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Nucleophilic attack on η^3-allyl and η^2-tetrahydroborate complexes of ruthenium(II)

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Reaction of $[Ru(CO)(\eta^3\text{-}C_3H_5)Cl(PMe_2Ph)_2]$, **1**, with CO and Ag^+ yielded **2A** and **2B**, isomers of $[Ru(CO)_2(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]^+$. Treatment of **2B** with BH_4^- gave $[Ru(CO)_2(CH_2CH_2CH_2)(PMe_2Ph)_2]$, **7**, and $[Ru(\eta^2\text{-}BH_4)(CO)H(PMe_2Ph)_2]$, **6**, subsequently obtained from $[Ru_2(CO)_2Cl_4(PMe_2Ph)_4]$ and $NaBH_4$. Chloride attacked the metal in **2B**, yielding $[Ru(CO)_2(\eta^1\text{-}C_3H_5)Cl(PMe_2Ph)_2]$, **8**, which then reformed **1**. Lability of the Ru–HB bond *trans* to hydride allowed nucleophilic access to the metal in **6**, with low-temperature formation of $[Ru(\eta^1\text{-}BH_4)(CO)H(L)(PMe_2Ph)_2]$ (**11**, **12**, **13**, L = PMe_2Ph, CO, 4-methylpyridine, respectively). On warming with excess L, these gave $H_3B{\cdot}L$ and $[Ru(CO)(H)_2L(PMe_2Ph)_2]$ (**5**, **4**, **14**, respectively). For L = C_2H_4, low-temperature NMR studies revealed a rapid equilibrium between **6**, C_2H_4 and $[Ru(\eta^1\text{-}BH_4)(CO)(\eta^2\text{-}C_2H_4)H(PMe_2Ph)_2]$, **16**, with slower conversion to $[Ru(\eta^2\text{-}BH_4)(CO)Et(PMe_2Ph)_2]$, **17**.

Introduction

The η^3-allyl and η^2-tetrahydroborate ligands share an ability to change their hapticity to η^1.[1] In consequence, reactions of nucleophiles with complexes containing these ligands can theoretically result either in a change to the η^1 binding mode, allowing the nucleophile to attach itself to the metal, or in direct attack on the allyl or tetrahydroborate ligand. This paper describes the results of a project initially intended to determine whether nucleophilic attack on an η^3-allyl complex of ruthenium(II) could be used to generate a ruthenacyclobutane.

Ruthenium(II) has been shown[2] to form a range of complexes $[Ru(CO)_2(R^1)R^2(PMe_2Ph)_2]$ containing two η^1-bonded organic ligands. In the past, symmetrical dialkyl and diaryl complexes ($R^1 = R^2$) were prepared by treating the *cct*-P isomer of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with the appropriate organo-lithium reagent, while unsymmetrical complexes were produced by converting *ttt*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ to $[Ru(CO)_2(R^1)Cl(PMe_2Ph)_2]$ with HgR^1_2, and then using LiR^2 to replace the remaining chloride ligand. An attempt was made to synthesise the ruthenacyclopentane complex $[Ru(CO)_2(CH_2CH_2CH_2CH_2)(PMe_2Ph)_2]$ by treating $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with $LiCH_2CH_2CH_2CH_2Li$ at 243 K.[3] An IR spectrum of the reaction mixture suggested that the desired product had been formed. The complex failed to survive the subsequent work-up procedure, but during this procedure cyclopentanone was formed. Since all the other species $[Ru(CO)_2(R^1)R^2(PMe_2Ph)_2]$ were found to eliminate the ketones R^1R^2CO in solution (although in most instances slowly enough to allow the complexes to be isolated and characterised), this result provided further evidence that $[Ru(CO)_2(CH_2CH_2CH_2CH_2)(PMe_2Ph)_2]$ *had* initially been formed.[3]

This paper reports an attempt to obtain the corresponding ruthenacyclobutane, $[Ru(CO)_2(CH_2CH_2CH_2)(PMe_2Ph)_2]$, by a different route, involving nucleophilic attack by hydride ion on the η^3-allyl complex, $[Ru(CO)_2(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]^+$. This requires not only that the attack should occur on the allyl ligand (rather than – for example – on the metal or on a carbonyl ligand) but also that the nucleophile should attack the central carbon atom in the allyl ligand. Davies, Green and Mingos[4] noted that nucleophiles attack an "open" unsaturated organic ligand at a terminal carbon atom, at any rate in cases where the ligand is "even" (*e.g.* butadiene). The rationale proposed for this was that the LUMO for the ligand, with which the nucleophile would interact, was concentrated mainly on the terminal carbon atoms. The situation for complexes in which the organic ligand is "odd" (and in particular for the η^3-allyl ligand) is less clear-cut, with examples of attack on both the terminal[5–7] and the central[7–11] carbon atoms. Although other groups[12,13] have since suggested somewhat different theoretical approaches, it was originally proposed[4] that the site of attack on the allyl ligand was determined by the electron-supplying or -withdrawing nature of the rest of the complex, making a prediction for $[Ru(CO)_2(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]^+$, which contains both predominantly σ-donor and π-acceptor ligands, particularly difficult.

The reaction intended to produce the ruthenacyclobutane used BH_4^- as a source of hydride ion. Unexpectedly it yielded, as a minor product, a tetrahydroborate complex of ruthenium(II), and this paper also describes the characterisation of this complex and a study of its own reactions with nucleophiles.

Results and discussion

The NMR data for all new ruthenium complexes and for adducts of BH_3 are collected in Table 1. Unless indicated otherwise, all ^{31}P, ^{13}C and ^{11}B data refer to spectra recorded with full proton decoupling. IR and elemental analysis data are given in the experimental section: IR data are limited to bands due to C–O stretching modes and those assigned to BH_4^- ligands.

(i) The formation and isomerisation of $[Ru(CO)_2(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]^+$

The uncharged η^3-allyl complex $[Ru(CO)(\eta^3\text{-}C_3H_5)Cl(PMe_2Ph)_2]$, **1**, was prepared as described in the literature.[14] The ligand arrangement in **1** is shown in Scheme 1. A CO-saturated solution of **1** in propanone was treated with $AgBF_4$ at room temperature. After filtration to remove AgCl, the solvent was removed from the filtrate. NMR spectra of a CD_3COCD_3 solution of the residue showed it to be a mixture of two species, **2A** and **2B**, assumed to be cations with BF_4^- counter-ions. At room temperature, the concentration of **2A** steadily decreased, while that of **2B** increased, with eventual complete conversion to **2B**. Although the BF_4^- salt of **2B** could not be isolated in crystalline form, treatment with $NaBPh_4$ in propanone solution yielded crystals for which elemental analysis results were in agreement with the formula $[Ru(CO)_2(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]BPh_4$.

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Table 1 NMR data for new complexes and for BH_3 adducts[a]

Nucleus	δ (ppm) (multiplicity, area)	Assignment	Coupling constants/Hz	Assignment
2A, 237 K, CD_3COCD_3				
^{31}P	−1.5 (d)	PMe_2Ph	33.2	$^2J_{PP}$
	6.3 (d)	PMe_2Ph	33.2	$^2J_{PP}$
^1H	1.30 (d, 3)	P*Me*$_2$Ph	9.6	$^2J_{PH}$
	1.41 (d, 3)	P*Me*$_2$Ph	9.2	$^2J_{PH}$
	2.16 (d, 1)[b]	H^b	6.2	$^3J_{HbHc}$
	2.25 (d, 3)	P*Me*$_2$Ph	9.9	$^2J_{PH}$
	2.33 (d, 3)	P*Me*$_2$Ph	9.9	$^2J_{PH}$
	2.53 (d, 1)	H^a	12.1	$^3J_{HaHc}$
	2.79 (dd, 1)	H^e	12.1, 3.6	$^3J_{HcHe}$, $^3J_{PH}$
	3.28 (d, 1)[b]	H^d	7.5	$^3J_{HcHd}$
	4.51 (m, 1)	H^c	6.3[c]	$^3J_{PH}$
^{13}C	8.8 (d)	P*Me*$_2$Ph	30.5	$^1J_{PC}$
	14.3 (d)	P*Me*$_2$Ph	33.2	$^1J_{PC}$
	19.2 (d)	P*Me*$_2$Ph	34.1	$^1J_{PC}$
	19.9 (d)	P*Me*$_2$Ph	33.2	$^1J_{PC}$
	44.3 (d)	C^a	13.5	$^2J_{PC}$
	47.9 (s)	C^c		
	104.9 (d)	C^b	2.7	$^2J_{PC}$
	193.1 (dd)	C^e	88.0, 12.6	$^2J_{PC}$, $^2J_{PC}$
	198.4 (dd)	C^d	18.0, 4.5	$^2J_{PC}$, $^2J_{PC}$
2B, 293 K, CD_3COCD_3				
^{31}P	−0.3 (d)	PMe_2Ph	223.2	$^2J_{PP}$
	13.0 (d)	PMe_2Ph	223.2	$^2J_{PP}$
^1H	1.91 (dddt, 2)	H^a	12.1, 12.1, 3.8, 2.7	$^3J_{HaHc}$, $^3J_{PH}$, $^3J_{PH}$, $\lvert^2J_{HaHb} + {}^4J_{HaHb}\rvert$
	1.97 (dd, 6)	P*Me*$_2$Ph	9.9, 2.2	$^2J_{PH}$, $^4J_{PH}$
	2.10 (dd, 6)	P*Me*$_2$Ph	9.2, 2.1	$^2J_{PH}$, $^4J_{PH}$
	2.94 (dtt, 2)	H^b	7.6, 2.7, 1.6	$^3J_{HbHc}$, $\lvert^2J_{HaHb} + {}^4J_{HaHb}\rvert$, $^2J_{PH} = {}^2J_{PH}$
	4.53 (tdt, 1)	H^c	12.1, 9.1, 7.6	$^3J_{HaHc}$, $^3J_{PHc}$, $^3J_{HbHc}$
^{13}C	15.7 (d)	P*Me*$_2$Ph	32.1	$^1J_{PC}$
	16.0 (d)	P*Me*$_2$Ph	32.1	$^1J_{PC}$
	49.1 (s)	C^a		
	105.8 (br)	C^b		
	198.1 (dd)	CO	14.1, 12.8	$^2J_{PC}$, $^2J_{PC}$
3, 273 K, CD_3COCD_3				
^{31}P	7.5 (s)	PMe_2Ph		
^1H	1.74 (d, 6)	P*Me*$_2$Ph	9.1	$^2J_{PH}$
	1.86 (d, 6)	P*Me*$_2$Ph	9.1	$^2J_{PH}$
	1.88[d]	H^a		
	3.37 (d, 2)	H^b	6.7	$^3J_{HbHc}$
	5.01 (tt, 1)	H^c	12.1, 6.7	$^3J_{HaHc}$, $^3J_{HbHc}$
^{13}C	14.6 (dd)[e]	P*Me*$_2$Ph	29.3, 5.5	$^1J_{PC}$, $^3J_{PC}$
	17.0 (dd)[e]	P*Me*$_2$Ph	31.4, 7.8	$^1J_{PC}$, $^3J_{PC}$
	56.4 (m)[e]	C^a	27.3	$\lvert^2J_{PC} + {}^2J_{PC}\rvert$
	103.4 (br)	C^b		
	202.5 (t)	CO	16.4	$^2J_{PC}$
6, 300 K, $CD_3C_6D_5$				
^{31}P	12.2 (s)	PMe_2Ph		
^1H	−13.86 (t, 1)	H^a	20.5	$^2J_{PH}$
	−7.4 (br, 1)	H^b		
	−5.1 (br, 1)	H^c		
	1.54 (t, 6)	P*Me*$_2$Ph	6.2	$\lvert^2J_{PH} + {}^4J_{PH}\rvert$
	1.56 (t, 6)	P*Me*$_2$Ph	6.2	$\lvert^2J_{PH} + {}^4J_{PH}\rvert$
	4.6 (br, 2)	H^d		
^{13}C	18.0 (t)	P*Me*$_2$Ph	29.9	$\lvert^1J_{PC} + {}^3J_{PC}\rvert$
	19.7 (t)	P*Me*$_2$Ph	31.1	$\lvert^1J_{PC} + {}^3J_{PC}\rvert$
	203.7 (t)	CO	13.5	$^2J_{PC}$
^{11}B	14.4 (br)	BH_4		
7, 270 K, CD_3COCD_3				
^{31}P	10.7 (s)	PMe_2Ph		
^1H	−0.44 (tt, 4)	H^a	11.9, 8.0	$^3J_{PH}$, $^3J_{HaHb}$
	1.93 (t, 12)	P*Me*$_2$Ph	6.5	$\lvert^2J_{PH} + {}^4J_{PH}\rvert$
	2.99 (quin, 2)	H^b	8.0	$^3J_{HaHb}$
^{13}C	−17.7 (t)	C^a	8.3	$^2J_{PC}$

Table 1 (*Contd.*)

Nucleus	δ (ppm) (multiplicity, area)	Assignment	Coupling constants/Hz	Assignment
7, 270 K, CD_3COCD_3				
	16.2 (t)	P*Me*$_2$Ph	30.5	$\lvert {}^1J_{PC} + {}^3J_{PC}\rvert$
	36.1 (t)	C^b	3.2	${}^3J_{PC}$
	199.7 (t)	CO	10.3	${}^2J_{PC}$
8, 253 K, CD_3COCD_3				
^{31}P	2.4 (s)	PMe_2Ph		
^{1}H	1.76 (dtdd, 2)	H^a	8.7, 8.0, 1.5, 0.7	${}^3J_{HaHb}$, ${}^3J_{PH}$, ${}^4J_{HaHd}$, ${}^4J_{HaHc}$
	1.91 (t, 12)	P*Me*$_2$Ph	7.6	$\lvert {}^2J_{PH} + {}^4J_{PH}\rvert$
	4.25 (ddt, 1)	H^c	9.9, 2.7, 0.7	${}^3J_{HbHc}$, ${}^2J_{HcHd}$, ${}^4J_{HaHc}$
	4.49 (ddt, 1)	H^d	16.8, 2.7, 1.5	${}^3J_{HbHd}$, ${}^2J_{HcHd}$, ${}^4J_{HaHd}$
	5.96 (ddt, 1)	H^b	16.8, 9.9, 8.7	${}^3J_{HbHd}$, ${}^3J_{HbHc}$, ${}^3J_{HaHb}$
^{13}C	11.6 (t)	P*Me*$_2$Ph	31.8	$\lvert {}^1J_{PC} + {}^3J_{PC}\rvert$
	13.6 (t)	P*Me*$_2$Ph	32.4	$\lvert {}^1J_{PC} + {}^3J_{PC}\rvert$
	23.3 (t)	C^a	7.5	${}^2J_{PC}$
	103.6 (s)	C^c		
	149.4 (s)	C^b		
	191.5 (t)	CO	8.9	${}^2J_{PC}$
	198.8 (t)	CO	12.4	${}^2J_{PC}$
9, 250 K, $CD_3C_6D_5$				
^{31}P	18.1 (s)	PMe_2Ph		
^{1}H	1.54 (t)	P*Me*$_2$Ph	6.9	$\lvert {}^2J_{PH} + {}^4J_{PH}\rvert$
^{13}C	22.3 (t)	P*Me*$_2$Ph	34.0	$\lvert {}^1J_{PC} + {}^3J_{PC}\rvert$
	209.9 (t)	CO	15.1	${}^2J_{PC}$
10, 300 K, $CDCl_3$				
^{31}P	6.1 (s)	PMe_2Ph		
^{1}H	1.85 (t)	P*Me*$_2$Ph	7.2	$\lvert {}^2J_{PH} + {}^4J_{PH}\rvert$
^{13}C	11.8 (t)	P*Me*$_2$Ph	30.5	$\lvert {}^1J_{PC} + {}^3J_{PC}\rvert$
	204.3 (t)	CO	15.3	${}^2J_{PC}$
11, 213 K, $CD_3C_6D_5$				
^{31}P	−6.9 (t)	PMe_2Ph	21.4	${}^2J_{PP}$
	6.1 (d)	PMe_2Ph	21.4	${}^2J_{PP}$
^{1}H	−11.9 (br, 1)^f	H^b		
	−7.28 (dt, 1)	H^a	91.0, 26.3	${}^2J_{PH}$, ${}^2J_{PH}$
	1.06 (d, 6)	P*Me*$_2$Ph	7.2	${}^2J_{PH}$
	1.54 (t, 6)	P*Me*$_2$Ph	6.8	$\lvert {}^2J_{PH} + {}^4J_{PH}\rvert$
	1.64 (t, 6)	P*Me*$_2$Ph	6.8	$\lvert {}^2J_{PH} + {}^4J_{PH}\rvert$
	1.8 (br, 3)^g	H^c		
^{11}B	−28.9 (br)	BH_4		
12, 210 K, $CD_3C_6D_5$				
^{31}P	6.8 (s)	PMe_2Ph		
^{1}H	−10.9 (br, 1)	H^b		
	−6.21 (t, 1)	H^a	22.0	${}^2J_{PH}$
	1.48 (t, 6)	P*Me*$_2$Ph	7.0	$\lvert {}^2J_{PH} + {}^4J_{PH}\rvert$
	1.53 (t, 6)	P*Me*$_2$Ph	7.0	$\lvert {}^2J_{PH} + {}^4J_{PH}\rvert$
	1.6^h	H^c		
^{13}C	16.9 (t)	P*Me*$_2$Ph	32.0	$\lvert {}^1J_{PC} + {}^3J_{PC}\rvert$
	19.7 (t)	P*Me*$_2$Ph	35.5	$\lvert {}^1J_{PC} + {}^3J_{PC}\rvert$
	197.0 (t)	CO	8.0	${}^2J_{PC}$
	199.9 (t)	CO	11.0	${}^2J_{PC}$
13, 220 K, $CD_3C_6D_5$				
^{31}P	13.5 (s)	PMe_2Ph		
^{1}H	−11.43 (t, 1)	H^a	19.7	${}^2J_{PH}$
	−0.6 (br, 4)	H^b, H^c		
	1.48 (t, 6)	P*Me*$_2$Ph	5.8	$\lvert {}^2J_{PH} + {}^4J_{PH}\rvert$
	1.54 (s, 3)	4-*Me*Py		
	1.73 (t, 6)	P*Me*$_2$Ph	6.4	$\lvert {}^2J_{PH} + {}^4J_{PH}\rvert$
	5.71 (d, 1)	4-Me*Py*, H^m	5.3	${}^3J_{HH}$
	5.95 (d, 1)	4-Me*Py*, H^m	5.3	${}^3J_{HH}$
	7.76 (d, 1)	4-Me*Py*, H^o	5.3	${}^3J_{HH}$

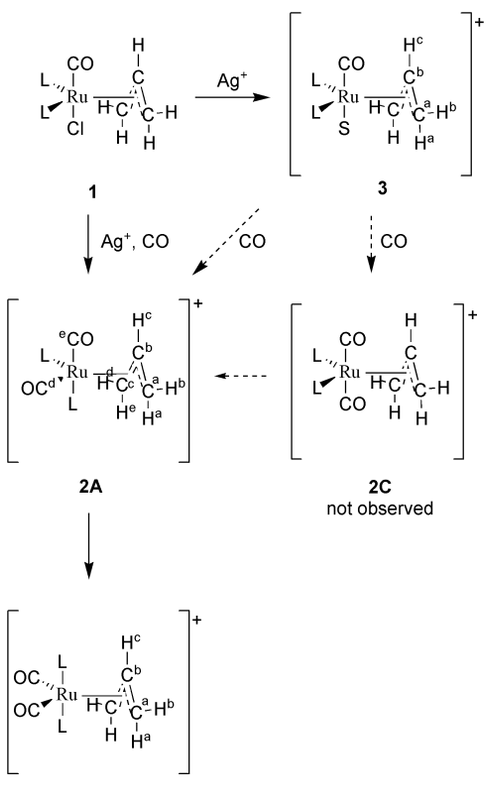
Table 1 (*Contd.*)

Nucleus	δ (ppm) (multiplicity, area)	Assignment	Coupling constants/Hz	Assignment
13, 220 K, $CD_3C_6D_5$				
	8.76 (d, 1)	4-Me*Py*, H^o	5.3	$^3J_{HH}$
^{13}C	14.8 (t)	P*Me*$_2$Ph	27.1	$\|^1J_{PC} + {}^3J_{PC}\|$
	18.9 (t)	P*Me*$_2$Ph	30.2	$\|^1J_{PC} + {}^3J_{PC}\|$
	20.0 (s)	4-*Me*Py		
	124.4 (s)	4-Me*Py*, C^m		
	125.2 (s)	4-Me*Py*, C^m		
	144.4 (s)	4-Me*Py*, C^p		
	154.1 (s)	4-Me*Py*, C^o		
	156.0 (s)	4-Me*Py*, C^o		
	206.1 (t)	CO	15.3	$^2J_{PC}$
14, 250 K, $CD_3C_6D_5$				
^{31}P	18.7 (s)	PMe$_2$Ph		
^{1}H	−15.01 (td, 1)	H^a	24.5, 7.0	$^2J_{PH}$, $^2J_{HH}$
	−4.46 (td, 1)	H^b	28.6, 7.0	$^2J_{PH}$, $^2J_{HH}$
	1.60 (s, 3)	4-*Me*Py		
	1.68 (t, 6)	P*Me*$_2$Ph	5.1	$\|^2J_{PH} + {}^4J_{PH}\|$
	1.72 (t, 6)	P*Me*$_2$Ph	5.4	$\|^2J_{PH} + {}^4J_{PH}\|$
	5.94 (d, 2)	4-Me*Py*, H^m	6.2	$^3J_{HH}$
	8.29 (d, 2)	4-Me*Py*, H^o	6.2	$^3J_{HH}$
^{13}C	19.9 (s)	4-*Me*Py		
	22.0 (t)	P*Me*$_2$Ph	28.8	$\|^1J_{PC} + {}^3J_{PC}\|$
	23.2 (t)	P*Me*$_2$Ph	33.0	$\|^1J_{PC} + {}^3J_{PC}\|$
	125.5 (s)	4-Me*Py*, C^m		
	144.5 (s)	4-Me*Py*, C^p		
	156.0 (s)	4-Me*Py*, C^o		
	205.0 (t)	CO	10.4	$^2J_{PC}$
15, 295 K, $CDCl_3$				
^{31}P	5.9 (s)	PMe$_2$Ph		
^{1}H	1.81 (t, 6)	P*Me*$_2$Ph	8.0	$\|^2J_{PH} + {}^4J_{PH}\|$
	1.92 (t, 6)	P*Me*$_2$Ph	7.0	$\|^2J_{PH} + {}^4J_{PH}\|$
	2.01 (s, 3)	4-*Me*Py		
	6.17 (d, 2)	4-Me*Py*, H^m	6.1	$^3J_{HH}$
	7.6 (br, 1)	4-Me*Py*, H^o		
	8.4 (br, 1)	4-Me*Py*, H^o		
^{13}C	10.6 (t)	P*Me*$_2$Ph	31.0	$\|^1J_{PC} + {}^3J_{PC}\|$
	13.9 (t)	P*Me*$_2$Ph	31.1	$\|^1J_{PC} + {}^3J_{PC}\|$
	21.0 (s)	4-*Me*Py		
	125.4 (s)	4-Me*Py*, C^m		
	147.9 (s)	4-Me*Py*, C^p		
	155.1 (br)	4-Me*Py*, C^o		
	201.9 (t)	CO	13.3	$^2J_{PC}$
16, 193 K, CD_3COCD_3				
^{31}P	10.2 (s)	PMe$_2$Ph		
^{1}H	−6.27 (t, 1)	H^a	25.9	$^2J_{PH}$
	0.2 (br, 4)	H^b, H^c		
	1.98 (t, 6)	P*Me*$_2$Ph	8.1	$\|^2J_{PH} + {}^4J_{PH}\|$
	1.99 (t, 6)	P*Me*$_2$Ph	7.9	$\|^2J_{PH} + {}^4J_{PH}\|$
	2.8 (br, 4)	C_2H_4		
17, 273 K, $CD_3C_6D_5$				
^{31}P	11.2 (s)	PMe$_2$Ph		
^{1}H	−5.8 (br, 1)^i	H^c		
	−5.5 (br, 1)^i	H^b		
	1.02 (t, 3)	CH_2CH_3	7.6	$^3J_{HH}$
	1.31 (qt, 2)	CH_2CH_3	7.6, 7.6	$^3J_{HH}$, $^3J_{PH}$
	1.52 (t, 6)	P*Me*$_2$Ph	6.0	$\|^2J_{PH} + {}^4J_{PH}\|$
	1.54 (t, 6)	P*Me*$_2$Ph	6.2	$\|^2J_{PH} + {}^4J_{PH}\|$
	4.1 (br, 2)	H^d		
^{13}C	6.2 (t)	CH_2CH_3	6.7	$^2J_{PC}$
	15.6 (t)	P*Me*$_2$Ph	28.4	$\|^1J_{PC} + {}^3J_{PC}\|$
	16.2 (t)	P*Me*$_2$Ph	28.8	$\|^1J_{PC} + {}^3J_{PC}\|$
	24.3 (s)	CH_2CH_3		
	205.5 (t)	CO	14.3	$^2J_{PC}$

Table 1 (*Contd.*)

	Nucleus	δ (ppm) (multiplicity, area)	Assignment	Coupling constants/Hz	Assignment
	$H_3B{\cdot}PMe_2Ph$, 300 K, $CD_3C_6D_5$				
	^{31}P	3.7 (q)	PMe_2Ph	55.0	$^1J_{PB}$
	^1H	0.99 (d, 6)	PMe_2Ph	10.2	$^2J_{PH}$
		1.54 (d, 3)[j]	BH_3	14.6	$^2J_{PH}$
	^{13}C	12.6 (d)	PMe_2Ph	38.0	$^1J_{PC}$
	^{11}B[k]	−34.5 (dq)	BH_3	55.0, 96.1	$^1J_{PB}$, $^1J_{BH}$
	$H_3B{\cdot}CO$, 300 K, $CD_3C_6D_5$				
	^1H	3.8 (br q)	BH_3	104.0	$^1J_{BH}$
	^{11}B[l]	−45.6 (q)	BH_3	104.0	$^1J_{BH}$
	$H_3B{\cdot}4$-MePy, 260 K, $CD_3C_6D_5$				
	^1H	1.56 (s, 3)	4-*Me*Py		
		3.4 (br, 3)[m]	BH_3		
		6.13 (d, 2)	4-Me*Py*, H^m	6.2	$^3J_{HH}$
		8.05 (d, 2)	4-Me*Py*, H^o	6.2	$^3J_{HH}$
	^{13}C[n]	20.3 (s)	4-*Me*Py		
		124.3 (s)	4-Me*Py*, C^m		
		146.1 (s)	4-Me*Py*, C^p		
		150.3 (s)	4-Me*Py*, C^o		
	^{11}B	−8.0 (br)	BH_3		

[a] Resonances for phenyl protons and carbon atoms omitted. Any coupling constants to boron are to ^{11}B. Labelling of hydrogen and carbon atoms is shown in the appropriate schemes. For the cationic complexes **2A** and **2B**, the counterion is BF_4^-. [b] Assignments for H^b and H^d may be reversed. [c] Values for other coupling constants already given. [d] Largely obscured. [e] Shows second-order effects due to magnetic inequivalence. [f] Observed on cooling to 203 K. [g] Observed on cooling to 184 K. [h] Detected by a ^1H–^1H COSY experiment. [i] Assignments for H^b and H^c may be reversed. [j] Only visible with ^{11}B decoupling. [k] Recorded at 250 K without ^1H decoupling. [l] Recorded without ^1H decoupling. [m] Sharpens to a 1 : 1 : 1 : 1 quartet ($|^1J_{BH}|$ = 104 Hz) at 300 K. [n] Recorded at 245 K.



Scheme 1 L = PMe_2Ph, S = solvent (propanone). The allyl ligand in **1**, **2A** and **3** may be inverted.

The NMR data for **2B** listed in Table 1 are for an isolated sample of its BF_4^- salt but do not differ significantly from those of the BPh_4^- salt. The assignments given in the table were supported by heteronuclear broad-band and selective decoupling experiments. It was clear from the spectra that the ligand arrangement in **2B** must be that shown in Scheme 1. The very strong coupling between the two inequivalent ^{31}P nuclei ($|^2J_{PP}|$ = 223.2 Hz) indicated that the PMe_2Ph ligands must be mutually *trans*, made inequivalent by the presence of the η^3-allyl ligand. Evidently any rotation of this ligand about its bond to the metal was slow on the NMR time-scale. The presence of a plane of symmetry in **2B** was clear from the pattern of resonances for the allyl ligand, and from the observation of a single doublet of doublets resonance for the carbonyl ligands, with slightly different coupling constants to the two ^{31}P nuclei. The IR spectrum of **2B** confirmed the mutually *cis* positioning of the carbonyl ligands.

It can be seen from Scheme 1 that the ligand arrangements in **1** and **2B** do not match. This observation, coupled with the fact that no NMR resonances other than those for **2B** were observed as those for **2A** disappeared, suggested that **2A** was an isomer of **2B**. The reaction was repeated in apparatus that was cooled in an ice–salt bath, and this temperature was maintained during the work-up procedure. NMR spectra were then recorded at 237 K. These spectra demonstrated that little **2B** had been formed and that conversion of **2A** to **2B** was very slow at this temperature. The spectra for **2A** were compatible with the formula $[Ru(CO)_2(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]^+$, but revealed a complete absence of symmetry in the complex. Once again the assignments given in Table 1 were based on detailed decoupling experiments. The value for $|^2J_{PP}|$, 33.2 Hz as opposed to 223.2

Hz for **2B**, indicated that the PMe_2Ph ligands were mutually *cis*, and the sizes of the coupling constants to phosphorus placed one carbonyl ligand ($|^2J_{PC}|$ = 88.0 and 12.6 Hz) *trans* to one PMe_2Ph ligand and the other ($|^2J_{PC}|$ = 18.0 and 4.5 Hz) *cis* to both PMe_2Ph ligands. Thus the ligand arrangement for **2A** (see Scheme 1) also did not match that in **1**.

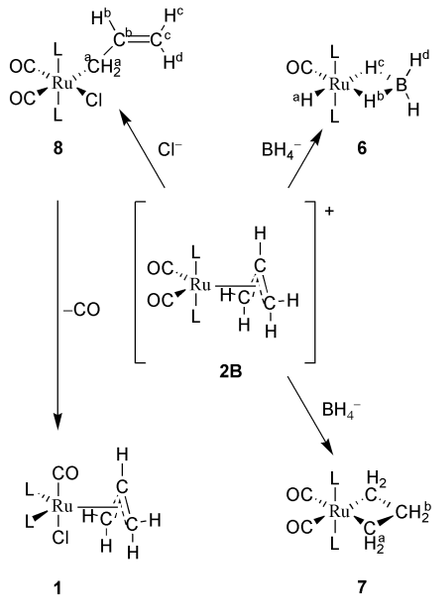
No clear evidence for the isomer of **2** (**2C** in Scheme 1) whose ligand arrangement *did* match that in **1** was obtained, even when the reaction between **1**, $AgBF_4$ and CO was carried out at even lower temperatures. In the absence of CO, however, **1** reacted with $AgBF_4$ in propanone solution to yield a species **3** which appeared on the basis of NMR evidence to contain PMe_2Ph, allyl and carbonyl ligands still in the same arrangement as for **1**. A ^{19}F NMR spectrum, recorded in CD_3COCD_3 solution, indicated that the BF_4^- ion was free in solution, so **3** may well be $[Ru(CO)(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2(S)]^+$, with a solvent molecule S in the site vacated by the chloride ligand (see Scheme 1). The solution of **3** was treated with CO at 213 K, and the temperature of the solution was raised until NMR spectra provided evidence of a reaction. Slow formation of **2A** was detected at 244 K, and further increase in temperature completed the conversion, with accompanying isomerisation of **2A** to **2B**. If isomer **2C** of $[Ru(CO)_2(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]^+$ *is* formed initially, it must rearrange very rapidly to **2A**. Given that **2B** is the thermodynamically preferred isomer, it might also be expected that **2C**, if formed, would rearrange directly to **2B** by a Berry[15] pseudorotation, bypassing **2A**.

Whether or not **2C** actually features in the reaction sequence, its instability relative to **2A** and **2B** probably relates to the presence of mutually *trans* carbonyl ligands. Transposing the positions of one carbonyl and one PMe_2Ph ligand, giving **2A**, removes this problem, but leaves the relatively bulky PMe_2Ph ligands close to one another. A second transposition, giving **2B**, moves them further apart. The isomerisations may well occur by way of $\eta^1\text{-}C_3H_5$ intermediates.

(ii) Nucleophilic attack on isomer 2B of $[Ru(CO)_2(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]^+$

The BF_4^- salt of **2B** was used for this reaction, and $NaBH_4$ was employed as a source of H^-: the solvent was ethanol. Both the reaction and the subsequent work-up were carried out in apparatus cooled in an ice–salt bath. After removal of the solvent under reduced pressure, extraction with a mixture of benzene and a little methylbenzene yielded a mixture of two major and two minor products. NMR spectra identified one major product as $[Ru(CO)_2(H)_2(PMe_2Ph)_2]$,[16] **4**, and one minor product as $[Ru(CO)(H)_2(PMe_2Ph)_3]$,[17] **5**. The other minor product, **6**, was tentatively assigned the formula $[Ru(\eta^2\text{-}BH_4)(CO)H(PMe_2Ph)_2]$ (see Scheme 2). A much better route to **6**, together with details of its characterisation, appears in the next section.

Attempts to obtain the other major product, **7**, in a completely pure state by both fractional crystallisation and chromatography were unsuccessful. In the hope of making the separation easier, a benzene solution of the product mixture was treated with CCl_4 to convert **4**, **5** and **6** to chloro-complexes, but unfortunately the CCl_4 also slowly decomposed **7**. Minor changes in reaction conditions yielded a sample of **7** contaminated only by **4**, and NMR spectra recorded on this sample, from which we could eliminate resonances due to **4**, allowed us to identify **7** as the metallacyclobutane $[Ru(CO)_2(CH_2CH_2CH_2)(PMe_2Ph)_2]$ (see Scheme 2), with mutually *trans* PMe_2Ph ligands. Selective decoupling at the frequency of the singlet resonance for the ^{31}P nuclei confirmed that two resonances in the ^1H NMR spectrum, of relative areas 3 : 1, belonged to **7**. The first, a triplet at δ 1.93, represented the methyl protons in the PMe_2Ph ligands, and the second, a triplet of triplets at δ −0.44, was assigned to the terminal CH_2 groups in the metallacycle. One of the triplet splittings ($|^3J_{PH}|$ = 11.9 Hz) was caused by the ^{31}P nuclei, and the other ($|^3J_{HH}|$ = 8.0 Hz) was shown by proton–proton decoupling to be the result of coupling to the central CH_2 protons in the metallacycle, represented by a quintet at δ 2.99. The ^{13}C NMR spectrum of **7** included triplet resonances at δ −17.7 ($|^2J_{PC}|$ = 8.3 Hz) and δ 36.1 ($|^3J_{PC}|$ = 3.2 Hz) for the terminal and central carbon atoms, respectively, in the metallacycle: both resonances were shown by a DEPT experiment to be due to CH_2 groups. There was also a triplet resonance at δ 199.7 for the carbonyl ligands in **7**. As expected, reaction of **2B** with $NaBD_4$ in EtOD yielded d_1-**7** $[Ru(CO)_2(CH_2CHDCH_2)(PMe_2Ph)_2]$. The resonances for the metallacyclobutane protons in d_1-**7** were at very similar chemical shifts to those for **7**, but with areas in a ratio of approximately 4 : 1.



Scheme 2 L = PMe_2Ph. Complexes **4** and **5** are also formed in the reaction with BH_4^-.

The formation of **7** provided clear evidence of nucleophilic attack at the central carbon atom of the η^3-allyl ligand in **2B**. The other major product, **4**, most likely resulted from the formation of the ruthenium(0) species $[Ru(CO)_2(PMe_2Ph)_2]$. Some H_2 was always produced during the reaction between **2B** and BH_4^- in ethanol, and the ease with which H_2 adds to such 16-electron ruthenium(0) species has been demonstrated for $[Ru(Me_2PCH_2CH_2PMe_2)_2]$, for which the rate constant for H_2 addition in cyclohexane solution at 300 K is 6.8×10^9 dm^3 mol^{-1} s^{-1}.[18] The precursor for $[Ru(CO)_2(PMe_2Ph)_2]$ could be the propene complex $[Ru(CO)_2(\eta^2\text{-}MeCH{=}CH_2)(PMe_2Ph)_2]$, formed by hydride attack on a terminal carbon atom in the allyl ligand in **2B**, but propene elimination could also occur from $[Ru(CO)_2(\eta^1\text{-}C_3H_5)H(PMe_2Ph)_2]$ formed by the switch of the allyl ligand to an η^1-bonding mode, accompanied by hydride or BH_4^- attack on the metal. Evidence in favour of this route was provided by a study of the reaction of the BF_4^- salt of **2B** with chloride ion (in the form of $[Me_4N]Cl$) in CD_3COCD_3 solution. The ultimate product was **1**, but at 279 K the formation of an intermediate species **8** was noted. Before conversion of **2B** to **8** was complete, there was some formation of **1**, but, by cooling the solution to 253 K at the point where the concentration of **8** was at its maximum, good NMR spectra were obtained for the complex. These revealed the presence of mutually *trans* PMe_2Ph ligands, two inequivalent carbonyl ligands, and an η^1-bonded allyl ligand. Assignment of the resonances for this ligand and determination of the relevant coupling constants were aided by selective decoupling, a ^1H–^1H COSY 2D spectrum and a DEPT experiment. As a test, the resonance at δ 5.96 for the proton on the β-carbon of the vinyl ligand was simulated using the values obtained for the coupling constants from the decoupling experiments, and a good match was achieved with the experimental version. We concluded (see Scheme 2)

that the final coordination site in **8** was occupied by a chloride ligand, making **8** [$Ru(CO)_2(\eta^1\text{-}C_3H_5)Cl(PMe_2Ph)_2$], an analogue of [$Ru(CO)_2(\eta^1\text{-}C_3H_5)H(PMe_2Ph)_2$], the species suggested as a precursor for [$Ru(CO)_2(PMe_2Ph)_2$] and hence for **4**. Evidently **8** then lost CO, allowing reversion of the allyl ligand to η^3-coordination and formation of [$Ru(CO)(\eta^3\text{-}C_3H_5)Cl(PMe_2Ph)_2$], intriguingly with a switch back to the ligand arrangement, **1**, from which the whole reaction sequence started (see Scheme 1).

One of the two minor products of the reaction between **2B** and BH_4^-, **5**, may well result from a little decomposition either of **4** or of [$Ru(CO)_2(PMe_2Ph)_2$] prior to the addition of H_2. The mechanism by which the other minor product, **6**, is formed may well involve an initial step similar to that for the formation of **4**, with attack by BH_4^- on the site made vacant by the switch of the allyl ligand in **2B** to η^1-bonding.

The metallacyclobutane [$Ru(CO)_2(CH_2CH_2CH_2)(PMe_2Ph)_2$], **7**, was significantly more stable than the metallacyclopentane [$Ru(CO)_2(CH_2CH_2CH_2CH_2)(PMe_2Ph)_2$],[3] surviving in solution for long periods at 270 K, a temperature at which the metallacyclopentane decomposes to give cyclopentanone. Treatment of a CD_3COCD_3 solution of **7** with CO at 270 K yielded [$Ru(CO)_3(PMe_2Ph)_2$], **9**, also obtainable by treating [$Ru(CO)_2(\eta^2\text{-}C_2H_4)(PMe_2Ph)_2$][16] with CO, but we were unable to identify an organic product of the reaction, either in the reaction mixture or by low-temperature trapping of any volatile materials expelled by the CO.

(iii) An alternative route to [$Ru(\eta^2\text{-}BH_4)(CO)H(PMe_2Ph)_2$], 6

A logical precursor to **6** appeared to be [$Ru_2(CO)_2Cl_4(PMe_2Ph)_4$], **10**, effectively two five-coordinate [$Ru(CO)Cl_2(PMe_2Ph)_2$] units held together by chloride bridges. It was hoped that **10** would react with $NaBH_4$ with replacement of two chloride ligands by hydride and the other two by BH_4^- ions. Complex **10** was obtained by passing N_2 through a solution of *ttt*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$][19] in refluxing ethanol, and characterised spectroscopically and by elemental analysis. Reaction with $NaBH_4$ in ethanol at 273 K, followed by removal of the solvent and benzene extraction of the residue, yielded **6** as an oil, obtainable in crystalline form from hexane solution. Elemental analysis and spectroscopic characterisation confirmed that **6** was [$Ru(\eta^2\text{-}BH_4)(CO)H(PMe_2Ph)_2$], with the ligand arrangement shown in Scheme 2. Similar complexes [$Ru(\eta^2\text{-}BH_4)(CO)HL_2$] but with much more bulky phosphines {L = $P(CHMe_2)_3$ or $PMe(CMe_3)_2$} have been prepared by Werner and Esteruelas,[20] and complexes [$Ru(\eta^2\text{-}BH_4)HL_3$] containing three monodentate or one terdentate phosphine ligand are known.[17,21–23]

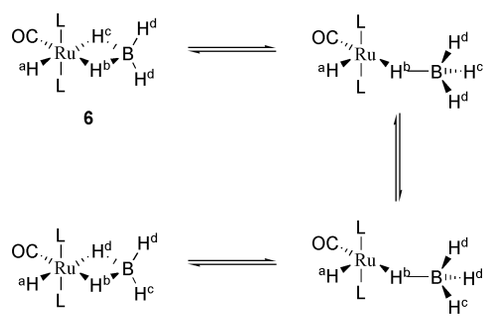
(iv) Fluxional motion in 6

The main spectroscopic interest in **6** and other complexes of this type relates to the BH_4^- ligand. In **6**, the two terminal hydrogens in this ligand are equivalent (H^d, giving a broad resonance at δ 4.6) whereas the two bridging hydrogens are inequivalent (H^b and H^c, broad resonances at δ −7.4 and −5.1, respectively). The evidence for the positions of the individual hydrogen atoms H^b and H^c (see Scheme 3) will be discussed shortly. The appearance of the three resonances was temperature-dependent for two separate reasons, (a) the effect of the quadrupolar ^{11}B and ^{10}B nuclei (80 and 20% abundant, respectively), and (b) fluxionality in the bonding between metal and BH_4^- ligand. In their pioneering study of $Zr(\eta^3\text{-}BH_4)_4$, where fluxionality causes all 16 hydrogens to appear equivalent even at low temperatures, Marks and Kolb[24] showed how the increase in the life-time of the ^{11}B nucleus in a particular spin-state with rising temperature made the fine structure in the ^1H NMR spectrum ($|^1J_{^{11}BH}|$ = *ca.* 90 Hz) become increasingly well resolved as the temperature was raised. In our studies of the ^1H NMR spectrum of **6** in $CD_3C_6D_5$ solution between 213 and 353 K, we were able to see only the first signs of this resolution in the resonances for the BH_4^- hydrogens before it was obscured by the onset of broadening due to fluxional motion. At 313 K this broadening was markedly greater for the terminal hydrogens, H^d, and for one bridging hydrogen, H^c, than for the other, H^b. The most obvious interpretation was that the Ru–H bond to H^c broke more readily than that to H^b, allowing scrambling of the H^c and H^d nuclei (see Scheme 3).

Table 2 T_1 values for protons in **6**[a]

	T_1/ms			
T/K	H^a	H^b	H^c	H^d
213	991	136	134	97
233	968	149	151	98
253	1296	216	191	141
273	1892	322	235	216

[a] Values for PMe_2Ph protons are not listed. Spectra were recorded in $CD_3C_6D_5$. Labelling of protons is shown in Scheme 3.



Scheme 3 L = PMe_2Ph.

Another indication of the preferential breaking of the Ru–H^c bond was provided by measurement of the spin–lattice relaxation times T_1 (see Table 2, which also includes values for the hydride ligand H^a for comparison). At 213 K the T_1 values for the two bridging hydrogens H^b and H^c were similar, whereas that for the terminal hydrogens H^d was appreciably lower, indicating – as expected – a stronger interaction with the boron nucleus. As the temperature was raised to 273 K, the increasing rate of the fluxional process which exchanged H^c and H^d caused their T_1 values to converge, with a widening gap between the values for H^b and H^c. A separate piece of evidence for a significant difference in the strength of the Ru–H^b and Ru–H^c bonds came from a ^1H–^{31}P HMQC experiment carried out to look for evidence of ^{31}P coupling to the BH_4^- hydrogen nuclei, not directly detectable in the ^1H NMR spectrum because of the breadth of the resonances. This experiment, run at 203 K, established that the ^{31}P nuclei were coupled to H^b, but gave no evidence of significant coupling to H^c or H^d.

Evidence of a similar fluxional process involving the terminal hydrogens and one bridging hydrogen has been noted by Meek[23] for [$Ru(\eta^2\text{-}BH_4)H\{PhP(CH_2CH_2CH_2PPh_2)_2\}$] and by Werner[20] for [$Ru(\eta^2\text{-}BH_4)(CO)HL_2$] {L = $P(CHMe_2)_3$ or $PMe(CMe_3)_2$}. In both instances one of the bridging hydrogens was *trans* to the hydride ligand (as is also the case for **6**). Meek concluded that this was the hydrogen involved in the fluxional motion, whereas Werner decided that it was not. We obtained both spectroscopic and (see later) chemical evidence to indicate that, in **6**, the bridging hydrogen involved, H^c, *was* the one *trans* to hydride. The spectroscopic evidence came from a ^1H–^1H 2D NOESY NMR experiment, carried out in $CD_3C_6D_5$ solution at 295 K. In such an experiment, the off-diagonal peaks due to the NOE effects are of the opposite phase to the diagonal peaks. Ignoring the cross-peaks involving hydrogen nuclei in the phosphine ligands, the spectrum showed only one such pair of peaks, linking the resonances for the hydride ligand H^a and the

bridging hydrogen H^b, the one not involved in the fluxional motion. Given this evidence of proximity, we concluded that H^a and H^b must be mutually *cis*, indicating that the bridging hydrogen H^c involved in the fluxional motion must be *trans* to H^a, as shown in Scheme 3.

Further increase in the temperature above 313 K caused the resonances for H^c and H^d to disappear, but the resonance for H^b now broadened rapidly. Evidently H^b also became involved in fluxional motion, perhaps by a separate process in which the Ru–H^b bond broke. This was confirmed by the NOESY experiment mentioned above, which showed off-diagonal peaks of the *same* phase as those on the diagonal (*i.e.* due to chemical exchange) connecting the terminal hydrogens H^d with both H^b and H^c.

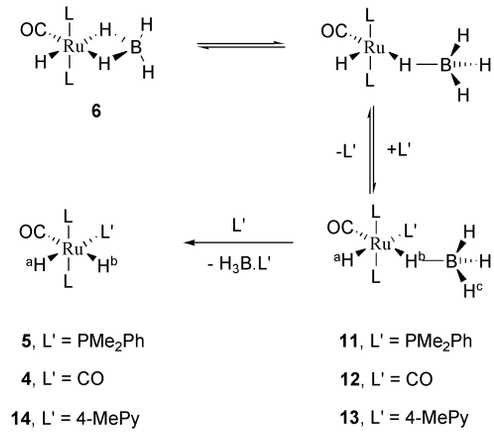
(v) Reactions of 6 with nucleophiles

In their early review of BH_4^- complexes, Marks and Kolb[24] mentioned the potential of the BH_4^- ligand to act as a "gatekeeper" in catalytic reaction sequences. Thus an η^2-bonded tetrahydroborate ligand could, by switching to the η^1-bonding mode, free a coordination site for the uptake of an organic substrate or other reactant. When the coordination site was no longer required, the BH_4^- ligand could revert to η^2-bonding. Clear-cut examples of this type of catalytic activity are, however, difficult to find. Indeed, an acid or base is often a component of the catalytic system, the role of the acid being to remove the entire BH_4^- ligand, while the base apparently removes BH_3 in the form of an adduct. This role of a base intrigued us, since – given the evident ease with which a metal–hydrogen bridge in an η^2-tetrahydroborate complex can be broken – there had to be a possibility that the base would occupy the vacant coordination site rather than abstracting BH_3. We were interested to determine what the *kinetic* products of such reactions were, and therefore carried out our studies at low temperatures.

When a $CD_3C_6D_5$ solution of **6** was treated with PMe_2Ph at 213 K, one major product, **11**, was formed. NMR spectra revealed the presence in **11** of three PMe_2Ph ligands in a *mer* arrangement, and a single hydride ligand whose resonance showed a triplet splitting of 26.3 Hz by the two equivalent ^{31}P nuclei but a doublet splitting of 91.0 Hz by the unique ^{31}P nucleus. It was not evident from the ^1H NMR spectrum recorded at 213 K what had happened to the BH_4^- ligand in **6**, but this became apparent when spectra were recorded at other temperatures. At 203 K a broad resonance, integrating for one proton, was detected at δ −11.9, and at 184 K this resonance had sharpened, and an additional, very broad resonance was seen at δ 1.8. These chemical shifts were in the regions expected for the bridging and terminal hydrogens, respectively, of an η^1-bonded BH_4^- ligand.[25,26] Both resonances disappeared on rewarming the solution to 213 K, but on further warming to 243 K a very broad resonance was observed at an intermediate chemical shift (*ca.* δ −1.7) and this sharpened on further increase in temperature. Studies of this variable temperature behaviour were curtailed by the increasing rate of a further reaction of **11** (see below), but it seemed clear that the η^1-tetrahydroborate ligand was undergoing scrambling of bridging and terminal hydrogens.

We were unable to obtain a satisfactory ^{13}C NMR spectrum of **11**, but the presence of a carbonyl ligand in the remaining coordination site was implied by the fact that both **6**, the precursor of **11**, and **5**, the species formed by its further reaction, were shown to contain a carbonyl ligand. We concluded that **11** was $[Ru(\eta^1\text{-}BH_4)(CO)H(PMe_2Ph)_3]$ with the ligand arrangement shown in Scheme 4. As the scheme shows, this ligand arrangement was consistent with the breaking of the Ru–H bond in **6** which was *trans* to the hydride ligand.

If the molar ratio of PMe_2Ph to **6** used in the experiment was at least 2 : 1, the effect of raising the temperature of the solution to 300 K was simply to cause complete conversion of **11** to



Scheme 4 L = PMe_2Ph.

$[Ru(CO)(H)_2(PMe_2Ph)_3]$, **5**,[17] and $H_3B{\cdot}PMe_2Ph$. As shown in Scheme 4, this corresponded to the abstraction of BH_3 from **11** without any alteration of the ligand arrangement around the metal. Interestingly, when the molar ratio of the reactants was 1 : 1, raising the temperature of the solution resulted in the disproportionation of **11** into equimolar quantities of **6**, **5** and $H_3B{\cdot}PMe_2Ph$.

The effect of bubbling CO through a $CD_3C_6D_5$ solution of **6** at 210 K was, as in the case of PMe_2Ph, to produce one major product, **12**. This was characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopies, and shown to contain two equivalent and mutually *trans* PMe_2Ph ligands, two inequivalent carbonyl ligands and a hydride ligand. A broad resonance in the ^1H NMR spectrum at δ −10.9, integrating for one proton, was assigned to the bridging hydrogen in an η^1-bonded BH_4^- ligand. The resonance for the three terminal hydrogens was not detected in the ^1H spectrum, but was shown to be at δ 1.6 by a 2D ^1H–^1H COSY NMR experiment which correlated this resonance with the bridging hydrogen resonance. Thus **12** was identified as $[Ru(\eta^1\text{-}BH_4)(CO)_2H(PMe_2Ph)_2]$ with the ligand arrangement shown in Scheme 4. As in the case of the reaction of **6** with PMe_2Ph, this ligand arrangement was consistent with the breaking of the Ru–H bond in **6** which was *trans* to the hydride ligand. The effect of raising the temperature of the solution to 300 K was to convert **12** to $[Ru(CO)_2(H)_2(PMe_2Ph)_2]$, **4**,[16] present in small quantities even at 210 K. The co-product of the conversion was identified as $H_3B{\cdot}CO$ on the basis of a quartet resonance ($|^1J_{HB}|$ = 104.0 Hz) at δ −45.6 in the proton-coupled ^{11}B NMR spectrum.[27] The splitting was lost on proton-decoupling, and the corresponding proton resonance was identified as a very broad 1 : 1 : 1 : 1 quartet at δ 3.8 in the ^1H spectrum. Again this corresponded to the abstraction of BH_3 from **12** with no change in the ligand arrangement around the metal.

The reaction of **6** with a third nucleophile, 4-methylpyridine, 4-MePy, was also investigated. Treating a $CD_3C_6D_5$ solution of **6** with an equimolar quantity of 4-MePy at 220 K yielded **13**, a complex shown by NMR spectroscopy to contain two mutually *trans* PMe_2Ph ligands, a hydride ligand, a carbonyl ligand and a 4-MePy ligand. A feature of the ^1H and ^{13}C NMR spectra was that each *ortho* and each *meta* proton and carbon atom in the 4-MePy ligand exhibited a separate resonance, establishing that at 220 K the rate of rotation of the ligand about the metal–nitrogen bond was slow on the NMR time-scale. The ^1H NMR spectrum also contained a very broad resonance at δ −0.6, which sharpened when the temperature of the solution was raised to 230 K: integration showed that it represented four hydrogens, implying that the final coordination site in **13** was occupied by an η^1-bonded BH_4^- ligand in which rapid exchange was occurring between bridging and terminal hydrogens. Lowering the temperature caused the resonance to collapse, and at 180 K a new broad resonance integrating for a single proton

(the bridging hydrogen) was detected at δ −8.5. The resonance for the three terminal hydrogens could not be detected (presumably it was still extremely broad), and further lowering in temperature was not practicable. The NMR data indicated that **13** was [Ru(η^1-BH_4)(CO)H(4-MePy)(PMe_2Ph)$_2$], but did not provide conclusive evidence of the ligand arrangement.

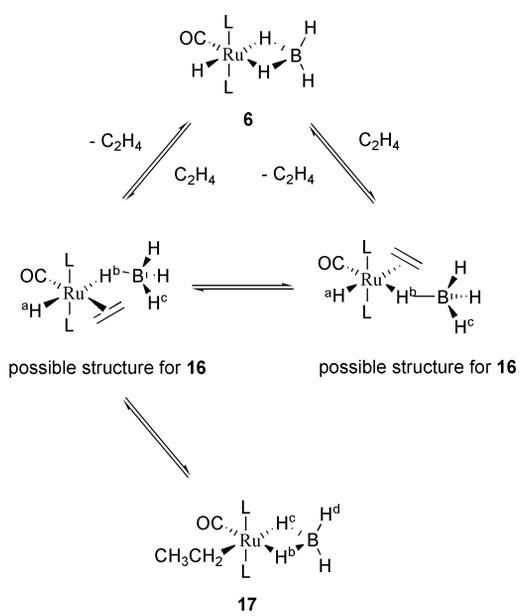
When a solution of **13** containing an equimolar amount of 4-methylpyridine was warmed to 273 K, the products were a new complex **14** and H_3B·4-MePy. Complex **14** was long-lived at low temperatures, but its stability at room temperature appeared to be more limited. NMR spectra recorded at 250 K indicated the presence of mutually *trans* PMe_2Ph ligands, two inequivalent hydride ligands, a carbonyl ligand and a 4-MePy ligand. This indicated that **14** was of [Ru(CO)(H)$_2$(4-MePy)(PMe_2Ph)$_2$], with the ligand arrangement shown in Scheme 4. Treatment of **14** with a little CCl_4 in C_6H_6 solution resulted in rapid conversion to its chloro-analogue, [Ru(CO)Cl_2(4-MePy)(PMe_2Ph)$_2$], **15**, characterised both spectroscopically and by elemental analysis. As in the case of [Ru(η^1-BH_4)(CO)H(PMe_2-Ph)$_3$], **11**, the effect of warming a solution of **13** in the absence of free 4-MePy was to cause it to disproportionate into **6**, **14** and H_3B·4-MePy, although some decomposition also occurred.

These results, achieved with three distinctly different nucleophiles, indicated, as shown in Scheme 4, that in each case the kinetic product of nucleophilic attack, **11**, **12** or **13**, resulted from the breaking of an Ru–H bond between metal and η^2-BH_4^- ligand in **6**, and the occupation by the nucleophile of the vacant coordination site. On raising the temperature of a solution of any of these η^1-BH_4^- complexes in the presence of an excess of the appropriate nucleophile, abstraction of BH_3 occurred, with complete conversion to **5**, **4** and **14** respectively. For the sequences **6**⟶**11**⟶**5** and **6**⟶**12**⟶**4**, the stereochemistry of the intermediates and final products corresponded to the initial breaking of the Ru–H bond *trans* to the hydride ligand, so that the nucleophile entered *trans* to this ligand, and the subsequent abstraction of BH_3 occurred without any change in the ligand arrangement around the metal. Since the ligand arrangement in **14** matched those in **5** and **4**, it seemed reasonable to suppose that the same was true for the sequence **6**⟶**13**⟶**14**.

The reaction of 6 with ethene

We were interested to discover whether ethene, as an example of an organic substrate, would react with **6** in the same manner as PMe_2Ph, CO and 4-methylpyridine. This reaction also was carried out under very mild conditions, by bubbling ethene through a CD_3COCD_3 solution of **6** at 195 K. NMR spectra subsequently recorded at 193 and 213 K indicated the establishment of an equilibrium between **6**, ethene and a new complex **16**, together with the slow formation of another complex, **17**. Lowering the temperature from 213 to 193 K shifted the equilibrium in favour of **16**: raising it to 213 K had the reverse effect, and also increased the rate of formation of **17**. When the reaction was repeated at 273 K, complete conversion to **17** was achieved, and **16** was not detected at all. ^{1}H and ^{31}P NMR spectra recorded at 193 K during the low-temperature study revealed that **16** contained mutually *trans* phosphine ligands and a hydride ligand, selective ^{31}P decoupling confirming that the appropriate ^{1}H resonances all belonged to the same species. A somewhat broadened peak at δ 2.8, integrating for four protons, also sharpened on selective ^{31}P decoupling, and this was tentatively assigned to the protons of an η^2-bonded ethene ligand. The incomplete conversion of **6** to **16**, even at 193 K, coupled with the slow conversion to **17**, prevented the recording of a good quality ^{13}C NMR spectrum, but crucially a resonance detected at δ 64.0 was correlated by a ^{1}H–^{13}C HMQC experiment to the δ 2.8 resonance in the ^{1}H spectrum, and was also shown by a DEPT experiment to be due to one or more carbon atoms each with two attached hydrogen atoms, thus confirming the presence of the ethene ligand. Finally, a very broad resonance, also integrating for four protons, was detected at δ 0.2 in the ^{1}H NMR spectrum. This was assigned as an averaged resonance for all the protons in an η^1-BH_4^- ligand (*cf.* the spectra of **11**, **12**, and **13**): evidently the scrambling of bridging and terminal BH_4^- protons was rapid even at 193 K. Although the quality of the ^{13}C NMR spectrum was insufficient to confirm the presence of a carbonyl ligand, the fact that both **6** and (see below) **17** contained such a ligand led us to conclude that this was also the case for **16**. Thus **16** was [Ru(η^1-BH_4)(CO)-(η^2-C_2H_4)H(PMe_2Ph)$_2$], the ethene equivalent of **11**, **12**, and **13**, although not necessarily with the same ligand arrangement (see below). Ruthenium complexes containing both a hydride and an ethene ligand appear to be rare: a recent report[28] gave only one example of an octahedral ruthenium(II) complex of this type, [Ru(η^2-C_2H_4)H($Me_2PCH_2CH_2PMe_2$)$_2$]$^+$:[29] in this complex the ethene and hydride ligands are mutually *trans*. Such a ligand arrangement would match those for **11**, **12** and **13**. There is, however, at least one known example of a similar species, [Ru(η^2-C_2H_4)H{P($CH_2CH_2PPh_2$)$_3$}]$^+$,[30] in which the geometry of the polydentate phosphorus ligand forces the hydride and ethene ligands to adopt mutually *cis* positions.

As mentioned above, complete conversion of **6** (and also of **16**) to **17** could be achieved in CD_3COCD_3 solution at 273 K, and the conversion was also carried out in $CD_3C_6D_5$. Under an atmosphere of N_2, however, **17** was easily reconverted to **6** on heating to 303 K. Complex **17** could not be isolated in a crystalline state and was stored at 253 K under ethene. NMR and IR spectra, recorded in the presence of free ethene in $CD_3C_6D_5$ and hexane respectively, clearly indicated both that **17** was [Ru(η^2-BH_4)(CO)Et(PMe_2Ph)$_2$] and that the ligand arrangement was that shown in Scheme 5. The BH_4^- ligand was represented in the ^{1}H NMR spectrum by a broad resonance for the two equivalent terminal protons at δ 4.1 and two overlapping broad resonances for the inequivalent bridging protons at δ −5.5 and −5.8. A variable temperature study in CD_3COCD_3 solution revealed that all three resonances were significantly sharper at 203 K, at which temperature the bridging proton resonances (at δ −5.9 and −6.2 in this solvent) did not overlap. On warming, the resonance for the terminal hydrogens and the bridging hydrogen resonance at δ −6.2 broadened more rapidly than that at δ −5.9, implying (as in the case of **6**) a preferential breaking of one of the two Ru–H bonds to the BH_4^- ligand. The resonances for the ethyl ligand in the ^{1}H NMR spectrum of **17** were a triplet for the methyl protons and an apparent sextet for the methylene protons, shown by selective decoupling to be



Scheme 5 L = PMe_2Ph.

the result of essentially equal splittings by both the methyl protons and the ^{31}P nuclei. The resonances for the ethyl carbon atoms in the ^{13}C spectrum, at δ 24.3 and 6.2, were shown by a DEPT experiment to belong to the methyl and methylene groups, respectively.

These results indicated the existence in solution (see Scheme 5) of a rapid equilibrium between **6**, ethene and **16**, and a slower one between **6**, ethene and **17**. If, however, **16** contains mutually *trans* hydride and ethene ligands, it clearly cannot be converted directly to **17**, but must be in equilibrium (directly or *via* **6**) with an unobserved second isomer in which hydride and ethene ligands are mutually *cis*.

Conclusions

The similarities in metal–ligand bonding between η^3-allyl complexes and η^2-tetrahydroborate complexes have been pointed out by Lauher and Hoffman,[31] and – as mentioned earlier – the η^3-allyl and η^2-tetrahydroborate ligands share the potential to decrease their hapticity,[1] liberating a vacant site on the metal for attack by a nucleophile. As illustrated by the reactions of **2B** with Cl^-, and of **6** with PMe_2Ph, CO, 4-methylpyridine and C_2H_4, this appears to be often the kinetically preferred pathway for reactions of nucleophiles with ruthenium(II) complexes containing either of these ligands. Only in the case of the reaction of **2B** with BH_4^- did we find evidence of a direct nucleophilic attack on the ligand itself, and even here other products which probably resulted from attack on the metal were obtained as well.

The willingness of BH_3 to act as a Lewis acid inevitably makes its abstraction from the resultant η^1-tetrahydroborate complexes by a second molecule of the nucleophile a likely subsequent reaction. The reaction of **6** with ethene, however, provided an example of reversion to the η^2-bonding mode, as a result of combination of the ethene and hydride ligands in the kinetic product **16** to give the ethyl ligand in **17**. Similarly, the η^1-bonded allyl ligand in the kinetic product of the reaction between **2B** and Cl^-, **8**, reverted to η^3-bonding by loss of CO, giving **1**.

The fact that we were able to detect an η^1-tetrahydroborate complex containing ethene and hydride ligands as a precursor to an η^2-tetrahydroborate complex containing an ethyl ligand provided a nice illustration of Marks' description of the tetrahydroborate ligand as a "gate-keeper",[24] and it would seem likely that the reactions of $[Ru(\eta^2\text{-}BH_4)H(PMe_3)_3]$ with alkynes RC≡CH, which have been shown by Kohlmann and Werner[21] to give vinyl complexes $[Ru(\eta^2\text{-}BH_4)(CH{=}CHR)(PMe_3)_3]$, went by way of similar but undetected η^1-tetrahydroborate intermediates, as the authors in fact suggested.

Experimental

Unless indicated otherwise, all experimental work was carried out under an atmosphere of N_2. The NMR spectra detailed in Table 1 were recorded on either a Bruker MSL 300 or a Bruker AMX 500 spectrometer. Details of the various NMR techniques used can be found in a review of 2D NMR experiments by Keeler[32] or in appropriate textbooks.[33,34] IR spectra were obtained using either a Perkin-Elmer PE 580B dual beam spectrometer or a Perkin-Elmer Paragon 1000 FTIR spectrometer. Complex **1** was prepared as described in the literature.[14]

Preparation of complex 2B

CO was bubbled through a solution of **1** (174 mg, 0.36 mmol) in propanone (30 cm^3), and then a solution of $AgBF_4$ (70 mg, 0.36 mmol) in the minimum amount of propanone was added. The reaction mixture, still under an atmosphere of CO and protected from light to avoid photodecomposition of silver salts, was stirred for several hours at room temperature. After filtration to remove the precipitate of AgCl, the solvent was removed from the filtrate under reduced pressure, and the residue dissolved in a little CD_3COCD_3. The solution was left at room temperature until NMR spectra indicated that conversion of the initially formed **2A** to **2B** was complete. After removal of the solvent under reduced pressure, the residue of the crude BF_4^- salt of **2B** was dissolved in propanone (30 cm^3) and stirred with $NaBPh_4$ (238 mg, 6.9 mmol) for 1 h. Removal of the solvent left a residue from which the BPh_4^- salt of **2B** was extracted into a small quantity of propanone, and obtained as a white solid on pumping off the propanone. The product was then recrystallised by dissolving it in the minimum of propanone, adding ethanol (3 cm^3) and cooling the solution to 273 K. The crystals were washed with ethanol (Found for BPh_4^- salt of **2B**: C, 68.2; H, 5.70. Calc. for $C_{45}H_{47}BO_2P_2Ru$: C, 68.1; H, 5.97%. IR in propanone solution: 2038, 1980 cm^{-1}.).

A solution containing **2A** contaminated by only a little **2B** was obtained by repeating the preparation, filtration and removal of the solvent from the filtrate at 270 K, and then redissolving the residue in CD_3COCD_3, also at 270 K. Complex **2A** was characterised by NMR spectroscopy at 237 K.

Preparation of complex 3 and its reaction with CO

The reaction between **1** (98 mg, 0.2 mmol) and $AgBF_4$ (40 mg, 0.2 mmol) in propanone (30 cm^3) was carried out as described for the preparation of **2B**, but under N_2 instead of CO. After filtration and removal of the solvent from the filtrate under reduced pressure, the residue, **3**, was dissolved in CD_3COCD_3 and characterised by NMR spectroscopy. The solution was then cooled to 213 K and saturated with CO. On stepwise increase in the temperature of the solution, the conversion of **3** to **2A** and then to **2B** was monitored by NMR spectroscopy.

Reaction of 2B with $NaBH_4$

This reaction was originally carried out by stirring the BF_4^- salt of **2B** (85 mg, 0.15 mmol) with a large excess of $NaBH_4$ in ethanol (20 cm^3) at 263 K for 30 min. The solvent was then removed under reduced pressure, and the residue extracted at 258 K with a 70 : 30 mixture of methylbenzene and benzene. The extract was filtered and the solvents removed under reduced pressure. ^{1}H and ^{31}P NMR spectra recorded on a CD_3COCD_3 solution of the residue revealed the presence of **4**, **5**, **6** and **7**, in an approximate molar ratio of 1 : 0.5 : 0.5 : 1. **4** and **5** were identified by comparison of their NMR spectra with those of authentic samples of the complexes.[16,17] An alternative preparation of **6** and its full characterisation are described below.

Changes in reaction conditions {typically 91 mg (0.16 mmol) of the BF_4^- salt of **2B**, a reduced amount of $NaBH_4$ (60 mg, 1.58 mmol), less ethanol (3 cm^3), a shorter reaction time (5 min) and a slightly higher reaction temperature (273 K)} virtually eliminated **5** and **6**, but we were still unable to achieve complete separation of **4** and **7**. **7** was characterised by NMR spectroscopy. The same technique was used to obtain a mixture of d_1-**7** and d_2-**4** [16] from **2B** and $NaBD_4$ in EtOD.

Reaction of 7 with CO

CO was bubbled through a CD_3COCD_3 solution of **4** and **7**, prepared as described above at 270 K. NMR studies indicated that **4** was unaffected by CO under these conditions, but **7** was converted to **9**, previously obtained by Bray[35] by treating $[Ru(CO)_2(\eta^2\text{-}C_2H_4)(PMe_2Ph)_2]$ [16] with CO.

Reaction of 2B with $[Me_4N]Cl$

A solution of the BF_4^- salt of **2B** (30 mg, 0.05 mmol) and $[Me_4N]Cl$ (6 mg, 0.55 mmol) in CD_3COCD_3 (1 cm^3) was made up at 279 K. The progress of the reaction was monitored at 279 K by NMR spectroscopy. At the point where the concentration

of the intermediate **8** was at its highest, the solution was cooled to 253 K to allow **8** to be characterised by NMR spectroscopy. The solution was then warmed up to room temperature, with complete conversion to **1**, identified by comparison of its ^{1}H and ^{31}P NMR spectra with those of an authentic sample of the complex.[14]

Preparation of complex 10

Nitrogen was bubbled through a stirred solution of *ttt*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] (100 mg, 0.20 mmol) in refluxing methanol (50 cm^3) for 2 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was recrystallised from a mixture of propanone and light petroleum (bp 353–373 K) (Found: C, 43.10; H, 4.83. Calc. for $C_{34}H_{44}Cl_4O_2P_4Ru_2$: C, 42.87; H, 4.66%. IR in $CHCl_3$ solution: 1955 cm^{-1}.).

Preparation of complex 6

An ethanol (5 cm^3) suspension of **10** (100 mg, 0.10 mmol) was stirred with $NaBH_4$ (100 mg, 2.6 mmol) at 273 K for 30 min. The solvent was then removed from the resulting solution under reduced pressure, still at 273 K. The residual oil was extracted into benzene (4 × 5 cm^3) at a temperature just above its freezing point. The extract was filtered and the benzene removed under reduced pressure, still at the same temperature, leaving **6** as a yellow oil. Crystals of **6** could be obtained by dissolving the oil in the minimum quantity of hexane at 273 K and cooling the solution to 253 K (Found: C, 48.11; H, 6.29. Calc. for $C_{17}H_{27}BO_2P_2Ru$: C, 48.47; H, 6.46%. IR in hexane solution: 2435, 2413, 1952, 1172 cm^{-1}.).

Reaction of 6 with PMe_2Ph

A $CD_3C_6D_5$ (1 cm^3) solution of **6** (18 mg, 0.04 mmol) in an NMR tube was treated at 213 K with the desired amount of PMe_2Ph (6 mm^3 for an approximately 1 : 1 molar ratio of the reactants, 12 mm^3 for a 2 : 1 ratio). In both cases **11** was quickly formed: it was only stable at low temperatures and was characterised by NMR spectroscopy at 213 K. Warming the solution containing a 2 : 1 molar ratio of the reactants to 300 K resulted in conversion of **11** to $H_3B{\cdot}PMe_2Ph$ and **5**, identified by spectroscopic comparison with an authentic sample.[17] The same treatment of the solution containing a 1 : 1 molar ratio of the reactants caused a disproportionation of **11** to equimolar quantities of **6**, **5** and $H_3B{\cdot}PMe_2Ph$, but addition of more PMe_2Ph completed the conversion of **6** to **5** and $H_3B{\cdot}PMe_2Ph$.

Reaction of 6 with CO

Carbon monoxide was bubbled through a $CD_3C_6D_5$ (1 cm^3) solution of **6** (36 mg, 0.08 mmol) in an NMR tube for 10 min at 210 K. The CO flow was then stopped and the NMR tube was transferred to the probe of the spectrometer (also at 210 K). The product of the reaction, **12**, which was only stable at low temperatures, was characterised by NMR spectroscopy. Warming the solution to 300 K caused complete conversion of **12** to $H_3B{\cdot}CO$ and **4**, identified by comparison of its spectra with those of an authentic sample.[16]

Reaction of 6 with 4-methylpyridine (4-MePy)

A $CD_3C_6D_5$ (1 cm^3) solution of **6** (36 mg, 0.08 mmol) in an NMR tube was treated at 220 K with 4-MePy (either a roughly equimolar quantity, 8 mm^3, or an excess, 38 mm^3). Immediate conversion to **13** occurred: this complex, only stable at low temperatures, was characterised by NMR spectroscopy at 220 K. Warming the solution containing an excess of 4-MePy to 273 K yielded $H_3B{\cdot}$4-MePy and **14**. **14**, which was insufficiently stable at room temperature to be isolated, was characterised by NMR spectroscopy at 250 K and by conversion to its dichloro-analogue **15** (see below). Warming the other solution resulted in disproportionation of **14** to **6**, $H_3B{\cdot}$4MePy and **14**, although some decomposition also occurred. Addition of more 4-MePy then converted **6** to **14** and $H_3B{\cdot}$4MePy.

Conversion of 14 to 15

The reaction between **6** and 4-MePy (molar ratio 1 : 2) was carried out at 293 K using C_6H_6 (1 cm^3) plus a little C_6D_6 as the solvent. NMR spectra recorded immediately after addition confirmed that conversion to **14** was complete, and CCl_4 (20 mm^3) was added straight away to the solution. The resonances for **14** disappeared immediately. All volatile materials were removed under reduced pressure, and the residue was recrystallised from a 50 : 50 mixture of ethanol and light petroleum (bp 313–333 K). NMR spectra recorded on this material revealed the presence of an impurity, which was separated from the main product **15** by chromatography on a 20 × 1 cm alumina column, eluted with a 1 : 1 mixture of Et_2O and $CHCl_3$. Complex **15** was in the second band to be eluted, and was obtained as pale yellow crystals on removal of the solvent (Found: C, 48.65; H, 5.11; N, 2.72. Calc. for $C_{23}H_{29}Cl_2NOP_2Ru$: C, 48.51; H, 5.13; N, 2.46%. IR in $CHCl_3$ solution: 1966 cm^{-1}).

Reaction of 6 with ethene

Ethene was bubbled through a solution of **6** (45 mg, 0.1 mmol) in either $CD_3C_6D_5$ or CD_3COCD_3 (0.7 cm^3) in an NMR tube for 5 min at 195 K, and the solution was transferred to the pre-cooled probe of the NMR spectrometer. Spectra recorded at 193 K and 213 K established the existence of an equilibrium between **6**, ethene and a species **16**, which was only stable at low temperatures and was characterised by NMR spectra recorded at 193 K. Meanwhile slow conversion to **17** was also occurring, and on raising the temperature to 273 K (or simply by carrying out the whole reaction at 273 K) the conversion was completed. Slow evaporation of the solvent under a stream of nitrogen at 273 K left **17** as a light brown oil, which appeared on the basis of NMR spectra recorded at 273 K to be free of impurity, but that would not crystallise. The stability of **17** was limited, and it was stored under ethene at 253 K (IR in hexane solution: 2425, 2405, 1938, 1725, 1703, 1172 cm^{-1}).

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