Isomerization of Diastereoisomeric Alkene Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+$; the Alkene Enantioface bound to the Metal can 'flip' without Alkene Dissociation

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Deuterium labelling experiments show that the title reaction is intramolecular, and does not proceed by rotation of the =CHR terminus; a mechanism involving a C–H 'σ bond complex' is proposed.

The diastereoisomeric monosubstituted alkene complexes (*RS,SR*)- and (*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+ X^-$, $(\mathbf{1})^+ X^-$, differ in the alkene enantioface bound to rhenium, as shown in Newman-type projections (**I**) and (**II**) (Scheme 1).[1] We recently reported that these complexes equilibrate† to *ca.* 95:5 (*RS,SR*)/(*RR,SS*) diastereoisomer mixtures at 95 °C in chlorobenzene. At first glance, interconversion seemingly necessitates alkene dissociation, rotation, and reattachment. However, alternative pathways can be visualized. In particular, evidence has recently been obtained for 'σ bond complexes' of alkenes as reaction intermediates.[2] In this communication, we show that diastereoisomers of $(\mathbf{1})^+ X^-$ interconvert *without* alkene dissociation, and in all likelihood by a most unusual reaction co-ordinate.

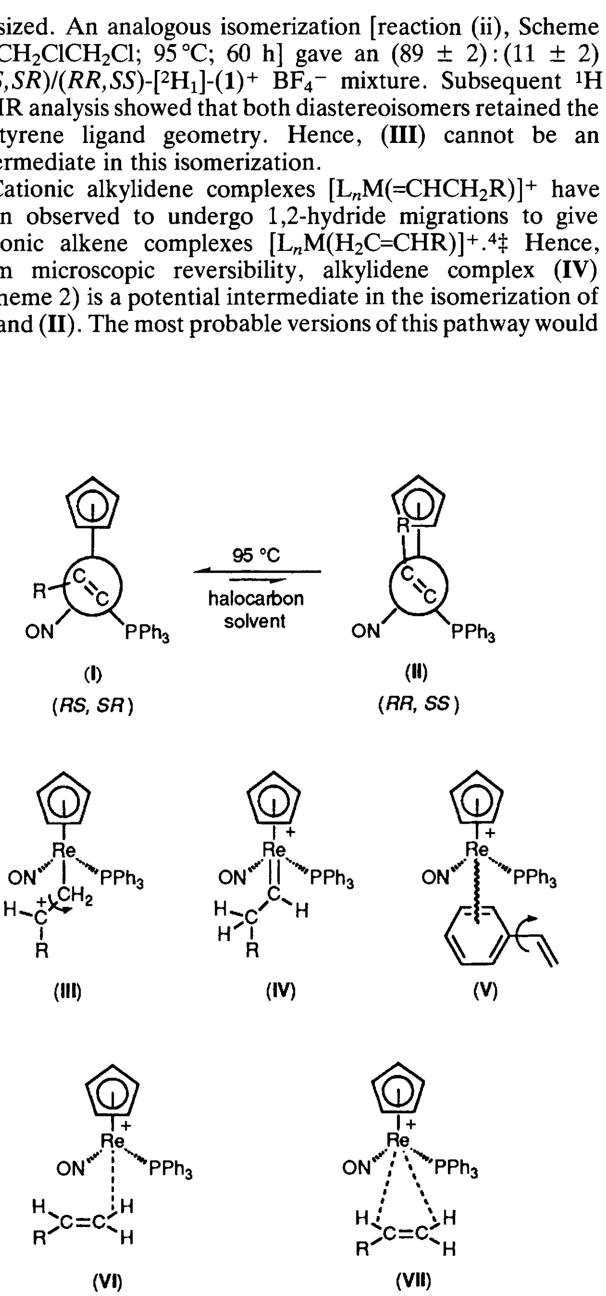
The styrene complex (*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHPh)]^+ BF_4^-$, (*RR,SS*)-$(\mathbf{1a})^+ BF_4^-$,[1b] was obtained as a pure diastereoisomer as previously described, and then heated in CD_2ClCD_2Cl at 95 °C (0.02 M; 48 h; septum-sealed NMR tube) in the presence of 10 equivalents of $[^2H_8]$styrene, $C_6D_5CD{=}CD_2$ [reaction (i), Scheme 2]. Isomerization† occurred to give an (89 ± 2) : (11 ± 2) (*RS,SR*)/(*RR,SS*)-$(\mathbf{1a})^+ BF_4^-$ diastereoisomer mixture, which was subsequently isolated in >99% yield. Careful ^1H NMR analysis of the well resolved 'vinylic' protons did not reveal any deuterium incorporation, and a FAB mass spectrum showed deuterium to be present at the natural abundance level. Thus, isomerization of (*RR,SS*)-$(\mathbf{1a})^+ BF_4^-$ must occur without styrene dissociation.

Identical results were achieved in similar experiments with other alkene complexes. Also, when the above isomerization of (*RR,SS*)-$(\mathbf{1a})^+BF_4^-$ was repeated in the presence of $P(C_6D_5)_3$ (2 equiv.), no label was incorporated into (*RS,SR*)-$(\mathbf{1a})^+ BF_4^-$ (at 55% conversion).

We next sought to address the possibility that (**I**) and (**II**) might interconvert by a configurational process involving *rhenium*. Both diastereoisomers of $(\mathbf{1a})^+ BF_4^+$ are readily available in optically active form, and optical purities are easily assayed with the chiral NMR shift reagent (+)-$Eu(hfc)_3$.[1b] Thus, (−)-(*SS*)-$(\mathbf{1a})^+ BF_4^-$ (≥98% enantiomeric excess, e.e.) was heated in PhCl at 95 °C (72 h). Subsequent ^1H NMR analysis showed *retention* of configuration at rhenium, with both (−)-(*SR*)- and (−)-(*SS*)-$(\mathbf{1a})^+ BF_4^-$ [(84 ± 2) : (16 ± 2)] being formed in ≥98% e.e. Hence, the isomerization pathway involves the alkene-based stereogenic centre.

We next sought to probe the possibility that isomerization might occur *via* the 'slipped,' carbocationic species (**III**) (Scheme 1). This pathway requires the *Z/E* scrambling of any alkene substituents. Hence, (*E*)-$[^2H_1]$styrene, (*E*)-PhCH=CHD, was prepared.[3] The corresponding labelled complex, (*E*)-(*RR,SS*)-$[^2H_1]$-$(\mathbf{1a})^+ BF_4^-$, was then synthesized. An analogous isomerization [reaction (ii), Scheme 2; CH_2ClCH_2Cl; 95 °C; 60 h] gave an (89 ± 2) : (11 ± 2) (*RS,SR*)/(*RR,SS*)-$[^2H_1]$-$(\mathbf{1})^+ BF_4^-$ mixture. Subsequent ^1H NMR analysis showed that both diastereoisomers retained the *E*-styrene ligand geometry. Hence, (**III**) cannot be an intermediate in this isomerization.

Cationic alkylidene complexes $[L_nM({=}CHCH_2R)]^+$ have been observed to undergo 1,2-hydride migrations to give cationic alkene complexes $[L_nM(H_2C{=}CHR)]^+$.[4]‡ Hence, from microscopic reversibility, alkylidene complex (**IV**) (Scheme 2) is a potential intermediate in the isomerization of (**I**) and (**II**). The most probable versions of this pathway would



Scheme 1. Some possible intermediates in the equilibration of alkene complex diastereoisomers (I) and (II).

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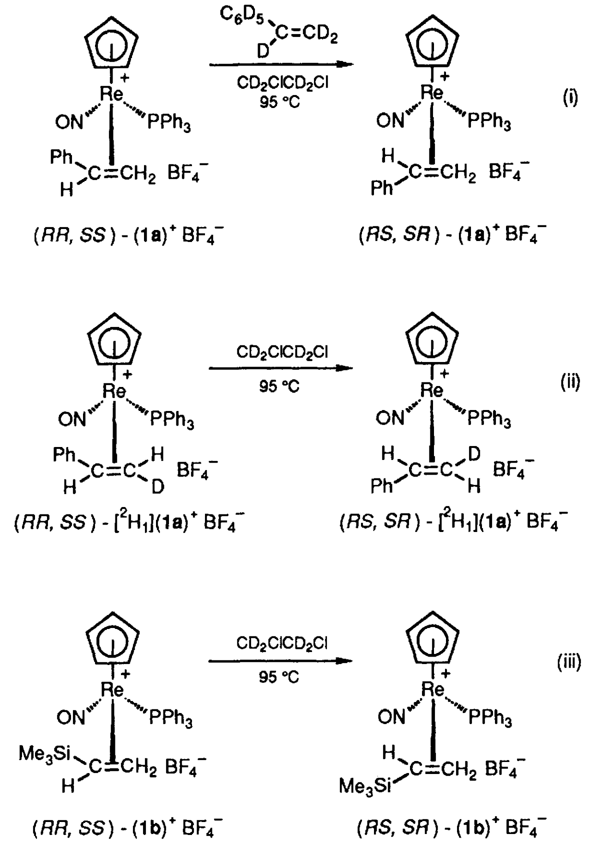
† In this paper, the term 'equilibration' is used to designate reactions that are purposefully run to thermal equilibrium, and 'isomerization' for those that may be halted short of equilibrium. Many mechanistic experiments are in the latter category. Quantitative equilibrium data will be given in our full paper.

‡ The propylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHCH_2Me)]^+ X^-$ cleanly isomerizes (65—85 °C; C_6D_5Cl) to a mixture of (*RS,SR*)/(*RR,SS*)-diastereoisomers of the propene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHMe)]^+X^-$; G. S. Bodner and C. Roger, unpublished data, University of Utah.



Scheme 2. Representative alkene complex isomerization experiments.

involve migration of one $=CH_2$ hydrogen to the $=CHR$ terminus, followed by return of the other hydrogen. This would scramble any deuterium label. Thus, $[^2H_2]$styrene, $PhCH=CD_2$, was prepared.[3] The corresponding labelled complex, (*RR,SS*)-$[^2H_2]$-(**1a**)$^+$ BF_4^-, was then synthesized. An analogous isomerization (CH_2ClCH_2Cl; 95 °C; 36 h) gave an (88 ± 2):(12 ± 2) (*RS,SR*)/(*RR,SS*)-$[^2H_2]$-(**1a**)$^+$ BF_4^- mixture. Subsequent ^1H and ^2H NMR analysis showed that both $=CD_2$ positions retained their original deuterium level, with no leakage into the $=CHR$ terminus.

Finally, we sought to address the possibility that styrene complex isomerization might occur *via* an η^2-arene intermediate such as (**V**) (Scheme 1).§ A 180° rotation of the vinyl group in (**V**), followed by a return of rhenium to the vinyl moiety, would interconvert diastereoisomers. We were unable to devise a direct probe for this pathway. Thus, a substrate lacking phenyl substituents (and allylic protons)¶ was sought. Reaction of the dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+$ BF_4^- (**2**) and trimethylsilylethylene, under conditions analogous[1b] to those used to prepare (**1a**)$^+$ BF_4^-, gave $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CHSiMe_3)]^+$ BF_4^-, (**1b**)$^+$ BF_4^-, as a (68 ± 2):(32 ± 2) mixture of (*RS,SR*)/(*RR,SS*)-diastereoisomers.|| Subsequent chromatography gave pure (*RR,SS*)-(**1b**)$^+$ BF_4^-, which was then heated at 95 °C in CD_2ClCD_2Cl (24 h). Isomerization to a >99:<1 (*RS,SR*)/(*RR,SS*)-(**1b**)$^+$ BF_4^- mixture occurred [reaction (iii), Scheme 2], as assayed by ^1H and ^{31}P NMR spectroscopy. Work-up gave (*RS,SR*)-(**1b**)$^+$ BF_4^- in >99% yield. Hence, a phenyl substituent is not required for isomerization.

In summary, the constraints imposed by the preceding experiments indicate that unusual, heretofore-unrecognized mechanisms are operative in the isomerization of diastereoisomeric rhenium alkene complexes (**1**)$^+$$BF_4^-$. We suggest that the results are best accommodated by the intermediacy of 'σ bond complexes' such as (**VI**) (Scheme 1; unidentate) or (**VII**) (bidentate), either as energy minima or transition states. Similar species have recently been proposed as intermediates in the oxidative addition of ethylene to iron atoms[2a] and the co-ordinatively unsaturated iridium fragment $[(\eta^5\text{-}C_5Me_5)Ir(PMe_3)]$.[2b] Additional mechanistic experiments, including rate studies, are in progress and will be reported in our full paper.

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References

1 (a) G. S. Bodner, J. M. Fernández, A. M. Arif, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1988, **110**, 4082; (b) G. S. Bodner, T.-S. Peng, A. M. Arif, and J. A. Gladysz, *Organometallics*, 1990, **9**, 1191.

2 (a) Z. H. Kafafi, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.*, 1985, **107**, 7550; (b) P. O. Stoutland and R. G. Bergman, *ibid.*, 1988, **110**, 5732; (c) see also M. Brookhart, M. L. H. Green, and L.-L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.

3 J. A. Labinger, D. W. Hart, W. E. Seibert III, and J. Schwartz, *J. Am. Chem. Soc.*, 1975, **97**, 3851.

4 Lead references: (a) R. S. Bly, R. K. Bly, M. M. Hossain, L. Leboida, and M. Raja, *J. Am. Chem. Soc.*, 1988, **110**, 7723; (b) M. Brookhart, J. R. Tucker, and G. R. Husk, *ibid.*, 1983, **105**, 258; (c) W. G. Hatton and J. A. Gladysz, *ibid.*, 1983, **105**, 1846.

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§ The η^2-benzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}C_6H_6)]^+$ BF_4^- can be generated in CH_2Cl_2 at −78 °C, but decomposes to (**2**) above −40 °C; S. K. Agbossou, G. S. Bodner, A. T. Patton, and J. A. Gladysz, *Organometallics*, 1990, **9**, 1184.

¶ When 'allylic' protons are present on the alkene ligand, additional isomerization mechanisms are possible. These base-catalysed pathways will be described in our full paper. See G. S. Bodner, K. Emerson, R. D. Larsen, and J. A. Gladysz, *Organometallics*, 1989, **8**, 2399.

|| Complex (**1b**)$^+$ BF_4^- was characterized by IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy, and microanalysis. Properties resembled those of (**1a**)$^+$ BF_4^-.[1b] The t-butylethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CHCMe_3)]^+BF_4^-$ was also synthesized [(84 ± 2):(16 ± 2) (*RS,SR*)/(*RR,SS*) mixture], but the minor diastereoisomer was not readily separable.