Nucleophilic Additions to the Chiral Rhenium Alkene Complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHR)]BF_4$ (R = H, Me, CH_2CH_2Me, Ph or CH_2Ph): Regio-, Diastereo- and Enantio-selectivities†

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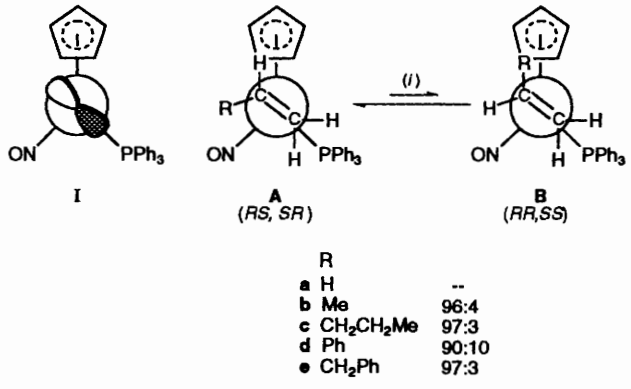
Reactions of alkene complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHR)]BF_4$ **1** (R = H **a**, Me **b**, CH_2CH_2Me **c**, Ph **d** or CH_2Ph **e**) and $LiCuMe_2$ in tetrahydrofuran (thf) at −80 °C gave the primary, β-branched alkyl complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CHMeR)]$ **2** (79–99%). No secondary alkyl complexes derived from additions to the unsubstituted $=CH_2$ termini were detected. Product diastereomer and enantiomer ratios matched those of the reactants. Thus, the additions are regiospecific, diastereospecific and enantiospecific. A chemical correlation involving $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\{CH_2CH(CD_3)Me\}]$ and a crystal structure determination [(*SR,RS*)-**2e**·0.5C_6H_{14}] show that attack occurs on the C=C face *anti* to the rhenium. Reactions of **1a** or **1b** (in thf) with NaOMe–MeOH gave predominantly the 2-methoxyalkyl complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\{CH_2CH(OMe)R\}]$ (R = H **4a** or Me **4b**) (92–97%). Analogous reactions of **1c** or **1d** gave 81–77:19–23 mixtures of **4c** or **4d** and the alkenyl complexes (*E*)-$[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH{=}CHR)]$ (85–71%). A similar reaction of **1e** gave mainly the allyl complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CH{=}CHPh)]$.

Metal-co-ordinated alkenes are strongly activated towards nucleophilic attack.[1–6] This well-known phenomenon plays a key role in several important catalytic processes,[1a] and has been the subject of detailed theoretical investigations.[4] Both stoichiometric and catalytic reactions see extensive use in organic syntheses, generally in cases that involve attack upon the C=C face *anti* to the metal.[1,5] However, there have been relatively few applications in enantioselective organic syntheses.[6]

We have conducted detailed studies of adducts of alkenes and the chiral rhenium Lewis acid $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)]^+$ **I**.[7–10] This sixteen-valence-electron fragment is also a strong π donor, with the d-orbital highest occupied molecular orbital (HOMO) depicted in Scheme 1. Importantly, **I** binds one enantioface of several classes of prochiral alkenes with very high thermodynamic selectivities.[7,8b,c] For example, monosubstituted alkene complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHR)]BF_4$ **1** can exist as two configurational diastereomers, as illustrated with the idealized structures **A** (*RS,SR*) and **B** (*RR,SS*) in Scheme 1.‡[7] The Re–(C=C) conformations maximize overlap of the HOMO of **I** and the C=C π* acceptor orbitals, while directing the larger =CHR terminus *anti* to the bulky PPh_3 ligand. The *RR,SS* diastereomer **B**, in which the =CH*R* substituent is *syn* to the cyclopentadienyl ligand, is less stable than the *RS,SR* diastereomer **A**, in which the =CH*R* substituent is *syn* to the small nitrosyl ligand. Representative equilibrium ratios are given in Scheme 1.[7b]

Both diastereomers of the monosubstituted alkene complexes **1** are generally available in diastereomerically and enantiomerically pure form. Thus, we sought to convert the co-ordinated alkenes to other ligands and ultimately optically active organic compounds. We anticipated, based upon precedent with related cyclopentadienyl iron complexes,[1,2,3c] that nucleophiles (Nu)



Scheme 1 The d orbital HOMO of the pyramidal 16-valence electron rhenium fragment $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)]^+$ **I** and idealized structures of diastereomeric monosubstituted alkene complexes of **I**: (*i*) 95–100 °C chlorohydrocarbon solvent

would preferentially add to the substituted =CHR terminus, and from a direction *anti* to rhenium, to give the primary, β-branched alkyl complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\{CH_2CH(Nu)R\}]$. We were also interested in several allied mechanistic issues, such as the factors affecting partitioning between alkene ligand addition and deprotonation with alkoxides,[9] and diastereoselection in additions to related π-aldehyde complexes.[11]

In this paper, we report (*i*) regiospecific§[12] additions of the

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

‡ The *R/S* nomenclature conventions have been detailed previously.[8b] All isomer ratios are normalized to 100, and error limits on each integer are ± 2; *e.g.*, 95:5 ≡ (95 ± 2):(5 ± 2).

§ Our usage of regiospecific follows the original definition.[12a] However, a cogent modification has been recently proposed,[12b] and our usage of diastereospecific and enantiospecific follows currently accepted definitions.[12b] In Scheme 3, enantiospecificity would have been best established by conducting one of the additions with an enantiomeric reactant, and isolating the enantiomeric product. However, the conversion of one reactant enantiomer to a non-racemic product would seem to require reciprocal behaviour for the other.

organocopper nucleophile $LiCuMe_2$ to the =CHR termini of monosubstituted alkene complexes **1**, (*ii*) data that show these additions to be diastereo- and enantio-specific,§[12] (*iii*) a chemical correlation and a crystal structure that establish attack upon the C=C face *anti* to rhenium, and (*iv*) complementary results with the oxygen nucleophile NaOMe, which in some cases also effects vinylic or allylic deprotonation of the alkene ligand. A portion of this work has been communicated.[10]

Results

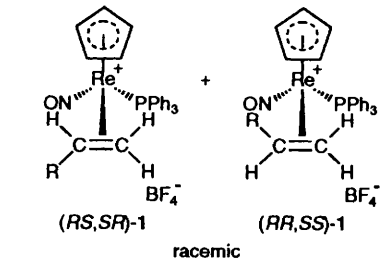
(1) *Scope of* $LiCuMe_2$ *Addition.*—As a starting point, the parent ethylene complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CH_2)]BF_4$ **1a**[13] and $LiCuMe_2$ (2 equivalents) were combined in tetrahydrofuran (thf) at −80 °C. Work-up gave the previously characterized *n*-propyl complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CH_2Me)]$ **2a**[14] in 79% yield (Scheme 2). The IR and ^1H NMR spectra were identical to those of an authentic sample. This simple reaction shows that alkene complexes of **I** are activated towards nucleophilic attack.

Next, a 95:5 mixture of (*RS,SR*):(*RR,SS*) diastereomers of the propene complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHMe)]BF_4$ **1b**[7a] and $LiCuMe_2$ were similarly treated. Work-up gave the previously characterized isobutyl complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CHMe_2)]$ **2b**[14] in 87% yield. This product is, as expected, derived from addition to the =CHMe terminus of co-ordinated propene. The crude reaction mixture was carefully analysed by ^1H NMR for the opposite regioisomer, the *sec*-butyl complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CHMeCH_2Me)]$. However, the triplet that would be expected for the CH_2CH_3 moiety (δ 0.80–0.85; detection limit < 2%) was not observed.

Analogous reactions were conducted with the pentene complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHCH_2CH_2Me)]BF_4$ **1c** [95:5 (*RS,SR*)/(*RR,SS*)],[7a] the styrene complex (*RS,SR*)-$[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHPh)]BF_4$ **1d**,[7a] and the allylbenzene complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHCH_2Ph)]BF_4$ **1e** [97:3 (*RS,SR*)/(*RR,SS*)].[7a] As summarized in Scheme 2, work-ups gave the new alkyl complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CHMeCH_2CH_2Me)]$ **2c** [82%; 95:5 (*SR,RS*)/(*SS,RR*)], (*SR,RS*)-$[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CHMePh)]$ (*SR,RS*)-**2d** (99%), and $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CHMeCH_2Ph)]$ **2e** [83%; 98:2 (*SR,RS*)/(*SS,RR*)]. No regioisomers were detected by ^1H or ^{31}P NMR. Hence, the addition of $LiCuMe_2$ to the monosubstituted alkene complexes **1** is, within detection limits, regiospecific. Complexes **2c**–**2e** were characterized by microanalysis, and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy (Experimental section). Configurations were assigned as described below.

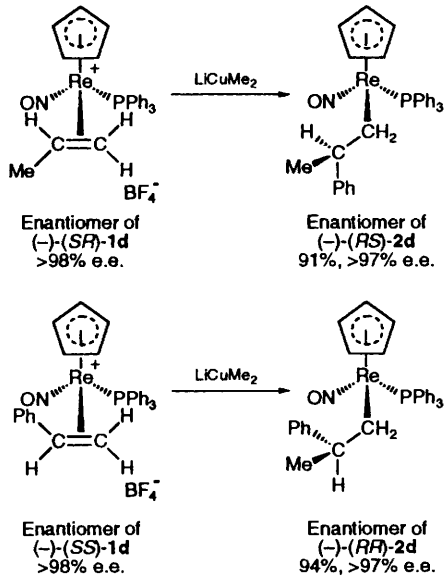
Significantly, the diastereomer ratios of isolated **2c**–**2e** closely matched those of precursors **1c**–**1e** (Scheme 2). This strongly suggested that $LiCuMe_2$ addition was also diastereospecific.§ As a test, the less stable styrene complex diastereomer, (*RR,SS*)-**1d**,[7a] was similarly treated (**1d'**, Scheme 2). Work-up gave (*SS,RR*)-**2d**, the diastereomer *opposite* to that obtained from (*RS,SR*)-**1d**, in >99% yield. Hence, addition is diastereospecific, as illustrated in Scheme 3 for the corresponding reactions with enantiomerically pure substrates (see below).

(2) *Stereochemistry of* $LiCuMe_2$ *Addition.*—We sought to assign configurations to the addition products **2**. The diastereotopic methyl groups of the isobutyl complex **2b** gave a single ^1H NMR signal (δ 0.913 d, $CDCl_3$), but well-separated ^{13}C NMR signals at δ 25.7 and 28.2 (50:50). Thus, a 95:5 mixture of (*RS,SR*):(*RR,SS*) diastereomers of **1b** was treated with the deuteriated organocopper nucleophile $MgICu(CD_3)_2$ (Scheme 4). Work-up gave the trideuterioisobutyl complex



	R	(*RS,SR*)-1:(*RR,SS*)-1	(*SR,RS*)-2:(*SS,RR*)-2	Yield
a	H	--	--	79%
b	Me	95:5	--	87%
c	CH_2CH_2Me	95:5	95:5	82%
d	Ph	>99:<1	>99:<1	99%
d'	Ph	<1:>99	<1:>99	>99%
e	CH_2Ph	97:3	98:2	83%

Scheme 2 Reactions of monosubstituted alkene complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHR)]BF_4$ **1** with $LiCuMe_2$; (*i*) $LiCuMe_2$, thf, −80 °C

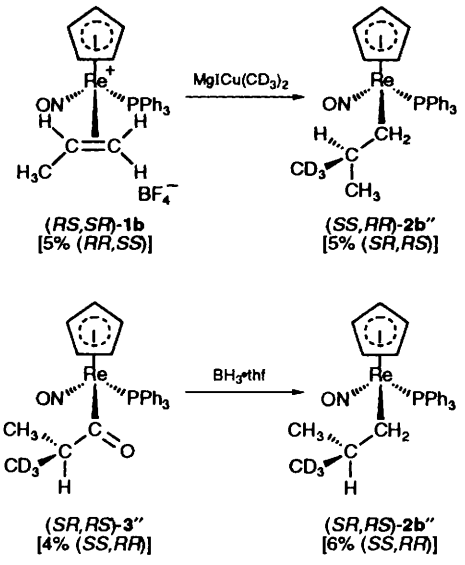


Scheme 3 Regio-, diastereo- and enantio-specific addition to the styrene complex **1d**; to facilitate comparison with other schemes, enantiomers of the complexes employed are depicted

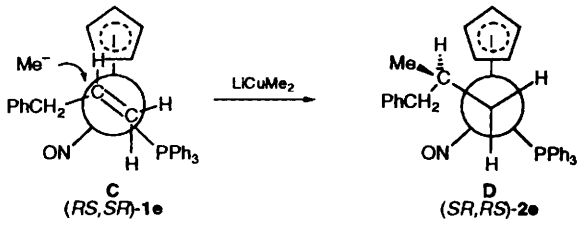
$[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\{CH_2CH(CD_3)Me\}]$ **2b″** in 96% yield. Integration of the ^{13}C NMR signals at δ 25.7 and 28.0* showed that **2b″** was a 95:5 mixture of diastereomers, in accord with a diastereospecific addition. A similar reaction with a 68:32 mixture of (*RS,SR*):(*RR,SS*) diastereomers of **1b** gave **2b″** that was a 70:30 mixture of diastereomers.

§ See footnote on p. 1857.

* The CD_3 resonances, which would be deuterium coupled (septet, $^1J_{CD}$ *ca.* 19 Hz), lacking nuclear Overhauser enhancement, and shifted downfield by *ca.* 1 ppm, were not observed.



Scheme 4 Reactions establishing the stereochemistry of addition to propene complex **1b**



Scheme 5 Addition of $LiCuMe_2$ to the allylbenzene complex (*RS,SR*)-**1e**

Independent syntheses of the diastereomers of **2b″** were next attempted. Importantly, the trideuterioisobutyryl complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\{COCHMe(CD_3)\}]$ **3″** had been previously prepared in diastereomerically enriched form by a route that allows assignment of configuration.[15] Also, acyl complexes of **I** are reduced by BH_3·thf to the corresponding alkyl complexes with retention at rhenium.[16] Accordingly, a 96:4 mixture of the (*SR,RS*):(*SS,RR*) diastereomers of **3″**[15b] was treated with BH_3·thf (Scheme 4). Work-up gave the trideuterioisobutyl complex **2b″** in 91% yield as a 94:6 (*SR,RS*):(*SS,RR*) diastereomer mixture, as assayed by integration of the ^{13}C NMR signals at δ 28.0 and 25.7.* Hence, the addition of $MgICu(CD_3)_2$ to (*RS,SR*)-**1b** and (*RR,SS*)-**1b** gives (*SS,RR*)-**2b″** and (*SR,RS*)-**2b″**, respectively. This requires attack on the C=C face *anti* to the rhenium.

Crystallographic proof of configuration was also sought. Thus, the 2-methyl-3-phenylpropyl complex (*SR,RS*)-**2e** derived from the allylbenzene complex (*RS,SR*)-**1e** (Scheme 5) was crystallized to diastereomeric purity. X-Ray data were collected, as summarized in Table 1, and refinement, described in the Experimental section, gave the structure shown in Fig. 1(*a*). The aliphatic protons on the alkyl ligand were located (but not included in the refinement). Atomic coordinates and selected bond lengths, bond angles and torsion angles are given in Tables 2 and 3.

Fig. 1 clearly shows that when rhenium has an *S* configuration, the carbon stereocentre has a *R* configuration. This relative stereochemistry requires nucleophilic attack on the C=C face of (*RS,SR*)-**1e** *anti* to the rhenium, as shown in Scheme 5. Furthermore, the Re–C(1)–C(2) conformation in the crystal closely corresponds to that which would be expected kinetically, as illustrated in Newman projection **D**. In this context, the Re–C(1) conformation directs the $CHMeCH_2Ph$ moiety into the least hindered interstice between the small

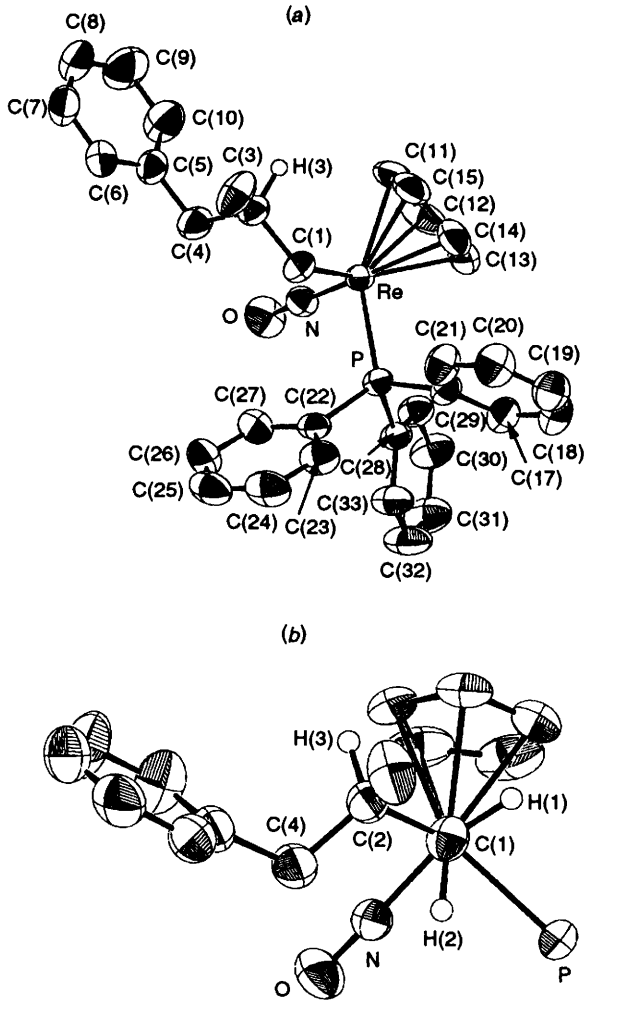


Fig. 1 (*a*) The crystal structure of (*SR,RS*)-**2e** with the numbering scheme; (*b*) Newman-type projection

nitrosyl and the medium cyclopentadienyl ligands, consistent with many previous crystal structures in this series of compounds.[17,18] The C(1)–C(2) conformation directs the smallest C(2) substituent, H(3), at the cyclopentadienyl ligand, in accord with other structures[17d] and diastereomeric equilibria[19] analysed previously.

(3) *Non-racemic Substrates.*—Since we envisioned eventual applications of the preceding additions in enantioselective organic syntheses, exploratory reactions with non-racemic reactants were conducted. Thus, the optically active styrene complexes (−)-(*SR*)-**1d** and (−)-(*SS*)-**1d** (>98% e.e.)[7a] were treated with $LiCuMe_2$ as shown in Scheme 3. Work-ups gave the optically active 2-phenylpropyl complexes (−)-(*RS*)-**2d** and (−)-(*RR*)-**2d**, respectively $\{[\alpha]_{589}^{25} - (180 \pm 3)$ and $-(126 \pm 3)°$, 0.44 mg cm^{-3} $CH_2Cl_2\}$,[20] in 91 and 94% yields.

Data on the enantiomeric purities of these products were sought. First, $CDCl_3$ solutions of racemic (*SR,RS*)-**2d** and (*SS,RR*)-**2d** were treated with the chiral NMR shift reagent (+)-[Eu(hfc)$_3$] {Hhfc = 3-trifluoromethylhydroxymethylene camphor (3-trifluoromethylhydroxymethylene-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one)} (3 equivalents). The cyclopentadienyl ^1H NMR signals exhibited near-baseline resolution (≈0.01 ppm). Next, (−)-(*RS*)-**2d** and (−)-(*RR*)-**2d** were similarly combined with (+)-[Eu(hfc)$_3$] in $CDCl_3$. No signals due to the opposite enantiomers were detected. When a $CDCl_3$ solution of (−)-(*RR*)-**2d** was spiked with 3% of the racemate, giving a

Table 1 Summary of the crystallographic data for (*SR,RS*)-[Re(η^5-C_5H_5)(NO)(PPh_3)($CH_2CHMeCH_2Ph$)]·0.5C_6H_{14} (*SR,RS*)-**2e**·0.5C_6H_{14}

Molecular formula	$C_{33}H_{33}NOPRe$
Formula weight	719.90
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.964(1)
b/Å	11.137(1)
c/Å	14.972(1)
β/°	101.92(1)
U/Å^3	1613.52
Z	2
D_c/g cm^{-3}	1.482 (15 °C)
D_{obs}/g cm^{-3} (CCl_4–CH_2I_2)	1.465 (22 °C)
Crystal dimensions/mm	0.27 × 0.21 × 0.18
λ(Cu-Kα)/Å	1.540 56
Data collection method	θ–2θ
Scan speed/° min^{-1}	Variable
Range of indices (*h*, *k*, *l*)	0–11, −13 to 13, −17 to 17
Scan range	0.8 + 0.14 tan θ
2θ Range/°	4.0–130.0
No. of reflections between standards	1 X-Ray hour
Total unique data	5717
Observed data, $I > 3\sigma(I)$	5484
μ/cm^{-1}	77.61
Minimum, maximum transmission (%)	57.05, 99.87
No. of variables	361
$R\{\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|\}$	0.0328
$R'\{[\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}\}$	0.0429
Weighting scheme, *w*	$1/\sigma(F)^2$
Goodness of fit	1.190
Maximum Δ/σ	0.014
Maximum Δρ/e Å^{-3}	0.630
F(000)	672

sample of ≈97% e.e., a resonance for the enantiomer (+)-(*SS*)-**2d** was easily observed. Hence, the optical purities of (−)-(*RS*)-**2d** and (−)-(*RR*)-**2d** are >97% e.e. This demonstrates that $LiCuMe_2$ addition is highly enantioselective, and in all probability enantiospecific.

(4) *Reactions with* NaOMe.—Methoxide ion has previously been observed to add to co-ordinated alkenes.[3] However, the bulkier alkoxide KOBu^t and monosubstituted alkene complexes **1** react to give either alkenyl or allyl complexes arising from vinylic or allylic deprotonation.[9] Product ratios are sensitive functions of the substrate and conditions. The former pathway, which was previously without precedent, has been the subject of a detailed mechanistic investigation.[9b] We wondered which of these diverse reactivity modes, which are summarized in Scheme 6, would be found with NaOMe.

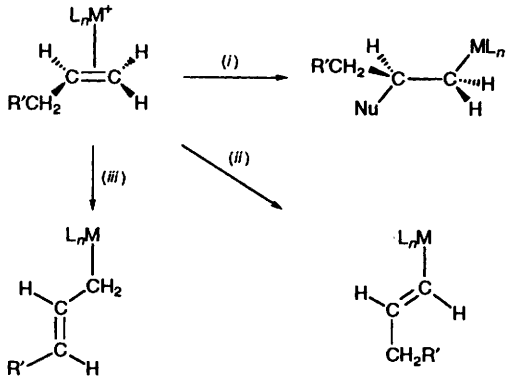
First, a thf solution of the ethylene complex **1a** and a MeOH solution of NaOMe (2 equivalents) were combined in an NMR tube at room temperature. A ^{31}P NMR spectrum showed the reaction to be complete within 10 minutes. Work-up gave the 2-methoxyethyl complex [Re(η^5-C_5H_5)(NO)(PPh_3)(CH_2CH_2-OMe)] **4a** in 92% yield (Scheme 7). At no stage was any trace of the previously reported ethenyl complex [Re(η^5-C_5H_5)(NO)(PPh_3)(CH=CH_2)] **5a**[15b] detected. Complex **4a** was characterized as described for the other new compounds above.

The propene complex **1b** [68:32 (*RS,SR*:*RR,SS*)] and NaOMe–MeOH reacted similarly (Scheme 7). Work-up gave a >99% yield of a 97:3 mixture of the 2-methoxypropyl complex [Re(η^5-C_5H_5)(NO)(PPh_3){CH_2CH(OMe)Me}] **4b** and the known propenyl complex (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)-(CH=CHMe)] **5b**.[15b] Complex **4b** was a 70:30 mixture of (*SR,RS*):(*SS,RR*) diastereomers, the configurations of which were assigned by analogy to the $LiCuMe_2$ additions. Attempted crystallization gave **4b** as a 77:23 (*SR,RS*):(*SS,RR*) mixture. Interestingly, when this sample was treated with HBF_4·OEt_2, the propene complex **1b** was regenerated as a 77:23

Table 2 Atomic coordinates for located atoms in (*SR,RS*)-**2e**·0.5C_6H_{14}*

Atom	*x*	*y*	*z*
Re	0.045 64(3)	0.533 01(3)	0.716 32(2)
P	0.274 3(2)	0.613 9(1)	0.741 1(1)
N	0.074 4(5)	0.418 2(5)	0.636 9(4)
O	0.089 9(6)	0.343 0(5)	0.578 0(4)
C(1)	0.100 5(7)	0.440 9(6)	0.841 1(4)
C(2)	−0.001 9(7)	0.335 2(6)	0.852 1(4)
C(3)	0.017(1)	0.316 6(7)	0.954 5(5)
C(4)	0.014 6(7)	0.218 7(7)	0.795 0(5)
C(5)	−0.091 8(7)	0.116 6(6)	0.799 0(5)
C(6)	−0.065 7(8)	0.031 1(7)	0.860 6(6)
C(7)	−0.167 7(9)	−0.059 2(7)	0.866 0(6)
C(8)	−0.293 3(9)	−0.065 7(7)	0.810 8(7)
C(9)	−0.321(1)	0.016 3(9)	0.748 9(8)
C(10)	−0.220 9(9)	0.108 4(8)	0.742 4(6)
C(11)	−0.188 5(7)	0.550 6(7)	0.703 1(6)
C(12)	−0.140 1(7)	0.612 0(8)	0.635 4(6)
C(13)	−0.044 2(8)	0.711 1(7)	0.681 9(7)
C(14)	−0.035 7(8)	0.705 2(7)	0.778 0(6)
C(15)	−0.123 4(7)	0.608 2(7)	0.790 4(5)
C(16)	0.305 8(6)	0.758 5(6)	0.813 1(4)
C(17)	0.324 7(8)	0.866 9(7)	0.776 0(5)
C(18)	0.335 8(9)	0.975 7(7)	0.832 2(7)
C(19)	0.331 7(9)	0.976 5(7)	0.923 3(6)
C(20)	0.311 0(9)	0.869 6(8)	0.959 9(5)
C(21)	0.298 4(9)	0.760 9(7)	0.905 2(5)
C(22)	0.409 8(6)	0.522 8(6)	0.793 4(4)
C(23)	0.512 2(7)	0.561 4(7)	0.870 5(5)
C(24)	0.610 3(8)	0.484 6(9)	0.905 2(6)
C(25)	0.605 2(8)	0.368 3(8)	0.863 5(6)
C(26)	0.503 6(8)	0.327 7(7)	0.784 9(6)
C(27)	0.407 2(7)	0.404 5(7)	0.750 9(5)
C(28)	0.332 5(6)	0.648 1(6)	0.637 3(4)
C(29)	0.236 5(7)	0.658 4(6)	0.558 2(5)
C(30)	0.278 3(8)	0.688 3(8)	0.478 2(5)
C(31)	0.416 7(9)	0.706 2(9)	0.478 5(5)
C(32)	0.513 5(8)	0.696 0(9)	0.557 5(6)
C(33)	0.471 4(7)	0.667 2(8)	0.637 6(5)
C(34)	0.313(2)	0.052(2)	0.559(1)
C(35)	0.161(3)	0.042(2)	0.495(1)
C(36)	0.082(3)	0.003(2)	0.540(1)
H(1)	0.109 3	0.527 3	0.894 5
H(2)	0.193 3	0.388 6	0.832 0
H(3)	−0.109 3	0.361 3	0.833 9
H(4)	−0.027 3	0.250 0	0.980 4
H(5)	0.027 3	0.388 6	1.000 0
H(6)	0.138 6	0.277 3	0.957 0
H(7)	0.027 3	0.220 7	0.728 5
H(8)	0.109 3	0.193 3	0.812 5

* Hydrogen atoms were not refined.

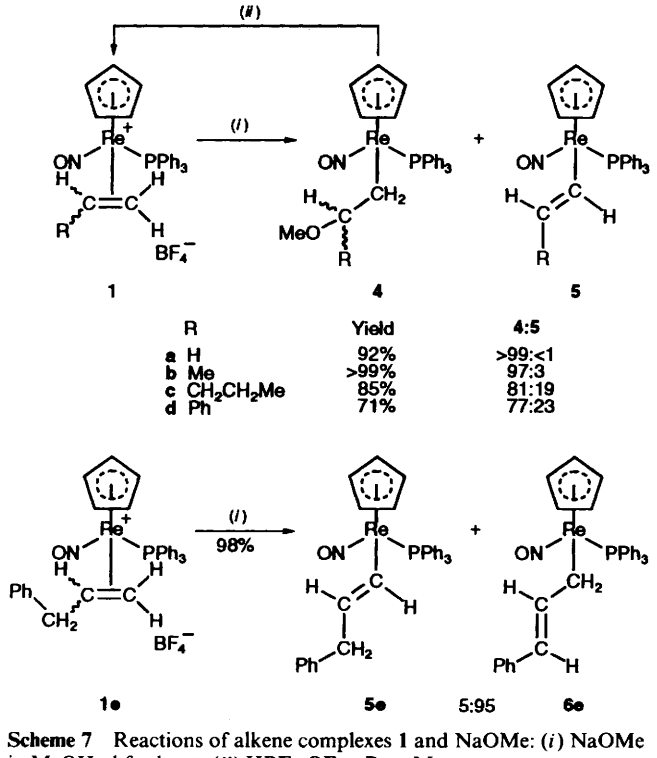


Scheme 6 Possible reactions of nucleophiles and/or bases with alkene complexes: (*i*) addition; (*ii*) vinylic deprotonation; (*iii*) allylic deprotonation

Table 3 Selected bond lengths (Å), bond angles and torsion angles (°) in (*SR,RS*)-**2e**·0.5C_6H_{14}[a]

Re–P	2.335(1)	Re–N	1.751(5)
Re–C(1)	2.195(6)	Re–C(11)	2.323(6)
Re–C(12)	2.269(7)	Re–C(13)	2.286(7)
Re–C(14)	2.326(7)	Re–C(15)	2.362(6)
N–O	1.206(6)	P–C(16)	1.830(6)
P–C(22)	1.831(6)	P–C(28)	1.827(6)
C(1)–C(2)	1.546(8)	C(2)–C(3)	1.538(9)
C(2)–C(4)	1.530(9)	C(4)–C(5)	1.514(9)
C(5)–C(6)	1.382(9)	C(5)–C(10)	1.38(1)
C(6)–C(7)	1.40(1)	C(7)–C(8)	1.34(1)
C(8)–C(9)	1.36(1)	C(9)–C(10)	1.40(1)
C(11)–C(12)	1.41(1)	C(11)–C(15)	1.41(1)
C(12)–C(13)	1.44(1)	C(13)–C(14)	1.43(1)
C(14)–C(15)	1.39(1)		
P–Re–N	91.3(2)	P–Re–C(1)	88.8(2)
N–Re–C(1)	98.4(2)	Re–P–C(16)	112.5(2)
Re–P–C(22)	118.3(2)	Re–P–C(28)	114.7(2)
Re–N–O	175.9(5)	Re–C(1)–C(2)	116.3(4)
C(1)–C(2)–C(3)	109.0(5)	C(1)–C(2)–C(4)	112.1(5)
C(2)–C(4)–C(5)	113.0(5)	C(4)–C(5)–C(6)	121.9(7)
C(4)–C(5)–C(10)	120.5(7)	C(6)–C(5)–C(10)	117.6(7)
C(5)–C(6)–C(7)	120.9(7)	C(6)–C(7)–C(8)	120.9(8)
C(7)–C(8)–C(9)	119.3(8)	C(8)–C(9)–C(10)	121.1(8)
C(5)–C(10)–C(9)	120.2(8)	C(12)–C(11)–C(15)	108.7(7)
C(11)–C(12)–C(13)	107.5(7)	C(12)–C(13)–C(14)	106.5(7)
C(13)–C(14)–C(15)	109.2(7)	C(11)–C(15)–C(14)	108.1(7)
CM[b]–Re–C(1)–C(2)	73.3(5)	CM–Re–C(1)–H(1)	−49.6
CM–Re–C(1)–H(2)	−176.8	P–Re–C(1)–C(2)	−162.5(5)
P–Re–C(1)–H(1)	74.6	P–Re–C(1)–H(2)	−52.6
N–Re–C(1)–C(2)	−71.4(5)	N–Re–C(1)–H(1)	165.7
N–Re–C(1)–H(2)	38.5	Re–C(1)–C(2)–C(3)	−156.9(5)
Re–C(1)–C(2)–C(4)	79.4(6)	Re–C(1)–C(2)–H(3)	−44.4
H(1)–C(1)–C(2)–C(3)	−44.2	H(1)–C(1)–C(2)–C(4)	−167.9
H(1)–C(1)–C(2)–H(3)	68.3	H(2)–C(1)–C(2)–C(3)	90.1
H(2)–C(1)–C(2)–C(4)	−33.6	H(2)–C(1)–C(2)–H(3)	−157.4
C(1)–C(2)–C(4)–C(5)	−157.6(6)	C(2)–C(4)–C(5)–C(6)	−94.6(8)

[a] Since hydrogen atom positions were not refined, estimated standard deviations are not given for the corresponding metrical parameters. [b] Cyclopentadienyl centroid.



Scheme 7 Reactions of alkene complexes **1** and NaOMe: (*i*) NaOMe in MeOH, thf solvent; (*ii*) HBF_4·OEt_2, R = Me

(*RS,SR*):(*RR,SS*) mixture (> 99%). This shows that methoxide addition and abstraction have the same stereochemistry—*i.e.*, transition states involving the C=C face *anti* to rhenium, or *antiperiplanar* Re–C–C–OMe conformations.

The pentene complex **1c** [97:3 (*RS,SR*):(*RR,SS*], which has a slightly bulkier C=C substituent than **1b**, was treated similarly with NaOMe–MeOH (Scheme 7). Work-up gave a 85% yield of a 81:19 mixture of the 2-methoxypentyl complex (*SR,RS*)-[Re(η^5-C_5H_5)(NO)(PPh_3){$CH_2CH(OMe)CH_2CH_2Me$}] **4c** and the known pentenyl complex (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)(CH=$CHCH_2CH_2Me$)] **5c**.[15b] Only a single diastereomer of the former was detected. The styrene complex (*RS,SR*)-**1d** and NaOMe–MeOH gave a 71% yield of a 77:23 mixture of the 2-methoxy-2-phenylethyl complex (*SR,RS*)-[Re(η^5-C_5H_5)(NO)(PPh_3){$CH_2CH(OMe)Ph$}] (*SR,RS*)-**4d** and the known styrenyl complex (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)(CH=CHPh)] **5d**.[9]

The allylbenzene complex **1e** is much more susceptible to allylic deprotonation by KOBu^t than **1b** or **1c**.[9b] Accordingly, as shown in Scheme 7, **1e** [97:3 (*RS,SR*:*RR,SS*)] and NaOMe–MeOH gave a 98% yield of a 5:95 mixture of the alkenyl complex (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)(CH=$CHCH_2Ph$)] **5e**[15b] and the allyl complex (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)-(CH_2CH=CHPh)] **6e**.[17b] A minor species, provisionally assigned as the addition product [Re(η^5-C_5H_5)(NO)(PPh_3)-{$CH_2CH(OMe)CH_2Ph$}] **4e** (< 3%), was also detected by NMR (Experimental section). An analogous reaction was conducted with a MeOH (instead of thf) solution of **1e**. However, a ^{31}P NMR spectrum showed that deprotonation was still incomplete after 6 h. Work-up after 12 hours gave a 3:97 mixture of **5e** and **6e** (99%). No **4e** was detected.

Discussion

The data in Schemes 2–4 establish that rhenium monosubstituted alkene complexes **1** undergo regio-, diastereo- and enantio-specific additions with the organocopper nucleophile $LiCuMe_2$. Although some exceptions exist,[2] many other monosubstituted alkene complexes undergo similarly regiospecific additions at the substituted =CHR terminus.[1,3] These are often analysed in the context of 'slippage'[4c]—a displacement of the metal from the C=C midpoint towards the $=CH_2$ terminus. This is thought to enhance the electrophilicity of the =CHR moiety. The crystal structures of the styrene complexes (*RS,SR*)-**1d** and (*RR,SS*)-**1d**, the allylbenzene complex (*RR,SS*)-**1e**, and the isopropylethylene complex (*RS,SR*)-$[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHCHMe_2)]BF_4$ (*RS,SR*)-**1f** have been determined.[7a,b,e] However, no unusual features are evident. The Re–CHR bonds in (*RS,SR*)-**1d**, (*RR,SS*)-**1d** and (*RS,SR*)-**1f** do appear to be slightly longer than the $Re–CH_2$ bonds [2.258(9) *vs.* 2.225(9) Å, 2.284(7) *vs.* 2.255(7) Å, 2.278(7) *vs.* 2.240(7) Å]. Unfortunately, the individual differences are not statistically meaningful.

The diastereospecificity can be attributed to a mechanistic requirement for addition to the C=C face *anti* to rhenium. This also has abundant precedent with other alkene complexes, especially those that are co-ordinatively saturated.[1–6] Interestingly, the corresponding π-aldehyde complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(\eta^2\text{-}O{=}CHR)]BF_4$ can be isolated as similar equilibrium mixtures of (*RS,SR*):(*RR,SS*) diastereomers.[11,21] However, nucleophilic additions generally give lower product diastereomer ratios. This suggests a fundamentally different mechanism of diastereoselection. Accordingly, rate studies indicate that isomerization to less stable σ-aldehyde complexes precedes nucleophilic attack.[11]

The data in Scheme 7 show that the monosubstituted alkene complexes **1** also undergo regiospecific additions with NaOMe. The styrene complex (*RS,SR*)-**1d** gives only one diastereomer of adduct **4d** (*SR,RS*), consistent with a diastereospecific addition. However, the diastereomer ratios of **4b** and **4c** [(*SR,RS*):(*SS,RR*) 70:30 and >99: < 1] appear to differ very slightly from those of precursors **1b**, **c** [(*RS,SR*):(*RR,SS*) 68:32 and 97:3]. We therefore suggest that the less stable *RR,SS* diastereomers of **1** may be more susceptible to competing vinylic deprotonation to the alkenyl complexes **5**. Related phenomena have been observed in reactions of **1** and KOBu^t.[9b] Phenyl substituents often accelerate π-bond-forming 1,2-eliminations. Hence, the dominance of allylic deprotonation with the allylbenzene complex **1e** is not surprising.

Several reactions that complement those in Schemes 2–4 and 7 have been reported. First, the hydride nucleophile $LiBHEt_3$ has been shown to add to the optically active ethylene complex (+)-(*R*)-**1a** (PF_6^- salt) to give the ethyl complex (+)-(*S*)-$[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2Me)]$.[13a] This transformation proceeds with at least 98% retention at rhenium. Secondly, σ complexes of the rhenium fragment **I** and cyclopentenone or cyclohexenone are easily isolated in enantiomerically pure form. These undergo *conjugate* additions of $LiCuMe_2$ and related nucleophiles. Under optimized conditions, 3-methylcycloalkanones of high enantiomeric purities can be isolated.[22] Thirdly, a variety of methods for detaching alkyl groups from **I** have been described.[16b,23] In an exploratory reaction, the alkyl complex **2e** and Br_2 were combined in CH_2Cl_2 at −30 °C. Work-up gave the bromide complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(Br)]$ and the alkyl bromide $PhCH_2CHMeCH_2Br$ (83%).[23b]

Finally, the reactivity of the rhenium monosubstituted alkene complexes **1** towards $LiCuMe_2$, NaOMe, and KOBu^t has now been fully delineated with respect to the nucleophilic addition and carbon–hydrogen bond activation processes shown in Scheme 6. With $LiCuMe_2$, only addition occurs. With NaOMe addition dominates, except in the case of allylbenzene complex **1e**. With the bulkier alkoxide KOBu^t only deprotonation occurs.[9b] However, under some conditions transient species derived from KOBu^t addition to the cyclopentadienyl ligand can be detected.[9b] Regardless, all of these reaction modes are of considerable interest and utility, and will be exploited in future publications from this laboratory.

Experimental

General.—General procedures were identical to those in a previous paper.[7b] The NMR spectra were recorded in $CDCl_3$ (**2**) or C_6D_6 (**4**) at ambient probe temperature and referenced to $Si(CH_3)_4$ (^1H, δ 0.0), $CDCl_3$ or C_6D_6 (^{13}C, δ 77.0 or 128.0), or external 85% H_3PO_4 (^{31}P, δ 0.0). All coupling constants (*J*) are in Hz. Positive-ion FAB mass spectra (MS) were obtained from samples in a 3-nitrobenzyl alcohol-$CHCl_3$ matrix under argon at 5 kV. Solvent and reagent data: thf, diethyl ether and benzene were distilled from Na–benzophenone; CH_2Cl_2 from P_2O_5; hexane from Na; MeOH from Mg–I_2; $CDCl_3$ was vacuum transferred from CaH_2; C_6D_6, vacuum transferred from Na; LiMe (1.4 mol dm^{-3} in diethyl ether, Aldrich) and $HBF_4{\cdot}OEt_2$ (Aldrich) were standardized before use;[13b,24] $MgICD_3$ (1.0 mol dm^{-3} in diethyl ether), NaOMe (4.37 mol dm^{-3} in MeOH) and $BH_3{\cdot}$thf (Aldrich) were used as received; $LiCuMe_2$ (0.20 mol dm^{-3}) and '$MgICu(CD_3)_2$' (0.20 mol dm^{-3}) were prepared from ethereal LiMe or $MgICD_3$ and a thf suspension of CuI at 0 °C.[25]

$[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CH_2Me)]$ **2a**.—A Schlenk flask was charged with $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CH_2)]BF_4$ **1a**[13] (13.2 mg, 0.020 mmol), thf (4 cm^3) and a stir bar and cooled to −80 °C (CO_2–acetone). Then $LiCuMe_2$ (0.20 mol dm^{-3}, 0.20 cm^3, 0.040 mmol) was added with stirring, and after 0.5 h the cold bath was removed. After 12 h solvent was removed by rotary evaporation, and benzene (5 cm^3) added, giving a brown solid and orange liquid. This mixture was filtered through a Celite plug (2 cm), which was rinsed with benzene, and solvent removed from the filtrate by rotary evaporation. The orange oil was chromatographed on a silica gel column (13.5 × 1.5 cm) with ethyl acetate–hexane (5:95 v/v). Solvent was removed from the orange band by rotary evaporation to give **2a**[14] as an orange-yellow powder (9.4 mg, 0.016 mmol, 79%). The IR and ^1H NMR spectra were identical to those of an authentic sample.

$[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CHMe_2)]$ **2b**.—The propene complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(H_2C{=}CHMe)]BF_4$ **1b**[7a,b] [67.2 mg, 0.100 mmol; 95:5 (*RS,SR*):(*RR,SS*)], thf (10 cm^3), and $LiCuMe_2$ (0.20 mol dm^{-3}, 1.00 cm^3, 0.20 mmol) were combined in a procedure analogous to that given for **2a**. An identical work-up gave **2b**[14] as an orange powder (52.0 mg, 0.087 mmol, 87%). The IR and ^1H NMR spectra were identical to those of an authentic sample. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 27.4 (s).

$[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\{CH_2CH(CD_3)Me\}]$ **2b″**.—*Method* (*a*). Complex **1b** [35.3 mg, 0.052 mmol; 95:5 (*RS,SR*):(*RR,SS*)], thf (2.0 cm^3) and $MgICu(CD_3)_2$ (0.20 mol dm^{-3}, 0.50 cm^3, 0.10 mmol) were combined in a procedure analogous to that given for **2b**. An identical work-up gave **2b″** as orange prisms [30.2 mg, 0.050 mmol, 96%; 95:5 (*SS,RR*):(*SR,RS*)] [Found: C, 53.80; (H + D) as H, 4.85. Calc. for $C_{27}H_{26}D_3NOPRe$: C, 53.70; (H + D) as H, 4.85%]. IR (cm^{-1}, thin film) ν_{NO} 1627vs. $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$) δ 25.7 and 28.0 ($CHCH_3$; 95:5); other data identical to that for **2b**.[14] FAB MS: *m/z* (relative intensity), (^{187}Re) 604 (M^+, 100), 544 ($M^+ - C_4H_6D_3$, 23%).

Method (*b*). Complex **1b** (16.8 mg, 0.025 mmol; 68:32 (*RS,SR*):(*RR,SS*), thf (0.5 cm^3) and $MgICu(CD_3)_2$ (0.20 mol dm^{-3}, 0.25 cm^3, 0.050 mmol) were combined as in method (*a*). An identical work-up gave **2b″** as orange prisms [13.1 mg, 0.022 mmol, 87%; 70:30 (*SS,RR*):(*SR,RS*)]. $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$) δ 25.7 and 28.0 ($CHCH_3$; 70:30).

Method (*c*). A two-necked flask was charged with [Re(η^5-C_5H_5)(NO)(PPh_3){COCH(CD_3)Me}] **3″**[15b] [61.8 mg, 0.100 mmol; 96:4 (*SR,RS*):(*SS,RR*)], thf (8 cm^3), and a stir bar, and fitted with a condenser, and BH_3·thf (1.0 mol dm^{-3} in thf, 1.0 cm^3, 1.0 mmol) was added with stirring. The solution was refluxed (4 h) and cooled to room temperature, MeOH (1 cm^3) added and work-up as in method (*a*) gave **2b″** as orange prisms [54.8 mg, 0.0091 mmol, 91%; 94:6 (*SR,RS*):(*SS,RR*)]. ^{13}C-{^{1}H} NMR ($CDCl_3$) δ 28.0 and 25.7 ($CHCH_3$; 94:6).

[Re(η^5-C_5H_5)(NO)(PPh_3)($CH_2CHMeCH_2CH_2Me$)] **2c**.—The pentene complex [Re(η^5-C_5H_5)(NO)(PPh_3)(CH_2=CH-CH_2CH_2Me)]BF_4 **1c**[7a] [35.0 mg, 0.050 mmol; 95:5 (*RS,SR*):(*RR,SS*)], thf (5 cm^3) and $LiCuMe_2$ (0.20 mol dm^{-3}, 0.50 cm^3, 0.10 mmol) were combined in a procedure analogous to that given for **2a**. An identical work-up gave **2c** as an orange-yellow powder [25.6 mg, 0.014 mmol, 82%; 95:5 (*SR,RS*):(*SS,RR*)], m.p. 146–147 °C (decomp.) (Found: C, 55.50; H, 5.30. Calc. for $C_{29}H_{33}NOPRe$: C, 55.40; H, 5.30%). IR (cm^{-1}, thin film) ν_{NO} 1628vs. FAB MS: *m/z* (relative intensity), (^{187}Re) 629 (M^+, 100), 544 ($M^+ - C_6H_{13}$, 87%). NMR, (*SR,RS*): ^{1}H, δ 7.48–7.30 (m, PPh_3), 4.89 (s, C_5H_5), 2.23 (m, ReC*H*H′), 1.63 (m, ReCH*H*′C*H*), 1.42–0.98 (m, C*H*H′ C*H*H′), 0.90 (d, J_{HH} = 6.1, $CHCH_3$), 0.83 (t, J_{HH} = 7.1, CHH′CH_3); ^{13}C-{^{1}H}, δ 136.6 (d, J_{CP} = 51.6, *i*-C of Ph), 133.7 (d, J_{CP} = 10.1, *o*-C of Ph), 129.8 (s, *p*-C of Ph), 128.2 (d, J_{CP} = 9.7, *m*-C of Ph), 89.7 (s, C_5H_5), 42.4 (s, $CH_2CH_2CH_3$),* 42.2 (s, $ReCH_2CH$),* 24.5 (s, $CHCH_3$), 20.3 (s, CH_2CH_3), 14.7 (s, CH_2CH_3), 0.0 (d, J_{CP} = 4.6, $ReCH_2$); ^{31}P-{^{1}H}, δ 24.6 (s). (*SS,RR*) (partial): ^{1}H, δ 4.88 (s, C_5H_5); ^{13}C-{^{1}H}, δ 89.8 (s, C_5H_5), 44.9 and 44.7 (s, $CHCH_2CH_2$), 22.6 (s, $CHCH_3$), 21.0 (s, CH_2CH_3), 14.7 (s, CH_2CH_3), 0.7 (d, J_{CP} = 4.2 Hz, $ReCH_2$).

[Re(η^5-C_5H_5)(NO)(PPh_3)($CH_2CHMePh$)] **2d**.—*Method* (*a*). The styrene complex (*RS,SR*)-[Re(η^5-C_5H_5)(NO)(PPh_3)(H_2-C=CHPh)]BF_4 (*RS,SR*)-**1d**[7a] (73.5 mg, 0.100 mmol), thf (10 cm^3) and $LiCuMe_2$ (0.20 mol dm^{-3}, 1.00 cm^3, 0.20 mmol) were combined in a procedure analogous to that given for **2a**. An identical work-up gave (*SR,RS*)-**2d** as an orange powder (66.2 mg, 0.100 mmol, >99%). Crystallization from hexane (−20 °C) gave orange prisms (61.0 mg, 0.092 mmol, 92%), m.p. 112–115 °C (Found: C, 57.75; H, 4.80; N, 2.05. Calc. for $C_{32}H_{31}NOPRe$: C, 58.00; H, 4.70; N, 2.10%). IR (cm^{-1}, thin film) ν_{NO} 1628vs. FAB MS: *m/z* (relative intensity), (^{187}Re) 663 (M^+, 17), 558 ($M^+ - C_8H_9$, 100), 544 ($M^+ - C_9H_{11}$, 21%).

Method (*b*). Complex (*RR,SS*)-**1d** (25.0 mg, 0.034 mmol),[7a] thf (3 cm^3) and $LiCuMe_2$ (0.20 mol dm^{-3}, 1.00 cm^3, 0.20 mmol) were combined as in method (*a*). An identical work-up and crystallization gave (*SS,RR*)-**2d** as an orange powder (22.6 mg, 0.034 mmol, >99%) or prisms (20.5 mg, 0.031 mmol, 91%), m.p. 185–186 °C (Found: C, 58.05; H, 4.75; N, 2.10). IR (cm^{-1}, thin film) ν_{NO} 1627vs. FAB MS: *m/z* (relative intensity), (^{187}Re) 663 (M^+, 14), 558 ($M^+ - C_8H_9$, 100), 544 ($M^+ - C_9H_{11}$, 19%).

Method (*c*). Complex (−)-(*SR*)-**1d** (36.7 mg, 0.050 mmol, >98% e.e.),[7a] thf (5 cm^3) and $LiCuMe_2$ (0.20 mol dm^{-3}, 0.50 cm^3, 0.10 mmol) were combined as in method (*a*). An identical work-up gave (−)-(*RS*)-**2d** as an orange powder (30.2 mg, 0.046 mmol, 91%). Reprecipitation from hexane (−20 °C) gave an orange powder, m.p. 140–142 °C, $[\alpha]_{589}^{25}$ −(180 ± 3)° (CH_2Cl_2, *c* 0.44 mg cm^{-3}).[20]

Method (*d*). Complex (−)-(*SS*)-**1d** (36.7 mg, 0.050 mmol, >98% e.e.),[7a] thf (5 cm^3) and $LiCuMe_2$ (0.20 mol dm^{-3}, 0.50 cm^3, 0.10 mmol) were combined as in method (*c*). An identical work-up gave (−)-(*RR*)-**2d** as an orange powder (31.1 mg, 0.047 mmol, 94%), which was similarly reprecipitated, m.p. 175–178 °C, $[\alpha]_{589}^{25}$ −(126 ± 3)° (CH_2Cl_2, *c* 0.44 mg cm^{-3}).[20]

NMR, (*SR,RS*): ^{1}H, δ 7.45–6.98 (m, Ph), 4.85 (s, C_5H_5), 2.97 (dd, J_{HH} = 6.6, 12.8, ReC*H*H′), 2.73 (ddq, J_{HH} = 6.6, 6.6, 6.9, C*H*CH_3), 1.96 (dd, J_{HH} = 6.6, 12.8, ReCH*H*′), 1.34 (d, J_{HH} = 6.9, CH_3); ^{13}C-{^{1}H}, δ 136.4 (d, J_{CP} = 52.0, *i*-C of PPh), 133.6 (d, J_{CP} = 10.4, *o*-C of PPh), 129.8 (s, *p*-C of PPh), 128.2 (d, J_{CP} = 9.8, *m*-C of PPh), 152.6, 127.6, 127.0 and 124.6 (s, CC_6H_5), 89.6 (s, C_5H_5), 48.3 (s, $CHCH_3$), 25.1 (s, CH_3), 1.2 (d, J_{CP} = 4.2, $ReCH_2$); ^{31}P-{^{1}H}, δ 26.7 (s). (*SS,RR*): ^{1}H, δ 7.50–7.10 (m, Ph), 4.67 (s, C_5H_5), 2.97 (dd, J_{HH} = 6.6, 13.7, ReC*H*H′), 2.51 (ddq, J_{HH} = 6.6, 6.6, 6.8, C*H*CH_3), 1.98 (dd, J_{HH} = 6.6, 13.7, ReCH*H*′), 1.24 (d, J_{HH} = 6.8, CH_3); ^{13}C-{^{1}H}, δ 136.3 (d, J_{CP} = 51.5, *i*-C of PPh), 133.6 (d, J_{CP} = 10.3, *o*-C of PPh), 129.8 (s, *p*-C of PPh), 128.1 (d, J_{CP} = 10.3, *m*-C of PPh), 152.3, 127.8, 126.8 and 124.8 (s, CC_6H_5), 89.5 (s, C_5H_5), 50.7 (s, $CHCH_3$), 25.9 (s, CH_3), 2.2 (d, J_{CP} = 4.2 Hz, $ReCH_2$); ^{31}P-{^{1}H}, δ 27.2 (s).

[Re(η^5-C_5H_5)(NO)(PPh_3)($CH_2CHMeCH_2Ph$)] **2e**.—The allylbenzene complex [Re(η^5-C_5H_5)(NO)(PPh_3)(CH_2=CH-CH_2Ph)]BF_4 **1e**[7a] [0.114 g, 0.153 mmol; (*RS,SR*):(*RR,SS*) 97:3], thf (10 cm^3) and $LiCuMe_2$ (0.20 mol dm^{-3}, 1.53 cm^3, 0.264 mmol) were combined in a procedure analogous to that given for **2a**. An identical work-up gave **2e** as an orange-yellow powder [85.9 mg, 0.127 mmol, 83%; (*SR,RS*):(*SS,RR*) 98:2] (Found: C, 58.60; H, 4.90. Calc. for $C_{33}H_{33}NOPRe$: C, 58.55; H, 4.90%). IR (cm^{-1}, thin film) ν_{NO} 1628vs. FAB MS: *m/z* (relative intensity), (^{187}Re) 677 (M^+, 85), 544 ($M^+ - C_{10}H_{13}$, 100%). Crystallization from hexane (−21 °C, 48 h) gave orange prisms of (*SR,RS*)-**2e**·0.5C_6H_{14}, m.p. 166–167 °C (decomp.), which were used for the X-ray studies (see below). NMR, (*SR,RS*): ^{1}H, δ 7.49–7.05 (m, Ph), 4.94 (s, C_5H_5), 3.05 (m, ReC*H*H′), 2.20 (m, ReCH*H*′), 1.87 (m, C*H*CH*H*′Ph), 0.82 (d, J_{HH} = 6.0, CH_3); ^{13}C-{^{1}H}, δ 136.4 (d, J_{CP} = 51.8, *i*-C of PPh), 133.6 (d, J_{CP} = 10.2, *o*-C of PPh), 129.9 (s, *p*-C of PPh), 128.2 (d, J_{CP} = 10.2, *m*-C of PPh), 143.7, 129.2, 127.7 and 124.9 (s, CC_6H_5), 89.7 (s, C_5H_5), 45.9 and 46.7 (s, $CHCH_2Ph$), 24.0 (s, CH_3), 0.8 (d, J_{CP} = 5.0, $ReCH_2$). (*SS,RR*) (partial): ^{1}H, δ 4.94 (s, C_5H_5), 1.01 (d, J_{HH} = 6.0, CH_3); ^{13}C-{^{1}H}, δ 143.6, 129.3, 127.8 and 125.1 (s, CC_6H_5), 89.7 (s, C_5H_5), 48.7 and 47.7 (s, $CHCH_2Ph$), 22.8 (s, CH_3), −0.8 (d, J_{CP} = 4.7 Hz, $ReCH_2$).

[Re(η^5-C_5H_5)(NO)(PPh_3)(CH_2CH_2OMe)] **4a**.—A 5 mm NMR tube was charged with **1a** (16.5 mg, 0.025 mmol) and thf (0.5 cm^3), and NaOMe–MeOH (4.37 mol dm^{-3}, 0.019 cm^3, 0.084 mmol) was added with shaking. After 10 min, a ^{31}P NMR spectrum showed the reaction to be complete. Solvent was removed under oil pump vacuum, and the residue was extracted with diethyl ether (1.0 cm^3). Solvent was removed under oil pump vacuum to give **4a** as an orange powder (13.8 mg, 0.023 mmol, 92%), m.p. 111–114 °C (Found: C, 51.75; H, 4.55; N, 2.25. Calc. for $C_{26}H_{27}NO_2PRe$: C, 51.80; H, 4.50; N, 2.30%). IR (cm^{-1}, thin film) ν_{NO} 1630vs. FAB MS: *m/z* (relative intensity), (^{187}Re) 572 ($M^+ - CH_3O$, 100), 544 ($M^+ - C_3H_7O$, 58%). NMR: ^{1}H, δ 7.71–6.92 (m, PPh_3), 4.55 (s, C_5H_5), 4.00 (m, ReCHH′C*H*H′), 3.38 (s, OCH_3), 2.83 (m, ReC*H*H′), 2.08 (m, ReCH*H*′); ^{13}C-{^{1}H}, δ 137.2 (d, J_{CP} = 51.3, *i*-C of Ph), 133.9 (d, J_{CP} = 10.5, *o*-C of Ph), 130.0 (s, *p*-C of Ph), 128.5 (s, *m*-C of Ph; one line obscured), 89.1 (s, CH_2OCH_3), 85.0 (s, C_5H_5), 57.1 (s, OCH_3), −9.8 (d, J_{CP} = 4.7 Hz, $ReCH_2$); ^{31}P-{^{1}H}, δ 26.3 (s).

Reaction of **1b** *and* NaOMe.—Complex **1b** [16.8 mg, 0.025 mmol; 68:32 (*RS,SR*:*RR,SS*)], thf (0.5 cm^3) and NaOMe–MeOH (4.37 mol dm^{-3}, 0.012 cm^3, 0.050 mmol) were combined in a procedure analogous to that given for **4a**. An identical work-up gave a mixture of [Re(η^5-C_5H_5)(NO)(PPh_3){CH_2-CH(OMe)Me}] **4b** [70:30 (*SR,RS*:*SS,RR*)] and (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)(CH=CHMe)] **5b**[9b,15b] as an orange powder (97:3; 15.4 mg, 0.025 mmol, >99%). The ^{1}H, ^{13}C-{^{1}H} and

* The resonances at δ 42.4 and 42.2 gave a triplet and doublet, respectively ($^1J_{CH}$ 126.6, 126.1 Hz), when a ^{13}C NMR spectrum was recorded without proton decoupling.

^{31}P-{^{1}H} NMR spectra of **5b** were identical to those of authentic samples. Reprecipitation from CH_2Cl_2–hexane gave **4b** [77:23 (*SR,RS*):(*SS,RR*)] as an orange powder, m.p. 134–137 °C. IR (cm^{-1}, thin film) ν_{NO} 1633vs. FAB MS: *m/z* (relative intensity), (^{187}Re) 586 ($M^+ - CH_3O$, 80), 544 ($M^+ - C_4H_9O$, 100%). NMR, (*SR,RS*)-**4b**: ^{1}H, δ 7.58–6.91 (m, PPh_3), 4.62 (s, C_5H_5), 3.79 (m, ReCHH'C*H*), 3.38 (s, OCH_3), 2.42 (dd, J_{HH} = 9.0, 9.0, ReC*H*H'), 2.37 (m, ReCH*H'*), 1.70 (d, J_{HH} = 5.8, CHCH_3); ^{13}C-{^{1}H}, δ 137.2 (d, J_{CP} = 51.1, *i*-C of Ph), 133.9 (d, J_{CP} = 10.1, *o*-C of Ph), 130.0 (s, *p*-C of Ph), 128.4 (d, J_{CP} = 10.7, *m*-C of Ph), 89.6 (s, C_5H_5), 85.9 (s, $ReCH_2CH$), 55.3 (s, OCH_3), 22.1 (s, $CHCH_3$), −1.5 (d, J_{CP} = 4.8, $ReCH_2$); ^{31}P-{^{1}H}, δ 26.3 (s). (*SS,RR*)-**4b** (partial): ^{1}H, δ 4.64 (s, C_5H_5), 3.87 (m, ReCHH'C*H*), 3.20 (s, OCH_3), 2.46 (dd, J_{HH} = 9.5, 9.5, ReC*H*H'), 1.93 (m, ReCH*H'*), 1.69 (d, J_{HH} = 5.3, CHCH_3); ^{13}C-{^{1}H}, δ 93.0 (s, $ReCH_2CH$), 90.2 (s, C_5H_5), 55.4 (s, OCH_3), 24.0 (s, $CHCH_3$), −4.5 (d, J_{CP} = 3.7 Hz, $ReCH_2$); ^{31}P-{^{1}H}, δ 27.2 (s).

Reaction of **1c** *and* NaOMe.—Complex **1c** [29.5 mg, 0.042 mmol; 97:3 (*RS,SR*):(*RR,SS*)], thf (0.5 cm^3) and NaOMe–MeOH (4.37 mol dm^{-3}, 0.019 cm^3, 0.084 mmol) were combined in a procedure analogous to that given for **4a**. An identical work-up gave a mixture of (*SR,RS*)-[Re(η^5-C_5H_5)(NO)(PPh_3){$CH_2CH(OMe)CH_2CH_2Me$}] **4c** and (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)(CH=$CHCH_2CH_2Me$)] **5c**[9b,15b] as an orange powder (81:19; 22.5 mg, *ca.* 0.036 mmol, *ca.* 85%). The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra of **5c** were identical to those of authentic samples. IR (cm^{-1}, thin film) ν_{NO} 1629vs. FAB MS: *m/z* (relative intensity), (^{187}Re) 614 ($M^+ - CH_3O$, 48), 544 ($M^+ - C_6H_{13}O$, 100%).

NMR, (*SR,RS*)-**4c**: ^{1}H, δ 7.80–6.90 (m, PPh_3), 4.68 (s, C_5H_5), 3.68 (m, ReCHH'C*H*), 3.38 (s, OCH_3), 2.52–1.32 (m, ReC*HH'*CHC*HH'CHH'*), 1.18 (t, J_{HH} = 7.3, CHH'CH_3); ^{13}C-{^{1}H}, δ 137.2 (d, J_{CP} = 51.6, *i*-C of Ph), 133.9 (d, J_{CP} = 10.5, *o*-C of Ph), 130.0 (s, *p*-C of Ph), 128.4 (d, J_{CP} = 11.4, *m*-C of Ph), 89.7 (s, C_5H_5), 89.5 (s, $ReCH_2CH$), 55.7 (s, OCH_3), 38.4 (s, $CH_2CH_2CH_3$), 23.2 (s, CH_2CH_3), 15.1 (s, CH_2CH_3), −4.6 (d, J_{CP} = 5.0 Hz, $ReCH_2$); ^{31}P-{^{1}H}, δ 26.2 (s).

Reaction of (*RS, SR*)-**1d** *and* NaOMe.—Complex (*RS,SR*)-**1d** (18.4 mg, 0.025 mmol), thf (0.5 cm^3) and NaOMe (4.37 mol dm^{-3}, 0.012 cm^3, 0.050 mmol) were combined in a procedure analogous to that given for **4a**. An identical work-up gave a mixture of (*SR,RS*)-[Re(η^5-C_5H_5)(NO)(PPh_3){CH_2CH-(OMe)Ph}] (*SR,RS*)-**4d** and (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)-(CH=CHPh)] **5d**,[9b] as an orange powder (77:23; 12.0 mg, *ca.* 0.018 mmol, *ca.* 71%). The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra of **5d** were identical to those of authentic samples. IR (cm^{-1}, thin film) ν_{NO} 1636vs. FAB MS: *m/z* (relative intensity), (^{187}Re) 648 ($M^+ - CH_3O$, 25), 544 ($M^+ - C_9H_{11}O$, 100%). NMR, (*SR,RS*)-**4d**: ^{1}H, δ 7.60–6.85 (m, Ph), 4.77 (s, C_5H_5), 4.61 (m, ReCHH'C*H*), 3.36 (s, OCH_3), 2.93 (ddd, J_{HH} = 13.0, 10.2, J_{HP} = 5.1, ReC*H*H'), 2.33 (dd, J_{HH} = 13.0, 7.9, ReCH*H'*); ^{13}C-{^{1}H}, δ 137.3 (d, J_{CP} = 50.7, *i*-C of Ph), 133.9 (d, J_{CP} = 10.1, *o*-C of Ph), 129.9 (s, *p*-C of Ph), 128.8 (s, *m*-C of Ph; one line obscured), 148.2, 126.8, 126.5 and 124.9 (s, CC_6H_5), 94.5 (s, $ReCH_2CH$), 89.7 (s, C_5H_5), 56.8 (s, OCH_3), 1.3 (d, J_{CP} = 3.8 Hz, $ReCH_2$); ^{31}P-{^{1}H}, δ 27.9 (s).

Reaction of **1e** *and* NaOMe.—Complex **1e** [18.7 mg, 0.025 mmol; 97:3 (*RS,SR*):(*RR,SS*)], thf (0.5 cm^3) and NaOMe–MeOH (4.37 mol dm^{-3}, 0.012 cm^3, 0.050 mmol) were combined in a procedure analogous to that given for **4a**. An identical work-up gave a mixture of (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)-(CH=$CHCH_2Ph$)] **5e**[9b,15b] and (*E*)-[Re(η^5-C_5H_5)(NO)(PPh_3)-(CH_2CH=CHPh)] **6e**[9b,17b] as an orange powder (5:95; 16.2 mg, 0.025 mmol, 98%). The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were identical to those of authentic samples. The sample contained traces of a third species, likely [Re(η^5-C_5H_5)(NO)-(PPh_3){$CH_2CH(OMe)CH_2Ph$}] **4e** [< 3%; NMR: ^{1}H, δ 4.68; ^{31}P-{^{1}H}, δ 26.2].

Reaction of **4b** *and* HBF_4·OEt_2.—A 5 mm NMR tube was charged with **4b** [16.7 mg, 0.027 mmol; 77:23 (*SR,RS*):(*SS,RR*)] and CH_2Cl_2 (0.5 cm^3), and cooled to −80 °C, and HBF_4·OEt_2 (3.2 μl, 0.030 mmol) was added. The tube was shaken and quickly transferred to a −80 °C NMR probe. A ^{31}P spectrum showed the reaction to be complete. The sample was warmed to room temperature and added to hexane (3 cm^3). Solvent was removed by rotary evaporation to give **1b** as a tan powder [18.1 mg, 0.027 mmol, >99%; 77:23 (*RS,SR*):(*RR,SS*)]. The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were identical to those of an authentic sample.

Crystallography.—Data were collected for (*SR,RS*)-**2e**·0.5 C_6H_{14} as outlined in Table 1 (Enraf-Nonius CAD4 diffractometer). Cell constants were obtained from 23 reflections with 15 < 2θ < 30°. The space group was determined from least-squares refinement. Standard reflections showed 20.0% decay during data collection. Lorentz, polarization, anisotropic decay and empirical absorption (Ψ scans) corrections were applied. The structure was solved by standard heavy-atom techniques with the SDP–VAX package.[26] Non-hydrogen atoms were refined with anisotropic thermal parameters. Aliphatic hydrogen atoms [H(1)-H(8)] were located, and other hydrogen atom positions were calculated. These were added to the structure factor calculations but were not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[27]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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