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The stereochemical course of electrophilic cleavage of metal–carbon bonds at a chiral ruthenium centre. X-Ray crystal structure of [$(S)_{Ru}$-RuBr(CO)PPh_3{η-C_5H_4(neomenthyl)}]

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The stereochemical course of the cleavage of the metal–methyl bond in [RuMe(CO)PPh_3{η-C_5H_4(neomenthyl)}] by electrophiles has been investigated. Cleavage by hydrogen halides occurs predominantly with retention of configuration at the ruthenium whereas cleavage by halogens shows little stereoselectivity. These results have been rationalised by proposing that the reactions proceed *via* an oxidative addition mechanism involving a configurationally labile seven co-ordinate ruthenium(IV) intermediate. In the case of hydrogen halides, rapid reductive elimination of methane from the ruthenium(IV) intermediate does not allow significant epimerisation of the ruthenium centre whereas with halogens a slower reductive elimination of methyl halide results in significant epimerisation. The crystal structure of [$(S)_{Ru}$-RuBr(CO)PPh_3{η-C_5H_4(neomenthyl)}] is also reported.

Introduction

Organotransition metal complexes incorporating metal–carbon σ-bonds are of great importance as intermediates in the catalysis of organic reactions.[1] Moreover, such complexes are of great value as stoichiometric reagents in organic and organometallic synthesis.[2] Examples of this include the highly stereospecific transformations that have been achieved *via* the chiral transition metal complexes [Fe(η^5-C_5H_5)(CO)(PPh_3)-(COMe)][3] and [Re(η^5-C_5R_5)(NO)(PPh_3)R′] (where R = H or Me; R′ = Me, $COC_6H_3Me_2$-3,5, *etc.*).[4] A key step in many of these reactions is the final cleavage of the metal–carbon bonds by electrophilic reagents such as acids. Despite their importance, there have been relatively few studies on the mechanism and stereochemistry of such reactions and the studies that have been carried out have, not surprisingly, been concerned with the cleavage of iron–[5] and rhenium[6]–carbon bonds. As part of a study of the stereochemical course of reactions at a chiral ruthenium centre,[7] we report here the cleavage by electrophilic reagents of the ruthenium–methyl bond in the chiral complex [RuMe(CO)(PPh_3)(NmCp)] **1** (where NmCp = neomenthylcyclopentadienyl). This complex is particularly suitable for stereochemical studies since both diastereoisomers which differ in the configuration at the metal centre are readily synthesised optically pure and their absolute configurations have been established.[7b] Further, the metal centre is exceedingly configurationally stable, especially compared to analogous iron complexes.[8]

Results and discussion

As we have demonstrated previously,[7b] it is very easy to follow the stereochemical course of reactions of [RuMe(CO)(PPh_3)-(NmCp)] since the pattern of the four cyclopentadienyl protons in the ^{1}H NMR spectrum of compounds of the type [RuX-(CO)(PPh_3)(NmCp)] is very dependent upon the stereochemistry of the metal centre. Moreover, these protons come in a region of the ^{1}H NMR spectrum distinct from the Ph and neomenthyl groups. Thus, the optical purity of the initial starting material *i.e.* the ratio of the diastereoisomers which differ in configuration at the metal centre can be determined by integration of the ^{1}H NMR spectrum. In a similar way, the ^{31}P signal of the triphenylphosphine ligand also acts as a signpost of the metal stereochemistry.

The ruthenium–methyl bond of [RuMe(CO)(PPh_3)(NmCp)] was cleaved by both hydrogen halides HX and halogens X_2 to give the halide complexes [Ru]–X (where [Ru] = Ru(CO)-PPh_3(NmCp) and X = Cl, **2**; Br, **3**; or I, **4**). By a combination of X-ray crystallography and circular dichroism we have previously assigned the ^{1}H and ^{31}P NMR spectra of the starting methyl complex[7b] and also the iodo and chloro products[7c,d] to the absolute configurations of the ruthenium atoms. Herein, we report the crystal structure of the corresponding bromo complex [RuBr(CO)PPh_3(NmCp)] **3** and from this structure we can again assign the ^{1}H and ^{31}P NMR spectra of this compound to the absolute configuration of the ruthenium atom. Thus, for both the starting ruthenium methyl complex and all the ruthenium halide products, we are able to correlate the ^{1}H and ^{31}P NMR spectra with the absolute configuration of the ruthenium atom. Hence, for all the reactions involving cleavage of the ruthenium–methyl bond it was a relatively simple procedure to determine the stereochemical course of the cleavage reactions using ^{1}H and ^{31}P NMR spectroscopy. Before discussing the results, it is important to appreciate that the configuration at the ruthenium is defined by the ligand priority sequence I > Br > NmCp > Cl > PPh_3 > CO > Me.[9] Therefore, conversion of the ruthenium methyl complex to the corresponding halide complex *with retention of the stereochemistry at the ruthenium* would result in a change in the stereochemical descriptor for X = Br or I but not for X = Cl *i.e.* (*R*)-[Ru]–Me ⟶ (*S*)-[Ru]–X (X = I or Br) and (*R*)-[Ru]–Me ⟶ (*R*)-[Ru]–Cl *all* indicate retention of stereochemistry.

The stereochemical outcomes of the halogen-induced and hydrogen halide-induced cleavage reactions as determined by NMR are presented in Table 1 and it can be seen that they contrast sharply. Essentially, cleavage by hydrogen halides occurs predominantly with retention of configuration at the ruthenium whereas cleavage by halogens shows little stereoselectivity. Another significant result is that in the reaction of bromine with (*R*)-[RuMe(CO)(PPh_3)(NmCp)] which was stopped before it went to completion, the ruthenium centre in the unreacted ruthenium-methyl complex epimerised. The

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Table 1 Stereoselectivities of electrophilic cleavage reactions of [RuMe(CO)(PPh_3){η-C_5H_4(neomenthyl)}] *i.e.* [Ru]–Me[a]

Initial [Ru]–Me d.e. (major Ru configuration)	Electrophile (equivalents used)	Reaction time/h	Configuration of major product	Final d.e. of product
83% (*R*)	HI (1.04)	92	(*S*)-[Ru]–I	80%
81% (*S*)	HI (1.04)	92	(*R*)-[Ru]–I	67%
83% (*R*)	HBr (1.00)	48[b]	(*S*)-[Ru]–Br	83%
81% (*S*)	HBr (1.00)	48[b]	(*R*)-[Ru]–Br	71%
83% (*R*)	HCl (1.00)	168	(*R*)-[Ru]–Cl	72%
81% (*S*)	HCl (1.00)	168	(*S*)-[Ru]–Cl	71%
83% (*R*)	I_2 (1.11)	2	(*S*)-[Ru]–I	4%
81% (*S*)	I_2 (1.11)	2	(*R*)-[Ru]–I	5%
83% (*R*)	Br_2 (0.7)	<0.5	(*S*)-[Ru]–Br	26%
			(*RS*)-[Ru]–Me	0%
81% (*S*)	Br_2 (1.01)	<0.5	(*R*)-[Ru]–Br	13%
0% (*RS*)	ICl (1.00)	2	(*RS*)-[Ru]–I	—

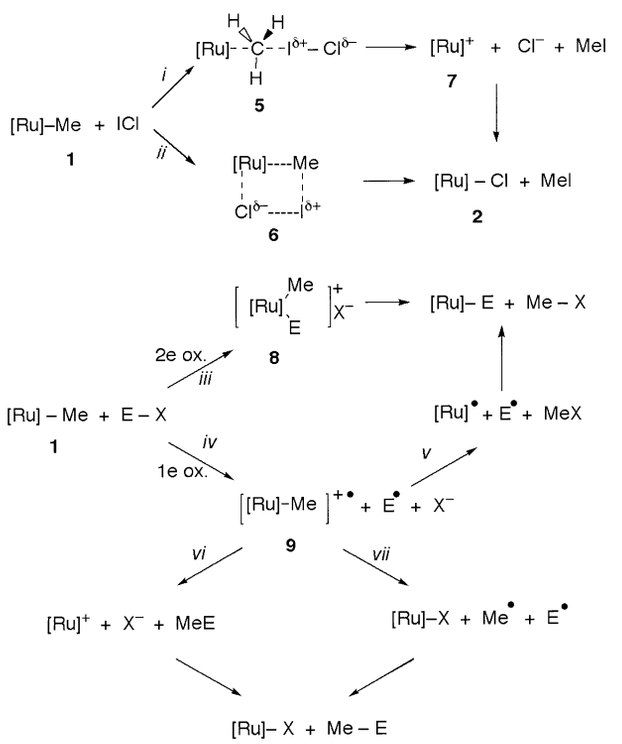
[a] At room temperature unless stated. [b] At 38 °C.

difference between the results obtained with (*R*)- and (*S*)-[RuMe(CO)(PPh_3)(NmCp)] indicates the small directing effect of the neomenthyl substituent. In keeping with this, we observed a comparable directing effect in the formation of the chiral ruthenium centre in reaction (1); again the diastereomeric

$$[RuX(CO)_2(NmCp)] + PPh_3 \longrightarrow [RuX(CO)(PPh_3)(NmCp)] + CO \quad (1)$$

excess increases with increasing size of the halogen (X = Cl, 6% d.e.; X = I, 19% d.e.).[7d]

In considering the mechanism of these cleavage reactions it should be noted that the reaction of [Ru]–Me with $I^{\delta+}$–$Cl^{\delta-}$ gave exclusively [Ru]–I. A S_E2 mechanism, proceeding *via* either a three-centred transition state **5** or a four-centred transition state **6** would be expected to lead to [Ru]–Cl (Scheme 1). It was



Scheme 1 Possible reaction pathways for cleavage of the ruthenium–methyl bond by electrophiles E–X. [Ru] = Ru(CO)PPh_3(NmCp).

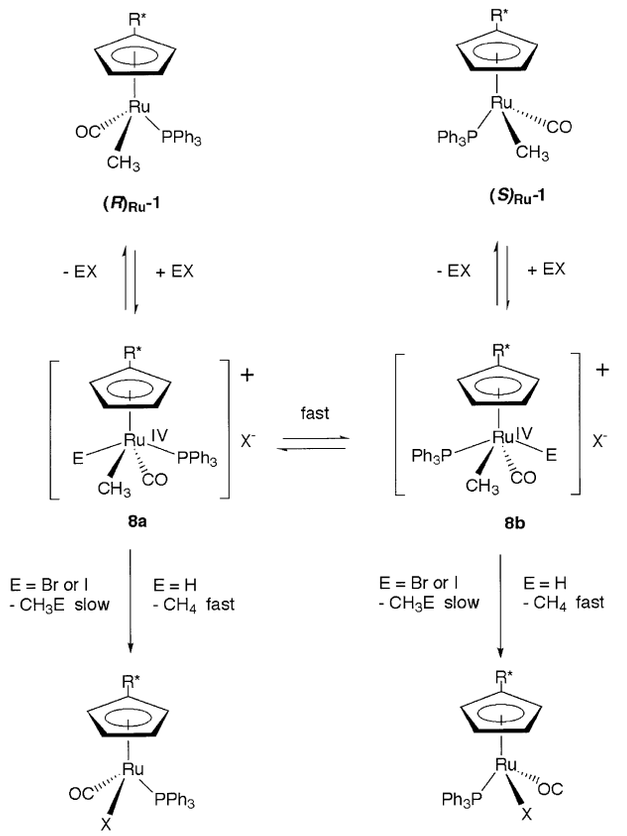
demonstrated that [Ru]–I was not formed as a result of metathesis of [Ru]–Cl with co-formed MeI by showing that no reaction occurred when a solution of the chloro-complex was stirred with MeI.

Further, a four-centred transition state (path ii) would be expected to lead to a high degree of retention and cannot explain the lack of selectivity observed in cleavage of the ruthenium–methyl bond by halogens. Similarly, path i would be expected to lead to a high degree of retention since there is strong evidence from our previous studies of complexes of the type [Ru(CO)L(PPh_3)(NmCp)]$^{n+}$ (where $n = 0$, L = Cl or I; $n = 1$, L = NCMe) and from theoretical calculations involving closely related systems[10] that the 16-electron pyramidal intermediate [Ru(CO)(PPh_3)(NmCp)]$^+$ **7** does not lose its stereochemical integrity before being attacked by the incoming nucleophile. Indeed we have shown that SO_2 insertion into the ruthenium–methyl bond of [RuMe(CO)(PPh_3)(NmCp)] proceeds *via* pathway i with ≥99% retention of configuration.[7b] Finally, neither of these mechanisms can explain the epimerisation of the unreacted starting material in the reaction of bromine with (*R*)-[RuMe(CO)(PPh_3)(NmCp)].†

In fact, the body of evidence suggests that for transition metals on the right hand side of the periodic table, metal–alkyl cleavage proceeds *via* one- and/or two-electron transfer reactions as shown in Scheme 1 (pathways iv and iii respectively).[11] In our case, if a 1e oxidation is involved then only pathways iv and v would give the observed product [Ru]–I from the cleavage of [Ru]–Me with ICl. However, if such a pathway is involved it must also explain the observed epimerisation of the unreacted starting material in the reaction of bromine with (*R*)-[RuMe(CO)(PPh_3)(NmCp)]. This would necessitate the radical cation [[Ru]–Me]$^{+\bullet}$ **9** being configurationally unstable. If, however, **9** is configurationally unstable it cannot be an intermediate in the stereospecific cleavage reactions of [RuMe(CO)(PPh_3)(NmCp)] with hydrogen halides.

A much more probable route for all these electrophilic cleavage reactions is pathway iii, the 2e transfer *i.e.* an oxidative addition mechanism depicted in Scheme 1, since this accounts for all the results including the dichotomy of stereochemical behaviour observed in the reactions of [RuMe(CO)(PPh_3)(NmCp)] with HX and X_2. The intimate details of this mechanism are shown in Scheme 2. Thus, we propose that addition of HX or X_2 to (*R*)- or (*S*)-[RuMe(CO)(PPh_3)(NmCp)] yields the seven co-ordinate ruthenium(IV) intermediates **8a** and **8b** respectively. Such seven co-ordinate complexes would be expected to be configurationally labile and to epimerise by intramolecular rearrangement without ligand dissociation.[12] For example, the geometrically similar molybdenum complexes [MoYL($CO)_2$Cp] (where Y = halide, H or alkyl; L =

† Although we have demonstrated that intermediates **5** or **6** are not involved in the electrophilic cleavage of [Ru]–Me by halogens we have not definitively excluded the possibility that they are involved in cleavage by hydrogen halides although all our data are consistent with both types of reaction occurring *via* a common oxidative addition mechanism.



Scheme 2 Proposed mechanism for the electrophilic cleavage of the ruthenium–methyl bond.

phosphine)[13] and [MoCl(CO)L_2Cp] (where L = $PMePh_2$ or PMe_2Ph)[14] undergo *cis–trans* interconversion *via* a pseudo-trigonal bipyramidal intermediate. Hence, if the ruthenium(IV) intermediates have a long enough life time then interconversion between the isomeric **8a** and **8b** before loss of EX will lead to epimerisation of the original (*R*)- or (*S*)-[RuMe(CO)(PPh_3)(NmCp)]. Similarly, the large degree of epimerisation of the products [RuX(CO)(PPh_3)(NmCp)] (X = Br or I) resulting from the reaction of (*R*)- or (*S*)-[RuMe(CO)(PPh_3)(NmCp)] with X_2 or ICl derives from the stereochemical lability of the ruthenium(IV) intermediates **8a** and **8b** and implies that, in this case, these ruthenium(IV) intermediates have a relatively long lifetime *i.e.* elimination of MeX is slow. In contrast, the relatively stereoselective cleavage of (*R*)- or (*S*)-[RuMe(CO)(PPh_3)(NmCp)] by HX implies that, in these cases, the lifetimes of **8a** and **8b** are relatively short *i.e.* elimination of CH_4 is relatively rapid. The rapid elimination of methane from organometallic complexes compared to the relatively slow elimination of methyl halides is precedented[15] and also expected given the paucity of stable metal-alkyl-hydrides compared to the numerous metal-alkyl-halide complexes.

Support for an oxidative addition mechanism comes from the detection of analogues of the intermediates **8a** and **8b** in related electrophilic cleavage reactions.[16] For example, in the reaction of [FeR(CO)$_2$Cp] with CF_3CO_2H to give [Fe(O_2CCF_3)(CO)$_2$Cp], the intermediacy of the iron(IV) complex [FeHR(CO)$_2$Cp][H(O_2CCF_3)$_2$] has been established.[17] Similarly, reaction of the electrophiles E–Br with [Os(Me)(CO)(PMe_2Ph)(C_5Me_5)] gives [OsE(Me)(CO)(PMe_2Ph)(C_5Me_5)]Br (**10a** E = Br; **10b** E = HgBr) and **10a** eliminates MeBr over 2 h at room temperature to give [OsBr(CO)(PMe_2Ph)(C_5Me_5)].[18] Although we have not detected ruthenium(IV) intermediates in the reactions reported herein, we have shown that the related complex, [RuBr(CO)$_2$(C_5Me_4Et)], readily oxidatively adds bromine to give the corresponding ruthenium(IV) complex.[19] Further support for an oxidative addition mechanism comes from the extensive synthetic and electrochemical studies carried out by Baird and co-workers on the electrophilic cleavage reactions of [RuR(CO)(PPh_3)(C_5H_5)] (R = Me or CH_2Ph).[11] It is also relevant to note that the oxidative addition mechanism proposed here is consistent with the retention of configuration at the carbon which is always observed on protonolysis of transition metal–alkyl bonds.[20] Electrophilic attack at the back side of the M–C bond would lead to inversion.

In conclusion, the study reported here provides strong evidence that the electrophilic cleavage reactions of ruthenium(II)-alkyl complexes with halogens and hydrogen halides proceeds *via* configurationally labile ruthenium(IV) intermediates. The implications of this for complexes containing a chiral ruthenium centre involved in catalytic or stoichiometric reactions which involve electrophilic cleavage of a ruthenium–alkyl bond is that there is little chance of the configuration of the ruthenium being retained. Certainly this will be true if halogens are used for the electrophilic cleavage; if hydrogen halides are used then the stereoselectivity of the cleavage reactions observed in this study suggest that after a relatively small number of reaction cycles the absolute configuration of the ruthenium centre will be compromised. The only way to avoid this is to devise diastereoisomers that have a large preference for one particular metal configuration (*i.e.* the equilibrium between the analogues of **8a** and **8b** lies predominantly in favour of one particular diastereoisomer) or which react at very different rates.

Description of structure

The molecular structure of (*S*)-[RuBr(CO)(PPh_3)(NmCp)] **3** is illustrated in Fig. 1 and Table 2 gives selected bond lengths and angles with estimated standard deviations.

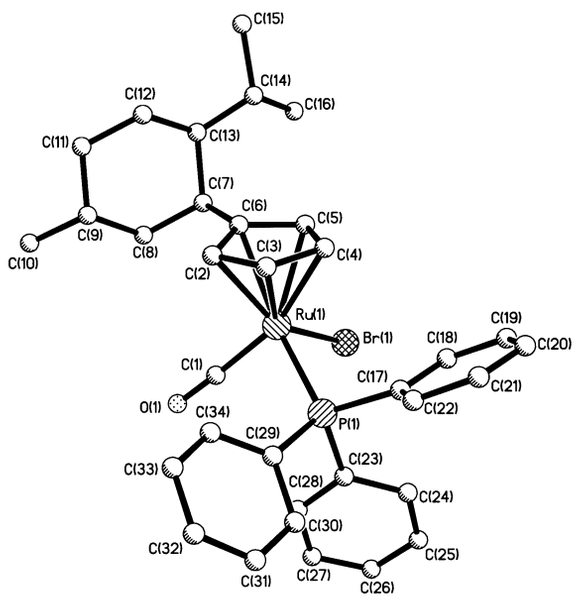


Fig. 1 Molecular structure of (*S*)-[RuBr(CO)(PPh_3)(NmCp)] **3** showing the atom numbering.

The molecule comprises a ruthenium(II) ion symmetrically bonded to a pentahapto neomenthylcyclopentadienyl ligand (r.m.s. deviation of five-membered ring atoms from mean plane 0.022 Å, ruthenium atom 1.87 Å from the mean plane). The other three ligands are a triphenylphosphine (r.m.s. deviations for the three phenyl groups are 0.006, 0.010 and 0.014 Å), a linear carbonyl and a bromine with the bond angles between these basal ligands all close to 90°. According to the Stanley–Baird convention[9] the absolute configuration of the chiral ruthenium atom is *S*. The neomenthyl substituent is positioned such that the bulky iso-propyl group to some extent avoids

Table 2 Selected bond lengths (Å) and angles (°) for (*S*)-[RuBr(CO)(PPh$_3$)(NmCp)] **3**

Ru–Br	2.576(4)	Ru–P	2.315(5)
Ru–C(1)	1.856(15)	Ru–C(2)	2.214(17)
Ru–C(3)	2.191(18)	Ru–C(4)	2.220(21)
Ru–C(5)	2.237(19)	Ru–C(6)	2.308(17)
Ru–Cp	1.87	C(1)–O	1.148(20)
P–C(17)	1.863(16)	P–C(23)	1.806(16)
P–C(29)	1.820(16)	C(2)–C(3)	1.413(27)
C(3)–C(4)	1.418(37)	C(4)–C(5)	1.422(26)
C(5)–C(6)	1.414(26)	C(6)–C(2)	1.477(27)
Br–Ru–P	90.5(1)	Br–Ru–C(1)	90.8(5)
P–Ru–C(1)	91.2(5)	Ru–C(1)–O	177.5(14)
Ru–P–C(17)	110.3(5)	Ru–P–C(23)	116.8(5)
Ru–P–C(29)	116.2(5)	C(17)–P–C(23)	105.6(7)
C(23)–P–C(29)	102.5(7)	C(29)–P–C(17)	104.1(7)

interactions with the basal ligands; thus, the neomenthyl substituent is twisted so that, although the iso-propyl group is on the opposite side of the cyclopentadienyl ring to the metal, it overlays the bromine [torsion angle C(2)–C(6)–C(7)–C(8) −26°]. Presumably the bulky bromine prevents the methyl group on the neomenthyl substituent from hanging directly below the cyclopentadienyl ring. There seem to be no significant interactions between the chiral neomenthyl substituent and the basal ligands. The observred Ru–Br bond length compares well with those reported for [Ru(η^5-C_5H_5)(CO)$_2$Br] (2.536 Å) and Ru(η^5-C_5Me_4Et)(CO)$_2$Br (2.544 Å).[21] The other bond lengths are very similar to those in [RuI(CO)(PPh$_3$)(NmCp)] **4**. In fact, the only significant differences between the structures of the iodo- and the bromo-complexes is that in **3** the neomenthyl substituent lies between the carbonyl and the bromine, almost opposite the bulky triphenylphosphine ligand, whereas in the iodo-complex the combination of the more bulky halide and the triphenylphosphine forces the neomenthyl substituent almost above the carbonyl ligand but displaced slightly towards the triphenylphosphine ligand.

Experimental

NMR spectra were recorded either with a Bruker AM250 spectrometer operating at 250.13 MHz (^{1}H) or at 62.90 MHz (^{13}C) or with a Bruker WH400 spectrometer operating at 400.13 MHz (^{1}H) or at 100.61 MHz (^{13}C), the ^{2}D-lock signal being used as an internal reference in either case. ^{31}P NMR spectra were recorded at 32.44 MHz on a Bruker WP80SY spectrometer with the ^{2}D-lock signal being used as an internal reference. All ^{31}P NMR and ^{13}CNMR spectra were run ^{1}H noise-decoupled. Diastereomeric excesses (d.e.) and reaction stereoselectivities were determined by use of ^{1}H NMR (250.13 MHz) and are quoted to an error of ±2%. Hydroiodic acid was purified as recommended.[22] Hydroiodic acid, hydrobromic acid and hydrochloric acid were standardised by titration against 0.1 M sodium hydroxide solution using phenolphthalein indicator. The epimers of [RuMe(CO)(PPh$_3$)(NmCp)], differing in the configuration at the ruthenium centre, were synthesised as described previously.[7b] All stereochemical studies were carried out in foil-wrapped flasks to exclude light although preliminary studies suggested that light had no effect upon the stereoselectivity of the reactions. The reaction products [RuX(CO)(PPh$_3$)(NmCp)] (X = Cl, Br or I) were identified by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy by reference to the spectra of authentic samples.

Reactions of [RuMe(CO)(PPh$_3$)(NmCp)] with hydrogen halides

These were carried out by a general procedure, described below for HI, using 50 mg of [RuMe(CO)(PPh$_3$)(NmCp)] and the experimental conditions given in Table 1.

Hydroiodic acid (4.25 cm^3 of a 0.2 M degassed aqueous solution, 0.85 mmol) was added to a solution of (*S*)-[RuMe(CO)(PPh$_3$)(NmCp)] (50 mg, 0.082 mmol, 81% d.e.) in dry dichloromethane (30 cm^3) under nitrogen and the mixture stirred at room temperature for 92 hours. The product mixture was washed with aqueous sodium carbonate (0.1 M, 1 × 30 cm^3) and water (3 × 30 cm^3) and the organic extract dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* yielded (*R*)-[RuI(CO)(PPh$_3$)(NmCp)] (59 mg, 100%) with 67% d.e., *i.e.* 83% stereoselectivity.

Similar treatment of (*R*)-[RuMe(CO)(PPh$_3$)(NmCp)] (83% d.e.) yielded (*S*)-[RuI(CO)(PPh$_3$)(NmCp)] in 98% yield and with 80% d.e., *i.e.* 96% stereoselectivity.

Reactions of [RuMe(CO)(PPh$_3$)(NmCp)] with halogens

These were carried out by a similar procedure, described below for I_2, using 50 mg of [RuMe(CO)(PPh$_3$)(NmCp)] and the experimental conditions given in Table 1.

Iodine (23 mg, 0.091 mmol) was added to a degassed solution of (*S*)-[RuMe(CO)(PPh$_3$)(NmCp)] (50 mg, 0.082 mmol, 81% d.e.) in dry dichloromethane (30 cm^3) under nitrogen and the reaction mixture stirred for two hours. Removal of the solvent *in vacuo* gave (*S*)-[RuI(CO)(PPh$_3$)(NmCp)] in quantitative yield with only 5% d.e., *i.e.* 6% stereoselectivity.

Similar treatment of (*R*)-[RuMe(CO)(PPh$_3$)(NmCp)] (83% d.e.) yielded (*S*)-[RuI(CO)(PPh$_3$)(NmCp)] with 4% d.e., *i.e.* 5% stereoselectivity.

Crystal structure determination of (*S*)-[RuBr(CO)(PPh$_3$)(NmCp)] 3

The compound was synthesised as described earlier[7b] and crystallised from dichloromethane–hexane as orange–red prisms.

Crystal data. $C_{34}H_{38}BrOPRu$, $M = 674.63$, crystal dimensions 0.50 × 0.40 × 0.30 mm, orthorhombic, a = 13.076(14), b = 14.175(22), c = 17.251(29) Å, U = 3198(8) Å^3; T = 293 K, D_c = 1.401 g cm^{-3}, space group $P2_12_12_1$ (D_2^4, no. 19), Z = 4; Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 17.90 cm^{-1}, $F(000)$ = 1375.83.

Three-dimensional, room temperature X-ray data were collected on a Nicolet R3 diffractometer in the range $3.5 < 2\theta < 50°$ by the ω scan method. The 2296 independent reflections for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of azimuthal scans. The structure was solved by standard Patterson and Fourier techniques and refined by blocked cascade least squares methods. Hydrogen atoms were placed in predicted positions, and refined in riding mode, with isotropic thermal parameters related to those of the supporting carbon atoms. Refinement converged at a final R of 0.0669 with allowance for anisotropic thermal motion of all non-hydrogen atoms. Complex scattering factors were taken from the program package SHELXTL[23] which, as implemented on the Nova 3 computer, was used throughout the structure solution and refinement. Unit weights were used throughout.

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References

1 (*a*) G. Consiglio, *Chimia*, 2001, **55**, 809; (*b*) A. Yamamoto, *J. Chem. Soc., Dalton Trans.*, 1999, 1027; (*c*) *Advanced Inorganic Chemistry*, eds. A. F. Cotton, G. Wilkinson, M. Bochmann and M. Caros, Wiley, New York, 6th edn., 1998; (*d*) K. Mashima, Y. Nakayama and A. Nakamura, *Adv. Polym. Sci.*, 1997, **133**, 1; (*e*) K. J. Cavell, *Coord. Chem. Rev.*, 1996, **155**, 209; (*f*) M. Bochmann,

Organometallics 1: Complexes with Transition Metal–Carbon σ-Bonds, Oxford University Press, New York, 1994.
2 (*a*) R. Fryatt and S. D. R. Christie, *J. Chem. Soc., Perkin Trans. 1*, 2002, 447; (*b*) B. C. G. Soderberg, *Coord. Chem. Rev.*, 2002, **224**, 171 and references therein.
3 (*a*) S. G. Davies, *Aldrichimica Acta*, 1990, **23**, 31; (*b*) S. G. Davies, *Pure Appl. Chem.*, 1988, **60**, 40 and references therein.
4 (*a*) W. E. Meyer, A. J. Amoroso, M. Jaeger, J. Le Bras, W. T. Wong and J. A. Gladysz, *J. Organomet. Chem.*, 2000, **616**, 44; (*b*) B. J. Boone, D. P. Klein, J. W. Seyler, N. Q. Mendez, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1996, **118**, 2411; (*c*) M. Uemura, *Kagaku Zokan (Kyoto)*, 1995, **124**, 193; (*d*) T. S. Peng, C. H. Winter and J. A. Gladysz, *Inorg. Chem.*, 1994, **33**, 2534; (*e*) E. J. O'Conner, M. Kobayashi, H. G. Floss and J. A. Gladysz, *J. Am. Chem. Soc.*, 1987, **109**, 4837.
5 (*a*) T. C. Flood, K. D. Campbell, H. H. Downs and S. Nakanishi, *Organometallics*, 1983, **2**, 1590; (*b*) S. L. Miles, D. L. Miles, R. Bau and T. C. Flood, *J. Am. Chem. Soc.*, 1978, **100**, 7278; (*c*) T. C. Flood and D. L. Miles, *J. Organomet. Chem.*, 1977, **127**, 33; (*d*) H. Brunner and G. Wallner, *Chem. Ber.*, 1976, **109**, 1053; (*e*) T. G. Attig and A. Wojcicki, *J. Am. Chem. Soc.*, 1974, **96**, 262; (*f*) P. Reich-Rohrwig and A. Wojcicki, *Inorg. Chem.*, 1974, **13**, 2457.
6 (*a*) M. Tilset, G. S. Boder, D. R. Senn, J. A. Gladysz and V. D. Parker, *J. Am. Chem. Soc.*, 1987, **109**, 7551; (*b*) P. C. Heah, A. T. Patton and J. A. Gladysz, *J. Am. Chem. Soc.*, 1986, **108**, 1185; (*c*) J. H. Merrifield, J. M. Fernández, W. E. Buhro and J. A. Gladysz, *Inorg. Chem.*, 1984, **23**, 4022.
7 (*a*) K. Tabatabaeian, P. Downing, H. Adams, B. E. Mann and C. Lindsay, to be submitted; (*b*) C. Lindsay, E. Cesarotti, H. Adams, N. A. Bailey and C. White, *Organometallics*, 1990, **9**, 2594; (*c*) E. Cesarotti, M. Angoletta, N. P. C. Walker, M. B. Hursthouse, R. Vefghi and C. White, *J. Organomet. Chem.*, 1985, **286**, 343; (*d*) E. Cesarotti, A. Chiesa, G. F. Ciani, A. Sironi, R. Vefghi and C. White, *J. Chem. Soc., Dalton Trans.*, 1984, 653.
8 H. Brunner, K. Fisch, P. G. Jones and J. Salbeck, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1521.
9 K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, 1975, **97**, 6598.
10 (*a*) T. R. Ward, O. Schafer, C. Daul and P. Hofmann, *Organometallics*, 1997, **16**, 3207; (*b*) P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 536.
11 (*a*) M. F. Joseph, J. A. Page and M. C. Baird, *Organometallics*, 1984, **3**, 1749; (*b*) M. F. Joseph, J. A. Page and M. C. Baird, *Inorg. Chim. Acta*, 1982, **64**, L121 and references therein.
12 (*a*) H. Brunner, *Eur. J. Inorg. Chem.*, 2001, 905; (*b*) H. Brunner, *Angew. Chem., Int. Ed.*, 1999, **38**, 1194.
13 J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, 1970, **92**, 5852.
14 G. Wright and R. J. Mawby, *J. Organomet. Chem.*, 1971, **29**, C29.
15 (*a*) V. V. Grushin, *Acc. Chem. Res.*, 1993, **26**, 279; (*b*) A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 3929; (*c*) W. D. Jones and F. J. Feher, *Organometallics*, 1983, **2**, 562; (*d*) J. Halpern, *Acc. Chem. Res.*, 1982, **15**, 332; (*e*) J. R. Norton, *Acc. Chem. Res.*, 1979, **12**, 139.
16 J. M. Fernández and J. A. Gladysz, *Inorg. Chem.*, 1986, **25**, 2.
17 N. De Luca and A. Wojcicki, *J. Organomet. Chem.*, 1980, **193**, 359.
18 (*a*) L. J. Johnston and M. C. Baird, *Organometallics*, 1988, **7**, 2469; (*b*) L. J. Sanderson and M. C. Baird, *J. Organomet. Chem.*, 1986, **307**, C1.
19 I. W. Nowell, K. Tabatabaian and C. White, *J. Chem. Soc., Chem. Commun.*, 1979, 547.
20 (*a*) E. J. O'Conner, M. Kobayashi, H. G. Floss and J. A. Gladysz, *J. Am. Chem. Soc.*, 1987, **109**, 837; (*b*) W. N. Rogers and M. C. Baird, *J. Organomet. Chem.*, 1979, **182**, C65; (*c*) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, 1979, **101**, 3043; (*d*) S. Komiya, T. Ito, M. Cowie, A. Yamamoto and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 3874; (*e*) J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 333; (*f*) M. P. Periasamy and H. M. Walborsky, *J. Am. Chem. Soc.*, 1975, **97**, 5930; (*g*) J. A. Labinger, D. W. Hart, W. E. Seibert III and J. Schwartz, *J. Am. Chem. Soc.*, 1975, **97**, 3851; (*h*) J. F. Normant, G. Cahiez, C. Chuit and J. Villieras, *J. Organomet. Chem.*, 1974, **77**, 269; (*i*) B. E. Mann, B. L. Shaw and N. Tucker, *Chem. Commun.*, 1970, 1333.
21 H. Adams, N. A. Bailey and C. White, *Inorg. Chem.*, 1983, **22**, 1155.
22 G. Bauer, ed., *Handbook of Preparative Inorganic Chemistry*, 2nd edn., vol. 1, Academic Press, London, 1967, p. 286.
23 G. M. Sheldrick, SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures and Diffraction Data, University of Göttingen, Göttingen, FRG, 1978; revision 4.1, Aug 1983.