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Transition metal hydride complexes as Lewis bases: preparation and crystal structure of (*RR,SS*)-$\{[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)]_2(\mu\text{-}H)\}PF_6 \cdot CH_2Cl_2$

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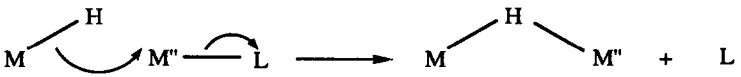
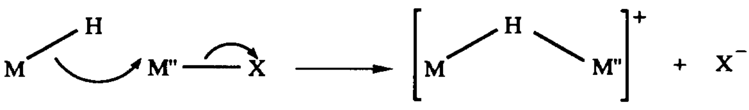
Abstract

Alkylation of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)H]$ (1) with Ph_3CPF_6, Et_3OBF_4, or Me_3OBF_4 leads to formation of the dimeric salts $\{[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)]_2(\mu\text{-}H)\}PF_6$ (2) and $\{[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)]_2(\mu\text{-}H)\}BF_4$ (3), respectively, with low diastereoselectivity. Hydrogenation of the molecular hydrogen complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(\eta^2\text{-}H_2)]PF_6$ (4) leads to the formation of 2 with high diastereoselectivity (*SS,RR* : *RS,SR* = 97 : 3). The reaction of the carbonyl hydride $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CO)H]$ (5) with Ph_3CPF_6 leads to a diastereomeric mixture of the cations $\{[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CO)]_2(\mu\text{-}H)\}PF_6$ (6). The major diastereomer of 2 has been characterised by a single crystal X-ray structural determination.

Introduction

Venanzi has introduced the concept of a metal hydride ligand acting as a Lewis base towards a coordinatively unsaturated metal centre which can function as a Lewis acid leading to a hydride bridged dinuclear product [1]. This type of process has been described as metal hydride coupling by Shapley [2].





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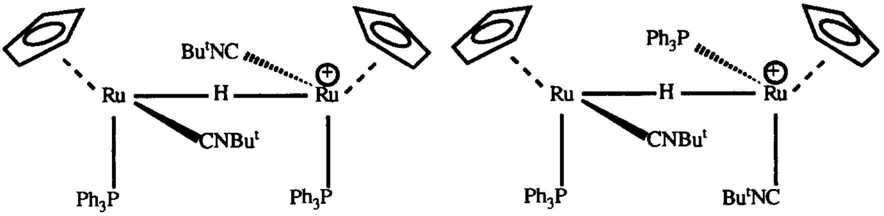
Paonessa and Trogler [3] have discussed this class of reaction and their 3*c*–2*e* representation of the bonding is in agreement with the formalism introduced earlier by one of us [4]. Recently this synthetic route has been developed by Caulton to prepare mixed metal trinuclear complexes containing a copper atom as the hub [5]. The cations $[(\eta^5\text{-}C_5H_5)M(CO)_3]^+$ (M = Mo, W) have been used as Lewis acid sites towards various Lewis bases including $[(\eta^5\text{-}C_5H_5)M(CO)_3H]$ (M = Mo, W) to yield hydride bridged cations [6]. Stone has prepared a reactive platinum dihydride species *in situ* which function as Lewis bases yielding hydrido bridged dimers of platinum [7]. In all of these cases the products have been achiral due to the symmetrical precursors employed. We were concerned to investigate whether diastereoselection would occur in this type of reaction if a suitable asymmetric precursor were used. We now report our results using the ruthenium complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)H]$ (**1**) as both the Lewis base and the source of the Lewis acid.

Results and discussion

In an extension of our studies on the protonation of the cyclopentadienylruthenium monohydrides $[(\eta^5\text{-}C_5H_5)Ru(L)(L'')H]$ [8], we reacted $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)H]$ (**1**) with carbonium ion sources. The anticipated products, *trans*-$[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(R)(H)]^+X^-$, were not observed spectroscopically at temperatures from 203–293 K. Reactions at room temperature were complete in minutes yielding red dichloromethane solutions from which the cation $\{[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)]_2(\mu\text{-}H)\}^+$ could be isolated as the hexafluorophosphate **2**, or tetrafluoroborate **3** salt. These salts can exist as *cis*- or *trans*-isomers which in fact constitute a diastereomeric pair. Since the starting material **1** was not homochiral two enantiomers of the *trans*-isomer will be present and can be labelled as (*SS,RR*). The *cis*-isomer is a meso compound and can be labelled as the (*SR,RS*) compound. The representations shown below are the (*SS*) and (*SR*) diastereomers as defined by the Stanley–Baird modification [9] of the Cahn–Ingold–Prelog rules [10].



SS (RR)   SR (RS)

The ratio of the two diastereomers was dependent on the carbonium ion source with the (*SS,RR*) isomer always predominating (see crystal structure section for assignment) and ranged from 66 : 34 for Me_3OBF_4 to 80 : 20 for Et_3OBF_4. We have been unable to separate the diastereomeric mixture and characterisation has been carried out on purified mixed samples. Crystallisation from dichloromethane–diethylether does not affect the isomer ratio for these samples although there may be some effect for samples of very high diasteromeric purity.

The infrared spectrum of **2** contains a band at 2097 cm^{-1} assignable to $\nu(C\equiv N)$. Each diastereomer exhibits *inter alia* a singlet for the cyclopentadienyl protons and a singlet for the tert-butyl group in the ^1H NMR spectrum, with those of the major product (*SS,RR*) at lower field than the resonances of the *meso* product. The high field ^1H NMR spectrum of **2** contains triplets at $\delta -21.68$ (J(PH) 16 Hz) and $\delta -24.24$ (J(PH) 12 Hz) assignable to the major and minor isomers respectively. Determination of the longitudinal relaxation times (T_1) of the bridging hydride ligand was carried out for a sample of **2**; the *trans*-isomer (*SS,RR*) gave a value of 1.3 s while the *cis*-isomer (*SR,SS*) gave 1.0 s. The difference in these values is significant and the relative order is intuitively correct but a lack of similar studies does not allow discussion at this time.

During an attempt to prepare single crystals of the dihydrogen complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(\eta^2\text{-}H_2)]PF_6$ (**4**) by slow diffusion of diethylether into a dichloromethane solution under hydrogen atmosphere we isolated small quantities of **2**. While at low pressures of hydrogen (1–3 atm) mainly decomposition products of **4** were obtained, the use of 17 atm hydrogen pressure gave a high yield of crystals of **2**. Spectroscopic analysis of the crystals showed them to be exclusively the major isomer of **2** by comparison with the mixtures prepared by alkylation. The mother liquor was a 97 : 3 mixture of the two diastereomers plus some minor impurities. Clearly at this composition fractional crystallisation is operative.

In order to understand this reaction a deuterodichloromethane solution of **2** with a 75 : 25 ratio of diastereomers which was sealed *in vacuo* was periodically monitored by ^1H NMR spectroscopy; the composition was unchanged after six months. Reaction of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(\eta^2\text{-}H_2)]PF_6$ (**4**) with one equivalent of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(H)]$ (**1**) in dichloromethane produced an 90 : 10 (*RR,SS*) : (*RS,SR*) mixture of **2**. Treatment of a dichloromethane solution of **4** with solid barium oxide gave a 75 : 25 (*RR,SS*) : (*RS,SR*) mixture of **2**. This reaction illustrates the acidity of the dihydrogen ligand relative to hydrogen gas or a normal metal hydride ligand. Indeed recent work by Morris suggests pK_a values of 4.6–9.2 for related compounds [11] compared with a pK_a value of ca. 38 for hydrogen gas [12].

These product ratios suggest the following mechanism for the formation of **2** by hydrogenation with the possibility that hydrogen gas itself is acting as a proton acceptor towards the cationic dihydrogen complex **4** in the first step (Fig. 1).

The approach of the metal hydride to the cationic complex is facilitated when the triphenylphosphine ligands are not occupying the same quadrant of space, leading to the *trans*-(*SS,RR*) product preferentially. When alkylating reagents are used to prepare **2** the lower selectivities can be rationalised by considering the nature of the electrophilic intermediate which is reacted with the metal hydride (Fig. 2). Whereas in the hydrogenation route the leaving group is dihydrogen, in the alkylation route the leaving group is either an alkane from a preformed alkyl hydride or alternatively an elimination reaction may be occurring where the carbonium ion occupies a region of space proximate to the hydride ligand; in either case an extra element of steric control will be present which acts to lower the selectivity.

Bercaw has reported the preparation of *trans*-$[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(H)(Me)]BF_4$ from the protonation of the neutral methyl precursor whose decomposition is rapid at room temperature presumably via a *cis*-intermediate [13]. Clearly the precise nature of the steric interactions cannot be described from the small selection of

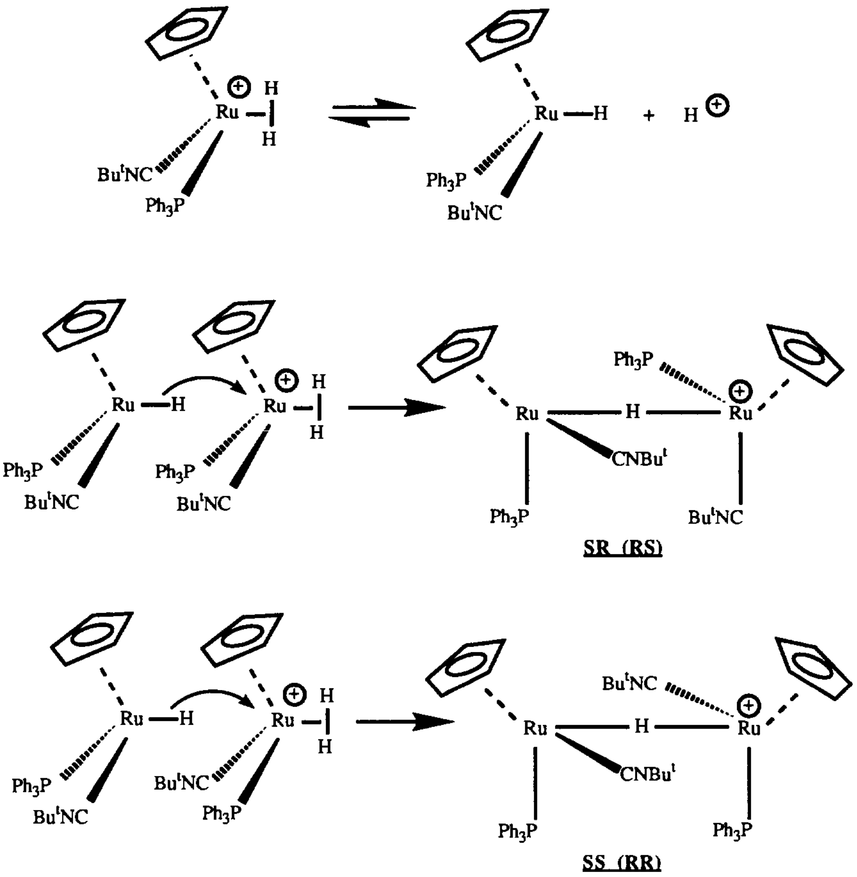
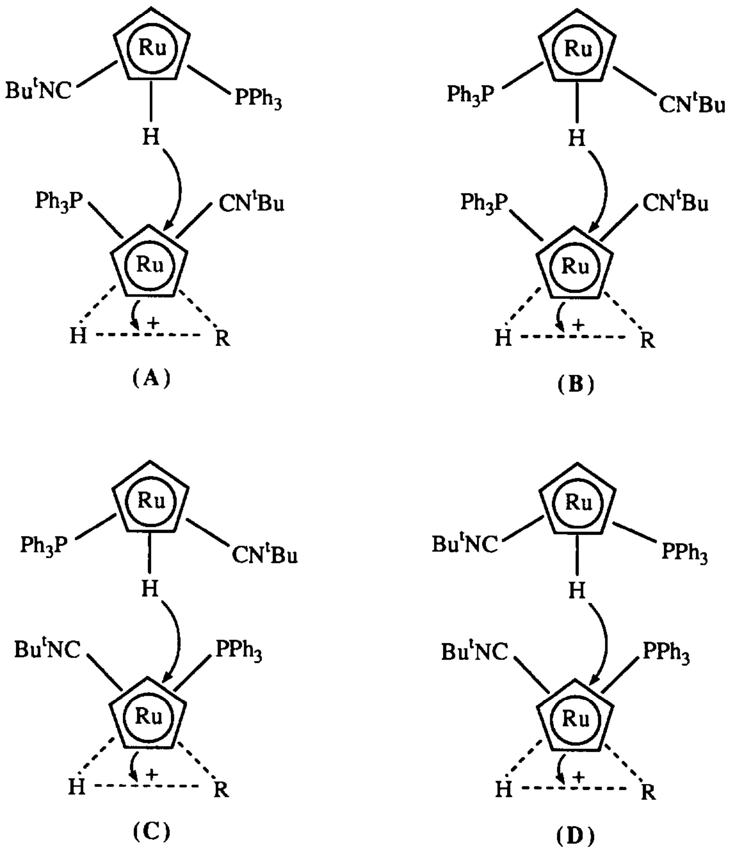


Fig. 1. Mechanism for the conversion of **4** to **2** under hydrogen.

carbonium ions used here but it is reasonable to suppose that some bending away from regular pseudo-octahedral and trigonal pyramidal geometries is involved.

Heinkey reported briefly [14] that treatment of $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)(CO)(H)]$ with half an equivalent of triphenylcarbenium tetrafluoroborate gave the dimeric product $\{[(\eta^5\text{-}C_5H_5)Ru(PMe_3)(CO)]_2(\mu\text{-}H)\}BF_4$ as a diastereomeric mixture of unstated composition which could be separated by fractional crystallisation. The pure *cis*-(*RS*,*SR*) diastereomer could be prepared by protonation of the precursor $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)(\mu\text{-}CO)_2]_2$. We treated $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CO)(H)]$ (**5**) with half an equivalent of triphenylcarbenium hexafluorophosphate and obtained a 60 : 40 diastereomeric mixture of **6** prior to fractional crystallisation; the major isomer appears to be the *trans*-(*RR*,*SS*) compound by spectroscopic comparisons with mixtures of **2**. In contrast to the reaction with **1**, use of one equivalent of triphenylcarbenium hexafluorophosphate causes the yield of **6** from **5** to be greatly lowered.

Gladyz has extensively investigated the rhenium Lewis acid fragment $[(\eta^5\text{-}C_5H_5)Re(PPh_3)(NO)]^+$, in particular its ability to preferentially react with one enantiomer of a racemic substrate [15]. One method of generation is the protonation of an alkyl precursor such as $[(\eta^5\text{-}C_5H_5)Re(PPh_3)(NO)(CH_2Ph)]$ where the *cis*-alkyl



Steric congestion : **A < B < C < D**

Product ratio's : **Trans > Cis**

Fig. 2. Intermediates in the alkylation of **1** to **2** and **3**.

hydride can be observed below −60 °C. This rhenium fragment has good enantiostability in halocarbon solvents where adduct formation takes place and it is possible that the reactive species in Fig. 2 is also a dichloromethane adduct since we have previously reported the preparation of such an *in situ* species [16].

*Solid state structure of **2***

The structure consists of isolated cation, anion and solvent molecular unit showing no unusually short intermolecular contacts. The cation has an exact C_2 molecular symmetry with each ruthenium coordinated by an η^5-cyclopentadienyl, a tert-butylisonitrile and a triphenylphosphine ligand and is shown in Fig. 3. Selected bond lengths and angles are given in Table 1. The hydride ligand which bridges the two metal centres lies on a crystallographic two-fold axis. Both metal centres have the same chirality and accordingly the (*RR,SS*) diastereomer is present. The ruthenium centres are linked by a $3c$–$2e$ bond involving the bridging hydride atom

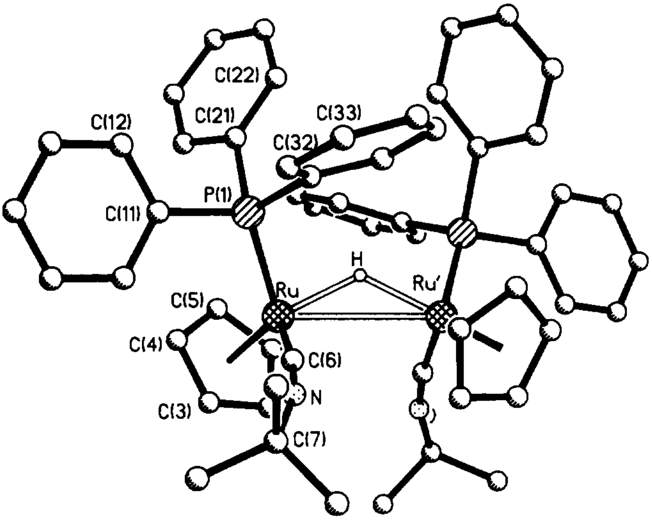


Fig. 3. Proposed molecular structure of the cation $\{[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)]_2(\mu\text{-}H)\}$ in **2**.

in the cation and the Ru–Ru separation in **2** is 3.180(1) Å which compares with values of 2.632(2) and 2.865(2) Å for the single 2*c*–2*e* metal to metal bonds in $\{[Ru(CO)_2(P\{^tBu_2\}\text{-}p\text{-}C_6H_4Me)]_2(\mu\text{-}Cl)_2\}$ and $\{(\mu^2\text{-}\eta^3:\eta^1,\eta^2\text{-}C_8H_8)[Ru(CO)_3]_2\}$ respectively [17,18]. The only published example of a similar 3*c*–2*e* hydrido bridge between two ruthenium atoms is the dimer $\{Ru_2(\mu\text{-}H)(CO)_4(\eta^5\text{-}C_5R_5)(\eta^5\text{-}C_5R'_5)\}$ containing two highly functionalised ring systems where a metal to metal separation of 3.223 Å was found [19]. The Ru–Ru separation in the triply halide bridged compounds $\{[Ru(P^nBu_3)_2(Cl)]_2(\mu\text{-}Cl)_3\}$ and $\{[Ru(PEt_2Ph)_3]_2(\mu\text{-}Cl)_3\}[RuCl_3(PEt_2Ph)_3]$ are 3.115 and 3.443(3) Å respectively [20,21]; both of these dinuclear compounds do not formally contain a direct metal to metal bond although the first contains an odd electron between the two centres.

The coordination sphere around the ruthenium centre in **2** is unexceptional with the Ru–P(1) and Ru–C(6) bond lengths of 2.300(1) and 1.926(5) Å respectively, similar to those in related compounds; e.g. 2.328(6) and 1.913(21) Å for $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(ICH_3)]PF_6$ [16], and 2.290(1) and 1.934(5) Å for $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(NH_3)]PF_6$ [22].

Table 1

Selected bond lengths (Å) and bond angles (°) for **2**

Ru–Ru′	3.180(1)		
Ru–C(1)	2.259(5)	Ru–C(2)	2.235(5)
Ru–C(3)	2.199(6)	Ru–C(4)	2.196(5)
Ru–C(5)	2.256(5)	Ru–H	1.779(22)
Ru–P(1)	2.300(1)	Ru–C(6)	1.926(5)
C(6)–N	1.166(6)	N–C(7)	1.454(7)
H–Ru–P(1)	84.6(12)	H–Ru–C(6)	100.4(7)
P(1)–Ru–C(6)	87.6(1)	Ru–C(6)–N	171.4(4)
C(6)–N–C(7)	169.9(5)		

Experimental

All reactions and preparations were carried out under nitrogen by standard Schlenk-tube techniques. Tetrahydrofuran was dried over sodium benzophenone ketyl and distilled prior to use. Diethylether and light petroleum ether (b.p. 40–60 ° C) were dried over sodium wire and distilled. Dichloromethane was dried over phosphorus pentoxide and distilled. All other solvents were used as supplied. Reactions performed at >1 atm pressure were carried out in Fischer–Porter bottles. Infrared spectra were recorded on a Perkin–Elmer 1710 FTIR instrument. Nuclear magnetic resonance spectra were recorded on Perkin–Elmer R32 (90 MHz, ^{1}H) and Bruker AC300 (300.13 MHz, ^{1}H; 121.49 MHz, ^{31}P; 75.47 MHz, ^{13}C) spectrometers. Elemental analyses were by Butterworth Laboratories, London. Fast Atom Bombardment (FAB) mass spectra were obtained on a Kratos Concept S1 spectrometer. Compounds **1**, **4** and **5** were prepared by simple modifications of literature methods [23,8,24]. Trialkyloxonium salts were purchased from Lancaster Synthesis and stored at −78 ° C. The solid trimethyloxonium tetrafluoroborate was pumped on under reduced pressure at −30 ° C immediately prior to use. Triphenylcarbenium hexafluorophosphate was prepared by a literature method [26] and stored at −30 ° C.

$\{[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)]_2(\mu\text{-}H)\}PF_6$ (2)

Triphenylcarbenium hexafluorophosphate (0.21 g, 0.55 mmol) was added to a cold (0 ° C) solution of **1** (0.28 g, 0.55 mmol) in dichloromethane (30 cm^3). The reactants were stirred at room temperature for 15 min yielding a deep red homogeneous solution. Filtration, concentration to 10 cm^3, and addition of diethyl ether (30 cm^3) to the stirred concentrate gave red crystals of **2** which were collected by filtration, washed with diethyl ether (5 cm^3) and dried *in vacuo*, yield 0.21 g (72%). (Found: C, 54.72; H, 4.84; N, 2.26. $C_{56}H_{59}F_6N_2P_3Ru_2 \cdot CH_2Cl_2$ calcd.: C, 54.59; H, 4.90; N, 2.23%). IR (Nujol): ν_{max} 2097s cm^{-1} (CN); ^{1}H NMR (CD_2Cl_2): δ 7.40 and 7.26 (m, 15H, Ph), 4.42 * and 4.32 (s, 5H, C_5H_5), 1.36 * and 1.17 (s, 9H, CMe_3), −21.68 * (t, J(PH) 16 Hz) and −24.24 (t, J(PH) 12 Hz)(1H, μ-H) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 55.5 * (s), 55.8 (s) ppm; * denotes signals of the major isomer (*RR,SS*) present as 75% in the product.

$\{[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)]_2(\mu\text{-}H)\}BF_4$ (3)

The use of trimethyloxonium tetrafluoroborate or triethyloxonium tetrafluoroborate (1.0 *M* in dichloromethane) in the above procedure gave crystalline **3** in 69 and 68% yield respectively. The percentage of the major isomer present in the product was Me_3OBF_4 (66) and Et_3OBF_4 (80).

Reaction of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(\eta^2\text{-}H_2)]PF_6$ *(4) with barium oxide*

A solution of **4** (0.2 g) in dichloromethane (20 cm^3) was stirred with barium oxide (0.2 g) at room temperature for 24 h. The resulting red solution was filtered and evaporated to dryness under reduced pressure to give a red solid. This was identified by its ^{1}H NMR spectrum as **2** containing 75% of the (*RR,SS*) diastereomer (*). ^{1}H NMR ($[CD_3]_2CO$): δ 7.53–7.29 (m, 15H, Ph), 4.59 * and 4.48 (s, 5H, C_5H_5), 1.40 * and 1.22 (s, 9H, CMe_3), −21.60 * (t, J(PH) 16 Hz) and −24.13 (t, J(PH) 13 Hz)(1 H, μ-H) ppm.

Reaction of equimolar 1 and 4

A solution of **1** (0.1 g, 0.20 mmol) in dichloromethane (10 cm^3) was rapidly added to a cold (0 °C) solution of **4** (0.12 g, 0.18 mmol) in dichloromethane (20 cm^3) with stirring. An immediate red colouration of the product solution was observed and the reactants were stirred for 15 min at room temperature. Work-up as above gave crystalline **2**, yield 0.13 g (62%) of which 90% was the (*RR,SS*) diastereomer by ^1H NMR spectroscopy.

Hydrogenation of 4

A solution of **4** (0.20 g, 0.30 mmol) in dichloromethane (ca. 5 cm^3) was filtered into a glass thimble placed inside a Fischer–Porter bottle containing diethyl ether (ca. 10 cm^3). The bottle was pressurised with hydrogen (250 psig) and allowed to stand in the dark for 14 days. The pressure was carefully released and large red well-formed crystals of **2** were isolated after decantation of the mother liquor, yield 0.09 g (51%).

Examination of a portion of the crystals by ^1H NMR spectroscopy showed them to be entirely the (*RR,SS*) diastereomer. The mother liquor was evaporated to dryness under reduced pressure and the residue examined; the diastereomer ratio (*RR,SS*):(*RS,SR*) was 97:3, traces of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(H)]$ and $[(\eta^5\text{-}C_5H_5)\text{-}Ru(PPh_3(H)_3]$ were also present [25].

Reaction of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CO)(H)]$ (5) with triphenylcarbenium hexafluorophosphate

Triphenylcarbenium hexafluorophosphate (0.10 g, 0.27 mmol) was added to a cold (0 °C) solution of **5** (0.25 g, 0.55 mmol) in dichloromethane (30 cm^3). The reactants were stirred at room temperature for 15 min yielding a deep red homogeneous solution. Filtration, concentration to 10 cm^3, and addition of diethylether (30 cm^3) to the stirred concentrate gave red crystals of **6** which were collected by filtration, washed with diethyl ether (5 cm^3) and dried *in vacuo*, yield 0.19 g (66%). IR (Nujol): ν_{max} 1965s cm^{-1} (CO); ^1H NMR (CD_2Cl_2): δ 7.79–6.98 (m, 15H, Ph), 5.13 and 5.00 * (s, 5H, C_5H_5), −19.53 * (t, *J*(PH) 15.5 Hz) and −22.70 (t, *J*(PH) 14 Hz)(1H, μ-H) ppm; * denotes signals of the major isomer (*RR,SS*) present as 60% in the product.

X-ray structure of 2

Red blocks were obtained by slow diffusion of diethylether into a dichloromethane solution of **1** under hydrogen gas (17 atm). A suitable crystal was mounted on a glass fibre with epoxy resin. Axial photographs and intensity data were collected on a Nicolet *P*3*m* diffractometer using graphite monochromatized Mo-K_α X-rays.

Crystal data. $C_{57}H_{61}N_2F_6P_3Cl_2Ru_2$, $\{[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)]_2(\mu\text{-}H)\}PF_6 \cdot CH_2Cl_2$, $M = 1254.1$, orthorhombic, space group *Pbcn* (No. 60), *a* 15.650(4) *b* 19.874(5) *c* 18.002(4) Å, $U = 5599(2)$ Å^3, D_c 1.49 g cm^{-3} for $Z = 4$. $F(000) = 2563.7$, μ(Mo-K_α) 7.67 cm^{-1}, *T* 20 °C, crystal size 0.35 × 0.30 × 0.25 mm. Cell dimensions were obtained from 15 centred reflections with 2θ values from 31 to 35°. Intensity data in the range $4 < 2\theta < 60°$ were collected using a θ–2θ scan technique. The intensities of three reflections measured periodically showed a decrease of less than 1% over the data collection. An empirical absorption correction was applied on the basis of 399 azimuthal scan data. A total of 7909 reflections were collected of which 6734 were independent, and 4799 for which $I > 2\sigma(I)$ were used in the refinement. One unique ruthenium atom was located from a Patterson map, indicating the crystallographic C_2 symmetry of the molecule. Subsequent electron-density difference syntheses located all remaining non-hydrogen atoms and allowed direct location of the bridging hydride on the two-fold axis, and which was refined without further constraints. Other hydrogen atoms were placed in calculated positions and

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**

	x	*y*	*z*	*U*
Ru	732(1)	2600(1)	1887(1)	32(1) [a]
P(1)	496(1)	3518(1)	1136(1)	36(1) [a]
C(1)	1676(3)	2375(3)	2803(3)	50(1) [a]
C(2)	1415(3)	1763(3)	2465(3)	54(2) [a]
C(3)	1670(4)	1793(3)	1708(3)	64(2) [a]
C(4)	2072(3)	2417(3)	1587(3)	59(2) [a]
C(5)	2085(3)	2774(3)	2275(3)	54(2) [a]
C(6)	−48(3)	2108(2)	1263(3)	41(1) [a]
N	−433(3)	1768(2)	856(2)	54(1) [a]
C(7)	−711(4)	1329(3)	256(3)	59(2) [a]
C(71)	−1268(5)	791(4)	567(4)	103(3)
C(72)	−1203(7)	1762(4)	−274(4)	137(5) [a]
C(73)	82(5)	1021(4)	−89(4)	121(4) [a]
C(11)	956(3)	3457(2)	193(2)	44(1) [a]
C(12)	1068(3)	4032(3)	−237(3)	54(2) [a]
C(13)	1379(4)	3981(3)	−955(3)	64(2) [a]
C(14)	1586(4)	3364(3)	−1247(3)	63(2) [a]
C(15)	1486(4)	2792(3)	−831(3)	63(2) [a]
C(16)	1170(3)	2838(3)	−102(3)	52(2) [a]
C(21)	981(3)	4317(2)	1440(3)	46(1) [a]
C(22)	515(4)	4884(3)	1630(3)	69(2) [a]
C(23)	942(6)	5460(3)	1887(4)	114(4) [a]
C(24)	1797(6)	5471(4)	1935(4)	110(4) [a]
C(25)	2270(5)	4924(4)	1723(4)	91(3) [a]
C(26)	1861(4)	4353(3)	1481(3)	69(2) [a]
C(31)	−619(3)	3736(2)	924(2)	41(1) [a]
C(32)	−942(4)	3704(3)	213(3)	63(2) [a]
C(33)	−1803(4)	3863(4)	83(4)	85(3) [a]
C(34)	−2325(4)	4068(3)	652(3)	73(2) [a]
C(35)	−2005(4)	4096(3)	1359(3)	65(2) [a]
C(36)	−1168(3)	3922(3)	1498(3)	51(2) [a]
P(2)	192(2)	260(1)	7463(2)	83(1)
F(1)	−380	−310	7820	186(6)
F(2)	364	−206	6768	138(4)
F(3)	18	725	8158	144(4)
F(4)	763	829	7105	128(3)
F(5)	−623	560	7063	168(5)
F(6)	1005	−41	7862	120(3)
C(50)	0	7738(7)	2500	138(5)
Cl(1)	677(2)	7278(2)	1977(2)	147(1) [a]
H	0	3002(25)	2500	29(14)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

with the exception of the solvent molecule hydrogen atom H(50a) were refined using a riding model. All non-hydrogen atoms of the cation and Cl(1) of the solvent were refined anisotropically. Isotropic parameters were refined for all atoms of the anion, the solvent carbon, C(50), and the bridging hydride: other hydrogen atoms were assigned fixed isotropic parameters set at 1.2 times the equivalent isotropic *U*-value of the carbon atom to which they were attached.

Space group symmetry required the presence of half an anion unit and half a solvent molecule per asymmetric unit. Refinement of the solvent molecule proceeded satisfactorily with C(50) constrained to lie on a crystallographic two-fold axis with half occupancy. The PF_6^- anion was found to be disordered over two positions close to, and related by the two fold axis. Unconstrained refinement of a rigid PF_6 octahedron (P–F = 1.58 Å) with site occupancy set to 0.5 for each atom converged with P(2) at 0.31 Å from the two-fold axis. The highest peak in the final difference map was 0.85 e Å^3. At convergence $R = 5.0\%$ and $R_w = 4.9\%$, $w = [\sigma^2(F) + 0.00035F^2]^{-1}$, $S = 1.49$ for 306 variables, $\Delta/\sigma < 0.02$.

Calculations were performed using SHELXTL program package on a Nicolet *R3m/E* structural determination system. The final positional parameters are given in Table 2.

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