Reactions of Diazo Compounds and Chiral Rhenium Alkylidene Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+ PF_6^-$; A Versatile and Highly Stereoselective Route to Alkene Complexes

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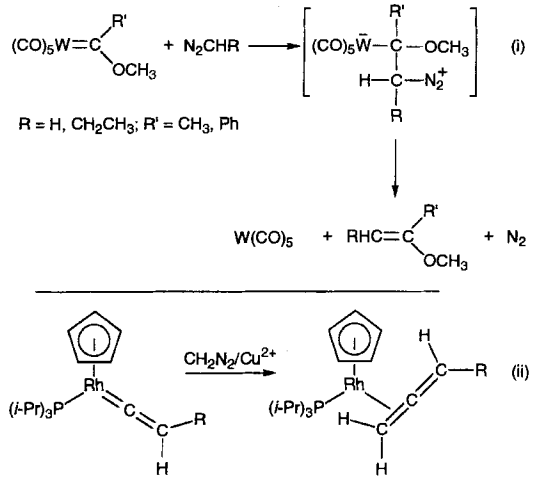
The methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+ PF_6^-$ or the $Re=CD_2$ analog react with diazo compounds N_2CHR [R = H, $Si(CH_3)_3$, COPh, $CO_2C_2H_5$] in CH_2Cl_2 at −80°C to give alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C=CHR)]^+ PF_6^-$ or $D_2C=CHR$ analogs. The two Re=C geometric isomers of benzylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHPh)]^+ PF_6^-$ and CH_2N_2 react to give opposite configurational diastereomers of styrene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C=CHPh)]^+ PF_6^-$. Stereochemical features of these reactions are analyzed in detail, and are interpreted in terms of models involving (a) attack of the diazo compound upon the Re=C face opposite to the bulky PPh_3 ligand, (b) an antiperiplanar disposition of the Re=C and $C-N_2$ bonds in the transition state, utilizing the diazo carbon face that minimizes interactions of the substituent (R) and cyclopentadienyl ligand, and (c) N_2 loss from the resulting intermediate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHR'CHRN_2)]^+ PF_6^-$ via a conformer with antiperiplanar P−Re−CHR′−C and Re−CHR′−CHR−N linkages, with anchimeric assistance of the rhenium fragment d orbital HOMO from the backside.

Numerous reactions of organometallic complexes and organic diazo compounds, N_2CRR', have been investigated[1−6]. Furthermore, transition metal catalyzed reactions of diazo compounds see wide use in organic synthesis[3]. Many of these transformations are believed to involve intermediate carbene or alkylidene complexes, $L_nM=CRR'$. Hence, reactions of alkylidene complexes and diazo compounds assume a special importance − especially in view of the diazo coupling products RR′C=CRR′ that form as undesired byproducts under some catalytic conditions.

Surprisingly, only a few reactions of alkylidene complexes or related species with diazo compounds appear to have been described[1,4−6]. In an important early report, Casey found that additions of diazo compounds to tungsten Fischer carbene complexes gave free alkenes as shown in eq. (i) of Scheme 1[4]. These were proposed to involve attack of the nucleophilic diazo carbon atoms upon the electrophilic carbene carbon atoms, followed by fragmentation of the resulting zwitterions. With other substrates, the diazo carbon atoms can be incorporated into coordinated C=C units, as illustrated for a rhodium vinylidene complex in eq. (ii) of Scheme 1[6].

Accordingly, we set out to study reactions of diazo compounds with alkylidene complexes of the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**)[7−10]. Our effort was also motivated by the potential for interesting reactions of diazo compounds with cumulene-bridged bimetallic complexes of the type $[Re=(C)_x=M]^{n+}$ that have recently become available[11]. Furthermore, we have had an extensive interest in the anticipated alkene complex products, which exhibit a number of unusual binding properties[12,13]. Such routes would complement existing syntheses, which generally involve pre-formed alkenes.

Scheme 1. Representative reactions of carbene or alkylidene-type complexes and diazo compounds



Rhenium alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+ PF_6^-$ are easily prepared by reactions of alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ with $Ph_3C^+ PF_6^-$[7,8], as illustrated in Scheme 2. The Re−C rotamer **II** is the most reactive, and the hydride ion is abstracted from a direction *anti* to the bulky PPh_3 ligand. This gives an "*sc*" Re=C geometric isomer[14] with the idealized structure **III**. The Re=C conformation allows a high degree of overlap between the CHR p acceptor orbital and the

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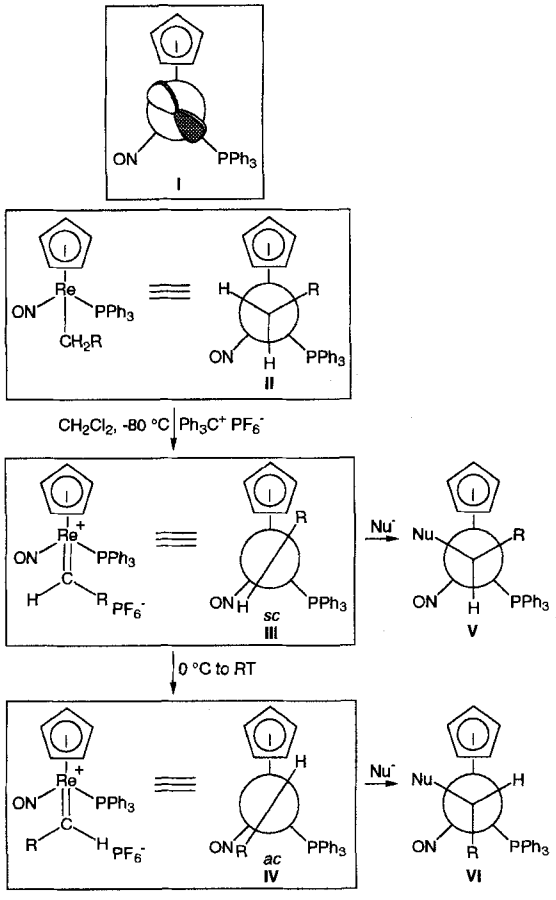
rhenium fragment d orbital HOMO shown in **I** (Scheme 2). An analogous interaction, equivalent to anchimeric assistance, should stabilize the predecessor transition state.

Scheme 2. Formation and reactions of rhenium alkylidene complexes



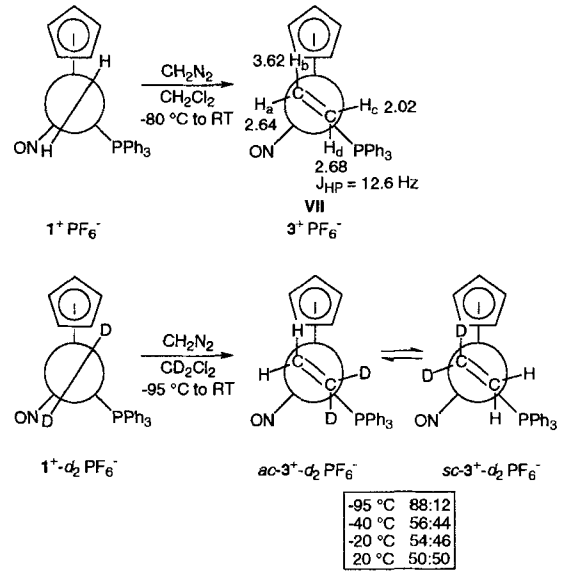
Upon warming to 0–20°C, **III** isomerizes to the more stable "*ac*" Re=C geometric isomer **IV** (Scheme 2). The basis for the divergent kinetic and thermodynamic selectivity has been analyzed previously[8d]. Reactions of **III** and **IV** with nucleophiles (Nu:$^-$ or Nu:) have been extensively studied[8,10a,b]. In each case, attack is highly diastereoselective, occurring predominantly from a direction *anti* to the bulky PPh_3 ligand to give adducts **V** and **VI**, respectively. Thus, either diastereomer of the addition product can be accessed. All of the preceding features, as well as new ones that control other types of stereoselectivity, come into play in reactions with diazo compounds, as detailed in the narrative below.

Results

1. Reactions of Diazomethane and Methylidene Complexes

The methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+$ PF_6^- (**1**$^+$ PF_6^-) was generated in CH_2Cl_2 at −80°C from the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**)[15] and Ph_3C^+ PF_6^-[7a]. Then freshly prepared ethereal CH_2N_2 was added (Scheme 3)[16a]. Workup gave the previously characterized ethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}CH_2)]^+$ PF_6^- (**3**$^+$ PF_6^-)[7b] in 86% yield. Based upon structures of analogous monosubstituted and disubstituted alkene complexes[12a,d,13], compound **3**$^+$ PF_6^- would be expected to adopt the Re−(C$\cdots$C) conformation shown in **VII** (Scheme 3). This maximizes overlap of the C=C π^* acceptor orbitals with the d orbital HOMO of the rhenium fragment **I**.

Scheme 3. Reactions of methylidene complex **1**$^+$-d_n PF_6^- and CH_2N_2



Regardless of Re−(C$\cdots$C) conformation, the four $\cdots$CH protons are inequivalent, and should give distinct ^{1}H-NMR signals. Extensive studies of other alkene complexes of **I** have established that protons in position H_d (see **VII**) give larger J_{HP} values (11–14 Hz) than those in positions H_c (4–6 Hz), H_b (<2 Hz), or H_a (<2 Hz)[12,13]. Thus, J_{HP} and J_{HH} values were determined by homonuclear decoupling (Experimental). One resonance (δ = 2.68) gave a large J_{HP} value (12.6 Hz) and was assigned to H_d. An upfield resonance (δ = 2.02) showed a small J_{HP} value (2.7 Hz) and was assigned to H_c. Two resonances (δ = 3.62, 2.64) gave no detectable phosphorus coupling, and were assigned on the basis of J_{HH} data and chemical shifts to H_b and H_a, respectively[12c,e].

We sought to probe the direction of CH_2N_2 attack. Thus, the deuteriomethylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CD_2)]^+$ PF_6^- (**1**$^+$-d_2 PF_6^-) was isolated as previously described[7a,b]. A CD_2Cl_2 solution of **1**$^+$-d_2 and a $[D_{10}]$ether solution of CH_2N_2 were combined in an NMR tube at −95°C. The tube was transferred to a −95°C NMR probe, and ^{1}H spectra were recorded. The formation of **3**$^+$-d_2 PF_6^- was complete within the 7-min transfer period. Integration of the $\cdots$CH resonances showed a 88:12 mixture of *ac*/*sc* Re−(C$\cdots$C) rotamers[14,17], as illustrated in Scheme 3.

When the probe was warmed to −40°C, the *ac*/*sc* ratio diminished to 56:44. At room temperature, a 50:50 mixture was present. When the sample was cooled again to −95°C, the *ac*/*sc* ratio remained 50:50. Thus, the equilibrium isotope effect is very close to unity. Workup gave **3**$^+$-d_2 PF_6^- in 95% yield. These data are consistent with preferential

CH_2N_2 attack from a direction *anti* to the PPh_3 ligand, commensurate with the precedent in Scheme 2. However, one other interpretation remains viable, as analyzed in the discussion section. In any event, rotation about the Re–(C=C) axis is rapid, in accord with the barrier determined by ^{13}C NMR for unlabeled **3**$^+$ PF_6^- earlier ($\Delta G^{\neq}$ = 16.4 kcal/mol, $CDCl_2CDCl_2$, 369 K)[12a]. Hence, the 88:12 *ac*/*sc* ratio represents a *lower bound* for the actual diastereoselectivity.

2. Reactions of Other Diazo Compounds and the Methylidene Complex

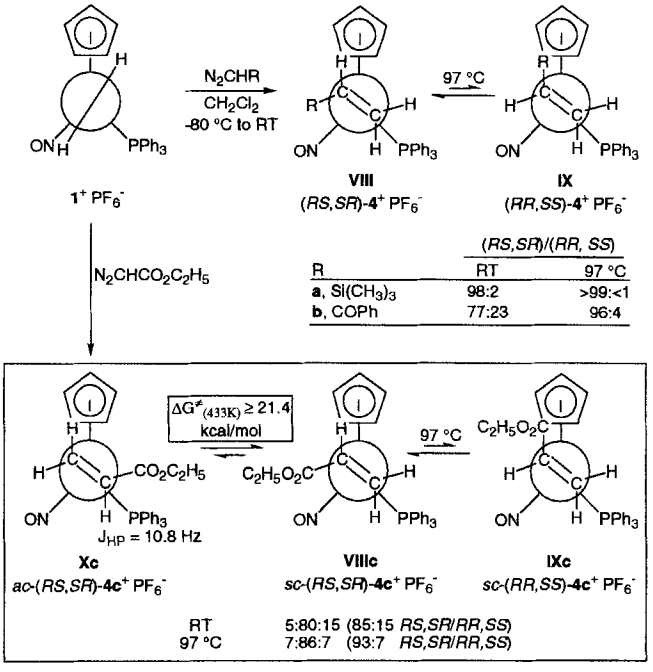
Analogous reactions of monosubstituted diazo compounds, N_2CHR, and methylidene complex **1**$^+$ PF_6^- should give monosubstituted alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}CHR)]^+$ PF_6^- (**4**$^+$ PF_6^-)[12a,b,d,13]. These can exist as two configurational diastereomers, (*RS,SR*) and (*RR,SS*), which differ in the C=C enantioface bound to rhenium. The (*RS,SR*)/(*RR,SS*) diastereomers equilibrate at 90–100°C in chlorinated solvents, and the former are much more stable (K_{eq} = 90:10 to >99:<1). Also, Re–(C=C) rotamers in which the larger =CHR termini are *anti* to the bulky PPh_3 ligands (*sc*) are greatly preferred. This in turn generates steric interactions between the =CH*R* substituents and the cyclopentadienyl ligands in the (*RR,SS*) diastereomers, accounting for the lower stability.

As summarized in Scheme 4, reactions of **1**$^+$ PF_6^- and diazo compounds N_2CHR [R = **a**, $Si(CH_3)_3$; **b**, COPh; **c**, $CO_2C_2H_5$] gave the expected monosubstituted alkene complexes **4a–c**$^+$ PF_6^-. With $N_2CHSi(CH_3)_3$, a 95:5 mixture of (trimethylsilyl)ethylene complex **4a**$^+$ PF_6^- and ethylene complex **3**$^+$ PF_6^- was obtained. The former was a 98:2 mixture of (*RS,SR*)/(*RR,SS*) diastereomers (**VIIIa/IXa**; Scheme 4). The latter is known to arise from the independent thermal coupling of **1**$^+$ PF_6^-[7b]. Chromatography gave **4a**$^+$ PF_6^- in 52% yield as a 99:1 (*RS,SR*)/(*RR,SS*) mixture. The IR and NMR (^1H, ^{31}P) spectra were identical with those of the previously reported tetrafluoroborate salt **4a**$^+$ BF_4^-[12b]. A $CHCl_2CHCl_2$ solution of **4a**$^+$ PF_6^- [(*RS,SR*)/(*RR,SS*) = 98:2] was kept at 97°C for 6 h. A ^{31}P-NMR spectrum showed a >99:<1 (*RS,SR*)/(*RR,SS*) equilibrium ratio, identical with that obtained earlier for **4a**$^+$ BF_4^-[12b].

With $N_2CHCOPh$, the new acrylophenone complex **4b**$^+$ PF_6^- was isolated in 86% yield as a 77:23 mixture of (*RS,SR*)/(*RR,SS*) diastereomers (**VIIIb/IXb**; Scheme 4). Complex **4b**$^+$ PF_6^- was characterized by microanalysis, and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, as summarized in the experimental section. Spectroscopic properties closely matched those of other C=C ligated vinyl ketone complexes of **I** (e.g., methyl vinyl ketone, ethyl vinyl ketone)[13], as more fully analyzed elsewhere[18]. A $CHCl_2CHCl_2$ solution of **4b**$^+$ PF_6^- was kept at 97°C and monitored periodically by ^{31}P NMR. After 135 h, a 96:4 (*RS,SR*)/(*RR,SS*) equilibrium ratio had been achieved[19a].

With $N_2CHCO_2C_2H_5$, the new ethyl acrylate complex **4c**$^+$ PF_6^- was isolated in 77% yield and characterized analogously to **4b**$^+$ PF_6^-. Surprisingly, a 5:80:15 mixture of three isomers was obtained (CD_2Cl_2). An analogous ^{31}P-NMR monitored reaction was complete within 7 min at –80°C, and gave a 9:78:13 mixture of isomers. When this sample was warmed to room temperature, a 4:83:13 mixture was obtained. When a $CHCl_2CHCl_2$ solution of the 5:80:15 mixture was kept at 97°C, equilibration occurred over the course of 230 h to give a 7:86:7 mixture[19b].

Scheme 4. Reactions of methylidene complex **1**$^+$ PF_6^- and monosubstituted diazo compounds N_2CHR



On the basis of NMR data, the three isomers were assigned as *ac*-(*RS,SR*)-**4c**$^+$ PF_6^-, *sc*-(*RS,SR*)-**4c**$^+$ PF_6^-, and *sc*-(*RR,SS*)-**4c**$^+$ PF_6^- (**Xc**, **VIIIc**, **IXc**; Scheme 4), respectively. The first two are *ac*/*sc* Re–(C=C) rotamers of the (*RS,SR*) diastereomer. Distinct rotamers have been previously observed for 1,2-disubstituted alkene complexes of **I**[12c,e,13], but not monosubstituted alkene complexes. As noted above, rotamers with the larger =CHR terminus *syn* to the bulky PPh_3 ligand (*ac*) would be expected to be less stable. Accordingly, the =CHCO ^1H-NMR signal of the minor species *ac*-(*RS,SR*)-**4c**$^+$ PF_6^- gave a large J_{HP} value (10.8 Hz), consistent with a proton in position d (see **VII**; Scheme 3).

Curiously, the NMR signals of *ac*-(*RS,SR*)-**4c**$^+$ PF_6^- and *sc*-(*RS,SR*)-**4c**$^+$ PF_6^- did not coalesce under the conditions assayed. For example, each rotamer showed broadened but distinct ^{31}P resonances in $CHCl_2CHCl_2$ at 160°C. Further heating gave decomposition. This bounds $\Delta G^{\neq}$(433 K) for any process capable of intercoverting the rotamers as ≥21.4 kcal/mol[20] – much higher than that for the $H_2C{=}CD_2$ ligand in **3**$^+$-d_2 PF_6^-[21]. The Re–(C=C) rotational barrier in the corresponding *cis*-1,2-dichloroethylene complex has been similarly bound as ≥17.5 kcal/mol (349 K)[12c]. This suggests that higher barriers may be associated with electron-withdrawing C=C substituents. However, we presently have no rationale as to why Re–(C=C) rotamers can be detected with (*RS,SR*)-**4c**$^+$ PF_6^-, but not with adducts of **I**

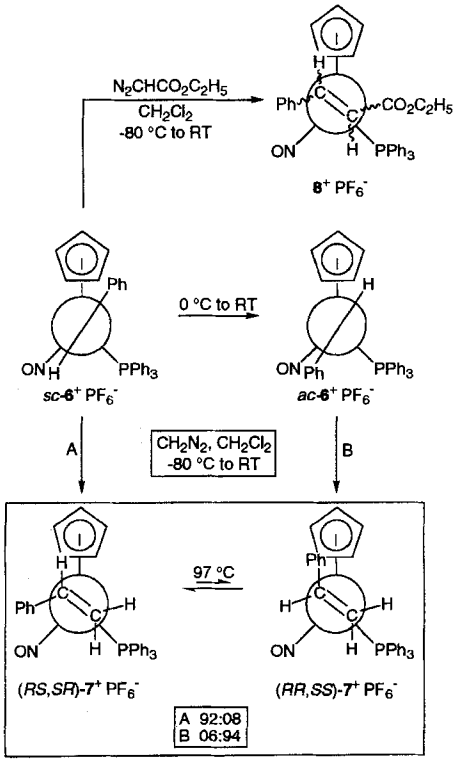
and other $H_2C{=}CHC(=O)X$ ligands (X = H, CH_3, C_2H_5, Ph)[13].

Most spectroscopic properties of **4c**$^+$ PF_6^- were similar to those of other $H_2C{=}CHC(=O)X$ complexes[13]. However, the $=CH_2$ ^{13}C-NMR signals of *sc*-(*RS,SR*)-**4c**$^+$ PF_6^- and *sc*-(*RR,SS*)-**4c**$^+$ PF_6^- (δ = 36.0, 37.8) were *downfield* of the $=CHC(=O)X$ signals (δ = 34.9, 36.3). In the other complexes, an opposite shielding trend was observed (δ = 34.7–36.9 and 38.5–44.2, respectively)[13]. The assignments in *sc*-(*RS,SR*)-**4c**$^+$ PF_6^- and *sc*-(*RR,SS*)-**4c**$^+$ PF_6^- were based upon the J_{CP} values (6.4–6.9 Hz) of the downfield resonances, which were characteristic of alkene carbon atoms *syn* to the PPh_3 ligand[12,13]. As a check, the $=CH(C=O)X$ ^1H resonance of *sc*-(*RS,SR*)-**4c**$^+$ PF_6^- was irradiated. Accordingly, only the upfield C=C ^{13}C resonance (δ = 34.9) was decoupled.

3. Reactions of Diazo Compounds and Other Complexes

The benzyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2Ph)$ (**5**) and Ph_3C^+ PF_6^- were allowed to react in CH_2Cl_2 at −80°C to give the less stable *sc* Re=C geometric isomer of benzylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHPh)]^+$ PF_6^- (*sc*-**6**$^+$ PF_6^-), as described above (Scheme 2)[8a]. Then CH_2N_2 was added as shown in path A of Scheme 5. Workup gave the previously characterized styrene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}CHPh)]^+$ PF_6^- (**7**$^+$ PF_6^-; 61%) as a 92:8 mixture of (*RS,SR*)/(*RR,SS*) diastereomers. The more stable Re=C geometric isomer, *ac*-**6**$^+$ PF_6^- (*ac*/*sc* ≥ 99:1), was similarly allowed to react (path B; Scheme 5). Workup gave **7**$^+$ PF_6^- (33%) as a 6:94 (*RS,SR*)/(*RR,SS*) mixture.

Scheme 5. Reactions of benzylidene complex **6**$^+$ PF_6^- and diazo compounds



The IR and NMR (^1H, ^{31}P) spectra of styrene complexes (*RS,SR*)-**7**$^+$ PF_6^- and (*RR,SS*)-**7**$^+$ PF_6^- were identical with those of authentic samples[12a]. Thus, CH_2N_2 addition is highly diastereoselective, transforming different geometric isomers of the reactant into different configurational diastereomers of the product. No attempts were made to optimize the isolated yields. However, reactions were spectroscopically quantitative.

Next, $CDCl_2CDCl_2$ solutions of the preceding samples of **7**$^+$ PF_6^- were kept at 97°C, and ^1H-NMR spectra were periodically recorded. After 31 h, the 6:94 (*RS,SR*)/(*RR,SS*) mixture had equilibrated to a 93:7 (*RS,SR*)/(*RR,SS*) mixture[19c]. There was no detectable change in the 92:8 (*RS,SR*)/(*RR,SS*) mixture after 24 h. These equilibrium ratios are close to that previously reported for the tetrafluoroborate **7**$^+$ BF_4^- [(*RS,SR*)/(*RR,SS*) = 90:10][12b,22].

A similar reaction of benzylidene complex *sc*-**6**$^+$ PF_6^- and the substituted diazo compound $N_2CHCO_2C_2H_5$ gave the ethyl cinnamate complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}PhHC{=}CHCO_2C_2H_5)]^+$ PF_6^- (**8**$^+$ PF_6^-) as a mixture of several isomers (Scheme 5). In this case, the alkene ligand is 1,2-disubstituted, which generates two stereocenters. The ν_{NO}- and ν_{CO}-IR values, and ^{31}P-NMR signal of the major isomer (δ = 4.8; 68%), were similar to those of *ac*-(*RS,SR*)-**4c**$^+$ PF_6^-. However, further purification attempts were unsuccessful. Additional data are given in the Experimental.

Reactions of other rhenium complexes and diazo compounds were also briefly investigated. First, the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+$ BF_4^- was generated in an NMR tube from methyl complex **2** and $HBF_4 \cdot OEt_2$ at −80°C[23]. Then ethereal CH_2N_2 was added, and the sample was warmed as ^{31}P-NMR spectra were recorded. These showed only the independent thermal decomposition of the dichloromethane complex. Finally, benzaldehyde and formaldehyde complexes of the formulae $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHR)]^+$ BF_4^-[24] were also treated with various diazo compounds. However, ^{31}P-NMR spectra always showed a multitude of products.

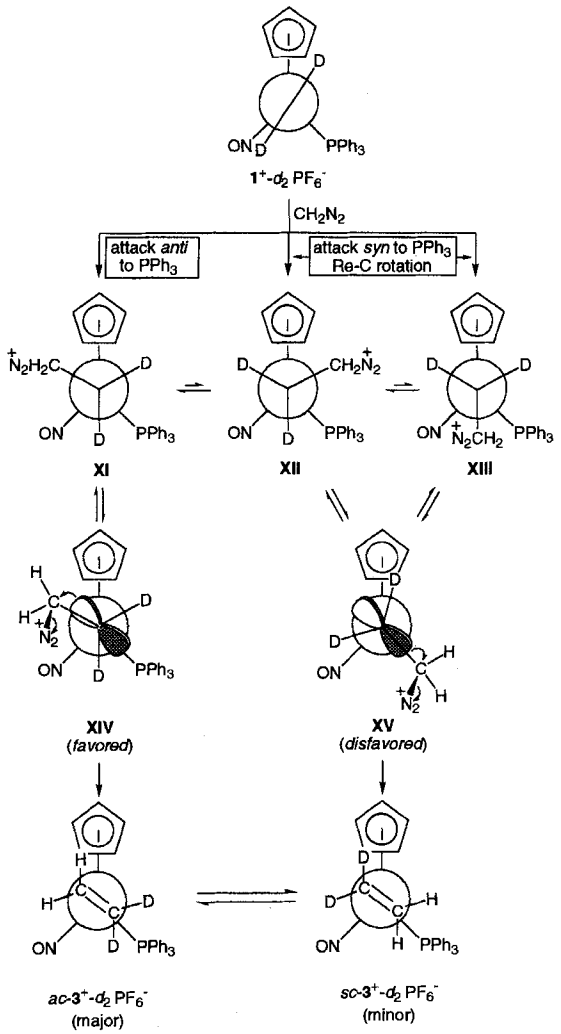
Discussion

The above results show that alkene complexes of the rhenium fragment **I** are easily prepared from alkylidene complexes and diazo compounds. These transformations are highly diastereoselective, the mechanistic implications of which are analyzed below. As a prelude, note the logical progression in Schemes 3–5. In Scheme 3, the alkylidene and diazo carbon atoms are symmetrically substituted ($=CH_2$). No new stereocenters are generated, but one conformational diastereomer of the product is greatly favored kinetically. In Scheme 4, the diazo carbon atom is unsymmetrically substituted, whereas in Scheme 5 the alkylidene carbon atom is unsymmetrically substituted. These are converted into alkene-based stereocenters. In each case, one configurational diastereomer dominates.

The reaction of deuteriomethylidene complex **1**$^+$-d_2 PF_6^- and CH_2N_2 would be expected to first give the addition product $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CD_2CH_2N_2)]^+$ PF_6^- (**10**$^+$

PF_6^-). Based upon the precedent in Scheme 2, CH_2N_2 attack should occur predominantly from a direction *anti* to the bulky PPh_3 ligand to give the Re–C rotamer **XI** shown in Scheme 6. Two less stable rotamers, **XII** and **XIII**, are also possible[10b]. These could form from **XI**, or by attack of CH_2N_2 *syn* to the PPh_3 ligand.

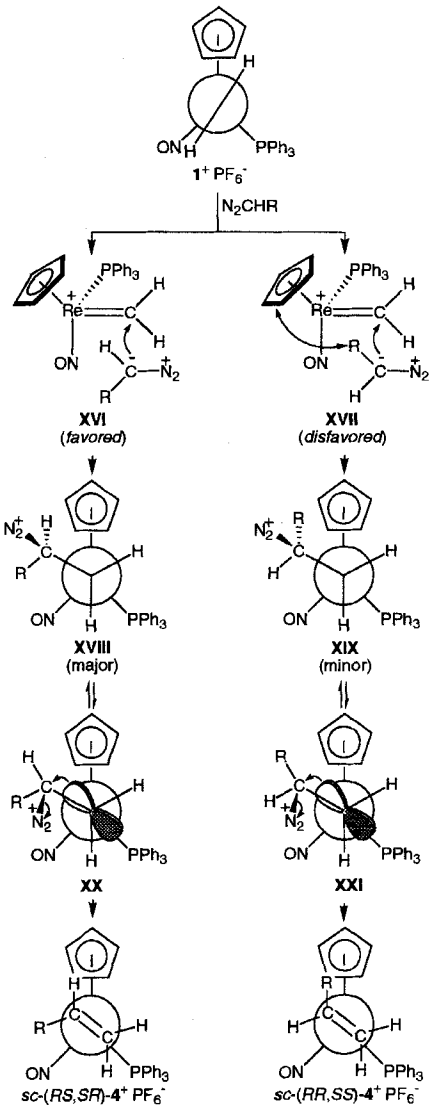
Scheme 6. Possible mechanisms of reaction of $\mathbf{1}^+$-d_2 PF_6^- and CH_2N_2



Regardless, subsequent N_2 loss should be anchimerically assisted by the rhenium fragment HOMO. This would maximize bonding in the transition state, lowering the energy. As shown in **XIV** and **XV** (Scheme 6), two variants are possible, both with antiperiplanar P–Re–CD_2–CH_2 and Re–CD_2–CH_2–N conformations. The former connects the most stable Re–C rotamer of $\mathbf{10}^+$ PF_6^-, **XI**, to the major Re–(C=C) rotamer of the product, *ac*-$\mathbf{3}^+$-d_2 PF_6^-. The latter requires eclipsing of the CH_2N_2 moiety and the PPh_3 ligand. Thus, it should be higher in energy. Accordingly, it would give the minor Re–(C=C) rotamer of the product, *sc*-$\mathbf{3}^+$-d_2 PF_6^-.

If the interconversion of Re–C rotamers **XI**, **XII**, and **XIII** is more rapid than N_2 loss – the familiar Curtin-Hammett limit[25] – the product *ac*/*sc* ratio will be a function of the relative energies of **XIV** and **XV**. In this situation, the data have no bearing on the direction of CH_2N_2 attack. Alternatively, **XI** might convert (via **XIV**) to *ac*-$\mathbf{3}^+$-d_2 PF_6^- much more rapidly than Re–C bond rotation. Rotamers **XII** and **XIII**, or precursor species, could behave similarly. In this limit, the *ac*/*sc* ratio would reflect the direction of CH_2N_2 attack. Our present data do not distinguish these possibilities. However, CH_2N_2 *must* preferentially attack the benzylidene carbon atom of $\mathbf{6}^+$ PF_6^- *anti* to the PPh_3 ligand, as analyzed below. Hence, analogous selectivity is highly probable in Schemes 3 and 6.

Scheme 7. Possible mechanisms of reaction of $\mathbf{1}^+$ PF_6^- and N_2CHR



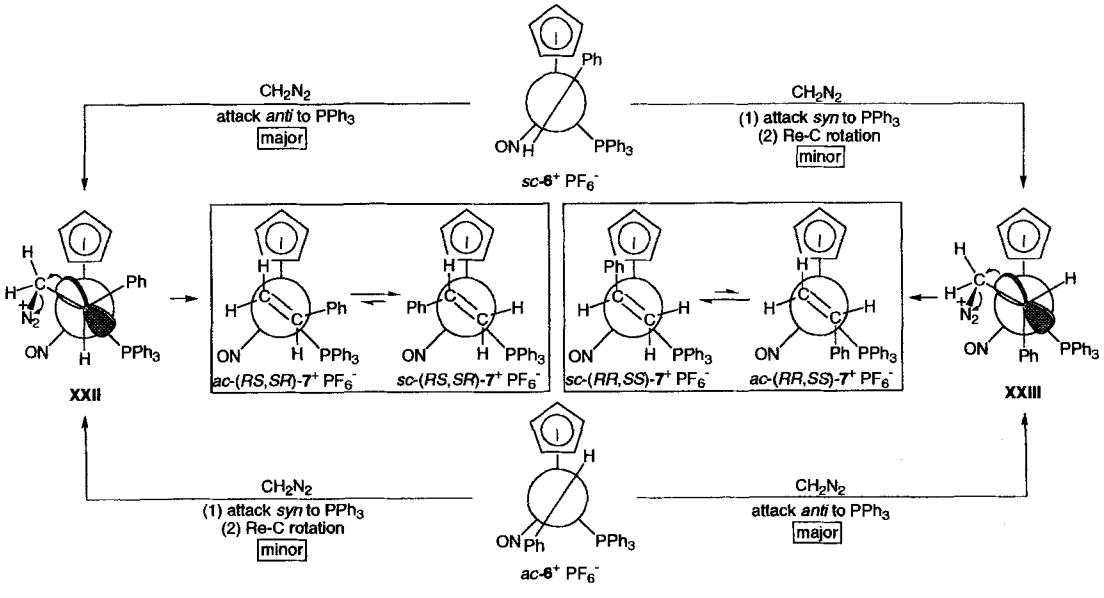
For the reactions of $\mathbf{1}^+$ PF_6^- and substituted diazo compounds N_2CHR (Scheme 4), we presume that (1) attack occurs *anti* to the PPh_3 ligand, and (2) N_2 loss entails transition states corresponding to **XIV**. The configurations of the alkene-based stereocenters of products $\mathbf{4}^+$ PF_6^- will then be determined by the face of the diazo carbon atom that participates in the initial carbon–carbon bond-forming step. As shown in Scheme 7, two diastereomeric intermediates, **XVIII** and **XIX**, can result. The former leads, via transition state **XX**, to the major products (*RS*,*SR*)-$\mathbf{4}^+$ PF_6^-.

The latter leads, via transition state **XXI**, to the minor products (*RR,SS*)-**4**$^+$ PF_6^-.

In structures **XIX** and **XXI**, steric interactions exist between the diazo carbon substituent (R) and the medium-sized cyclopentadienyl ligand. These interactions, which are absent in **XVIII** and **XX**, are similar to those that destabilize the (*RR,SS*) diastereomers of the products **4**$^+$ PF_6^-. Thus, **XVIII** and **XX** should be lower in energy. However, the (*RS,SR*)/(*RR,SS*) ratio will be controlled by the relative energies of the transition states preceding **XVIII** and **XIX**. By analogy to mechanisms proposed for additions of Wittig reagents to carbonyl groups[26], antiperiplanar dispositions of the Re=C and C–N_2 bonds would be likely, as shown in **XVI** and **XVII**. The latter would have destabilizing interactions between the diazo carbon substituent and cyclopentadienyl ligand similar to those in **XIX** and **XXI**. Hence, **XVI** should be the dominant pathway, in accord with the (*RS,SR*)/(*RR,SS*) ratios in Scheme 4 (98:2 to 77:23). As would be expected, the ratios roughly correlate with the sizes of the diazo substituents.

We presume that the dominant pathways in Schemes 6 and 7 will also apply to the reactions of benzylidene complexes **6**$^+$ PF_6^- and CH_2N_2 (Scheme 5). Now, the configurations of the alkene-based stereocenters in the resulting styrene complexes **7**$^+$ PF_6^- will be a function of the Re=C face that participates in the initial carbon–carbon bond-forming step. The formation of (*RS,SR*)-**7**$^+$ PF_6^- from *sc*-**6**$^+$ PF_6^-, and (*RR,SS*)-**7**$^+$ PF_6^- from *ac*-**6**$^+$ PF_6^-, *requires* CH_2N_2 attack *anti* to the PPh_3 ligand, as illustrated with transition states **XXII** and **XXIII** in Scheme 8.

Scheme 8. Possible mechanisms of reaction of **6**$^+$ PF_6^- and CH_2N_2

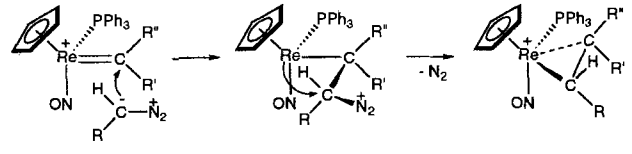


Interestingly, this model predicts that the *less* stable styrene complex Re–(C$\cdots$C) rotamers, *ac*-(*RS,SR*)-**7**$^+$ PF_6^- and *ac*-(*RR*,SS)-**7**$^+$ PF_6^-, should form initially. However, since it has not proved possible to detect Re–(C$\cdots$C) rotamers of either diastereomer by low-temperature NMR, this point cannot be tested. The minor styrene complex diastereomers might arise by attack *syn* to the PPh_3 ligand, as depicted in Scheme 8, or by other pathways. Earlier studies have shown that the hydride and carbon nucleophiles add to *sc*-**6**$^+$ PF_6^- and *ac*-**6**$^+$ PF_6^- with diastereoselectivities similar to those in Scheme 5[8b].

Conclusion

The data in Schemes 3–8, when taken together, provide a detailed picture of the stereochemical course of reactions of diazo compounds and alkylidene complexes of the rhenium fragment **I**. Key features are illustrated in the summary Scheme 9. These include (1) attack of the diazo compound upon the Re=C face opposite to the bulky PPh_3 ligand, (2) an antiperiplanar disposition of the Re=C and C–N_2 bonds in the transition state, (3) participation of the diazo carbon atom face that minimizes interactions of the substituent (R) and cyclopentadienyl ligand, and (4) N_2 loss from an intermediate with antiperiplanar P–Re–CHR′–CHR and Re–CHR′–CHR–N conformations, with anchimeric assistance of the rhenium fragment d orbital HOMO from the backside.

Scheme 9. Summary of dominant pathway for reactions of alkylidene complexes and diazo compounds



It should also be emphasized that the preceding transformations have preparative value. For example, an alkene ligand that might otherwise bind slowly to **I** or be difficult to synthesize can be assembled in the coordination sphere. Further, less stable diastereomers can be accessed directly, as established for (*RR,SS*)-**7**$^+$ PF_6^- in Scheme 5. Prep-

arations that utilize free alkenes always give chiefly the more stable diastereomer[12,13]. Extensions of the preceding chemistry are under active investigation, and will be reported in due course.

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Experimental

General: Experimental procedures and chemical sources were identical with those given earlier[12b,27]. Additional materials used were as follows: [D_{10}]ether (Janssen), used as received; Ph_3C^+ PF_6^- (Aldrich), recrystallized from CH_2Cl_2/ether; $CH_3N(NO)C(=NH)NHNO_2$ (CH_2N_2 precursor)[16a], $N_2CHSi(CH_3)_3$, $N_2CHCO_2C_2H_5$, used as received from Aldrich.

[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-H_2C=CH_2)]$^+$ PF_6^- (**3**$^+$ PF_6^-): A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**2**[15]; 0.289 g, 0.518 mmol), CH_2Cl_2 (10 ml), and a stir bar and was cooled to −80°C (acetone/CO_2). Then Ph_3C^+ PF_6^- (0.224 g, 0.577 mmol) in CH_2Cl_2 (5 ml) was added with stirring to generate [(η^5-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+$ PF_6^- (**1**$^+$ PF_6^-)[7a]. After 5 min, ethereal CH_2N_2 (ca. 4.0 mmol)[16a] was added. The cold bath was allowed to gradually warm. After 4 h, a tan solid had formed. Ether (20 ml) was added to the mixture. The solid was collected by filtration, washed with ether (2 × 5 ml), and dried under oil-pump vacuum to give **3**$^+$ PF_6^- (0.305 g, 0.444 mmol, 86%)[28]. – NMR (CD_2Cl_2): ^{1}H ($CHDCl_2$ as ref.): δ = 7.64–7.31 (m, 3 C_6H_5), 5.32 (s, C_5H_5), 3.62 (1 H, dd, J_{HH} = 9.9, 8.7), 2.68 (1 H, ddd, J_{HH} = 9.9, 8.7, J_{HP} = 12.6), 2.64 (1 H, dd, J_{HH} = 10.2, 8.7), 2.02 (1 H, ddd, J_{HH} = 10.2, 8.7, J_{HP} = 2.7)[29].

[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-H_2C=CD_2)]$^+$ PF_6^- (**3**$^+$-d_2 PF_6^-): Complex **1**$^+$-d_2 PF_6^- was isolated from the reaction of **2**-d_3 (>98% D by ^{1}H NMR) and Ph_3C^+ PF_6^- as described earlier[7a,b]. A 5-mm NMR tube was charged with **1**$^+$-d_2 PF_6^- (0.045 g, 0.056 mmol), capped with a septum, and cooled to −95°C (toluene/N_2). Then CD_2Cl_2 (0.8 ml) was slowly added. The tube was shaken until all solid had dissolved. Then a [D_{10}]ether CH_2N_2 solution (ca. 0.10 mmol)[16a] was added. The reaction was monitored by ^{1}H NMR (text; Scheme 3). The sample was added to ether (20 ml). A tan solid formed. The solvent was removed with a pipet, and the solid was washed with ether (2 × 3 ml) and dried under oil-pump vacuum to give **3**$^+$-d_2 PF_6^- (0.043 g, 0.053 mmol, 95%, 50:50 *ac*/*sc*)[14,17].

[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-H_2C=$CHSi(CH_3)_3$)]$^+$ PF_6^- (**4a**$^+$ PF_6^-): Complex **2** (0.163 g, 0.292 mmol), CH_2Cl_2 (5 ml), Ph_3C^+ PF_6^- (0.127 g, 0.327 mmol), and $N_2CHSi(CH_3)_3$ (220 µl, 0.440 mmol, 2 M in hexane) were combined in a procedure analogous to that given for **3**$^+$ PF_6^-. A similar workup gave a 95:5 mixture of **4a**$^+$ PF_6^- [98:2 (*RS,SR*)/(*RR,SS*)] and **3**$^+$ PF_6^- (0.161 g total), as asseyed by ^{31}P and ^{1}H NMR. Silica-gel chromatography [15 × 1.3 cm; CH_2Cl_2/acetone (95:5 v/v)] gave pure **4a**$^+$ PF_6^- [0.119 g, 0.151 mmol, 52%; 99:1 (*RS,SR*)/(*RR,SS*)], m.p. 218–223°C (dec.). – $C_{28}H_{32}F_6NOP_2ReSi$ (788.7): calcd. C 42.64, H 4.09; found C 42.77, H 4.05. – IR (thin film): $\tilde{\nu}$ = 1716 cm^{-1} (NO, vs). – NMR (CD_2Cl_2): (*RS,SR*)-**4a**$^+$ PF_6^-[27]: ^{1}H ($CHDCl_2$ as ref.): δ = 7.63–7.38 (m, 3 C_6H_5), 5.76 (d, J_{HP} = 0.6, C_5H_5), 2.92 (ddd, J_{HH} = 13.2, 14.4, J_{HP} = 1.5, =CHSi), 2.67 (ddd, J_{HH} = 2.7, 13.2, J_{HP} = 7.7, =CH_ZH_E), 2.47 (ddd, J_{HH} = 2.7, 14.4, J_{HP} = 9.8, =CH_ZH_E), 0.04 (s, 3 CH_3); ^{31}P{^{1}H}: δ = 8.8 (s). (*RR,SS*)-**4a**$^+$ PF_6^-: ^{1}H ($CHDCl_2$ as ref.): δ = 7.63–7.38 (m, 3 C_6H_5), 5.79 (d, J_{HP} = 0.6, C_5H_5), 3.19 (ddd, J_{HH} = 3.3, 11.4, J_{HP} = 15.0, =CH_ZH_E), 1.90 (ddd, J_{HH} = 11.4, 16.8, =CHSi), 1.55 (ddd, J_{HH} = 3.3, 16.8, J_{HP} = 3.3, =CH_ZH_E), 0.26 (s, 3 CH_3); ^{31}P{^{1}H}: δ = 11.6 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-H_2C=$CHCOPh$)]$^+$ PF_6^- (**4b**$^+$ PF_6^-): Complex **2** (0.447 g, 0.801 mmol), CH_2Cl_2 (5 ml), Ph_3C^+ PF_6^- (0.344 g, 0.886 mmol), and $N_2CHCOPh$ (prepared from PhCOCl and CH_2N_2[16]; 0.320 g, 2.19 mmol) were combined in a procedure analogous to that given for **3**$^+$ PF_6^-. A similar workup gave **4b**$^+$ PF_6^- [0.565 g, 0.688 mmol, 86%; 77:23 (*RS,SR*)/(*RR,SS*)], m.p. 222–229°C (dec.). – $C_{32}H_{28}F_6NO_2P_2Re$ (820.7): calcd. C 46.83, H 3.44; found C 47.04, H 3.46. – IR (thin film): $\tilde{\nu}$ = 1743 cm^{-1} (NO, vs), 1659 (CO, s). – NMR (CD_2Cl_2): (*RS,SR*)-**4b**$^+$ PF_6^-[27]: ^{1}H (TMS as ref.): δ = 8.15–7.38 (m, 4 C_6H_5), 5.82 (d, J_{HP} = 0.6, C_5H_5), 5.47 (ddd, J_{HH} = 8.4, 10.5, J_{HP} = 2.1, =CHCO), 3.28 (ddd, J_{HH} = 4.7, 10.5, J_{HP} = 11.5, =CH_ZH_E), 2.09 (ddd, J_{HH} = 4.7, 8.4, J_{HP} = 6.4, =CH_ZH_E); ^{13}C{^{1}H} (CD_2Cl_2 as ref.): δ = 193.8 (s, CO), 137.3 (s, CPh), 134.1 (s, CPh), 129.6 (s, CPh), 128.2 (s, CPh), 133.6 (d, J_{CP} = 10.2, *o*-PPh), 133.0 (d, J_{CP} = 2.7, *p*-PPh), 130.2 (d, J_{CP} = 11.3, *m*-PPh), 98.4 (s, C_5H_5), 38.5 (s, =*C*HCO), 35.7 (d, J_{CP} = 6.6, =CH_2)[30]; ^{31}P{^{1}H}: δ = 12.3 (s). (*RR,SS*)-**4b**$^+$ PF_6^-: ^{1}H (TMS as ref.): δ = 8.15–7.38 (m, 3 C_6H_5), 5.54 (d, J_{HP} = 0.6, C_5H_5), 4.55 (ddd, J_{HH} = 8.3, 12.6, J_{HP} = 1.4, =CHCO), 3.06 (ddd, J_{HH} = 4.6, 8.3, J_{HP} = 14.4, =CH_ZH_E), 2.63 (ddd, J_{HH} = 4.6, 12.6, J_{HP} = 4.6, =CH_ZH_E); ^{13}C{^{1}H} (CD_2Cl_2 as ref.): δ = 198.8 (s, CO), 137.0 (s, CPh), 134.7 (s, CPh), 130.4 (s, CPh), 128.7 (s, CPh), 133.5 (d, J_{CP} = 9.7, *o*-PPh), 133.3 (d, J_{CP} = 2.6, *p*-PPh), 130.0 (d, J_{CP} = 12.0, *m*-PPh), 99.8 (s, C_5H_5), 39.8 (s, =*C*HCO), 36.9 (d, J_{CP} = 6.9, =CH_2)[30]; ^{31}P{^{1}H}: δ = 11.1 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-H_2C=$CHCO_2C_2H_5$)]$^+$ PF_6^- (**4c**$^+$ PF_6^-): Complex **2** (0.216 g, 0.387 mmol), CH_2Cl_2 (3 ml), Ph_3C^+ PF_6^- (0.167 g, 0.430 mmol), and $N_2CHCO_2C_2H_5$ (200 µl, 1.91 mmol) were combined in a procedure analogous to that given for **3**$^+$ PF_6^-. A similar workup gave **4c**$^+$ PF_6^- [0.236 g, 0.299 mmol, 77%; 5:80:15 *ac*-(*RS,SR*)/*sc*-(*RS,SR*)/*sc*-(*RR,SS*)][14], m.p. 226–232°C (dec.). – $C_{28}H_{28}F_6NO_3P_2Re$ (788.6): calcd. C 42.64, H 3.58; found C 42.76, H 3.51. – IR (thin film): $\tilde{\nu}$ = 1747 cm^{-1} (NO, vs), 1710 (CO, s). – NMR (CD_2Cl_2): *sc*-(*RS,SR*)-**4c**$^+$ PF_6^-[27]: ^{1}H (TMS as ref.): δ = 7.64–7.36 (m, 3 C_6H_5), 5.88 (s, C_5H_5), 4.34 (m, =CHCO), 4.28–4.17 (m, OCHH′), 3.00 (ddd, J_{HH} = 4.8, 10.8, J_{HP} = 10.8, =CH_ZH_E), 2.03 (ddd, J_{HH} = 4.8, 9.6, J_{HP} = 6.9, =CH_ZH_E), 1.29 (dd, J_{HH} = 6.9, 6.9, CH_3); ^{13}C{^{1}H} (CD_2Cl_2 as ref.): δ = 171.8 (s, CO), 133.6 (d, J_{CP} = 10.2, *o*-Ph), 133.0 (d, J_{CP} = 2.6, *p*-Ph), 130.2 (d, J_{CP} = 11.7, *m*-Ph), 129.5 (d, J_{CP} = 60.3, *i*-Ph), 98.4 (s, C_5H_5), 61.7 (s, OCH_2), 36.0 (d, J_{CP} = 6.4, =CH_2), 34.9 (s, =*C*HCO), 14.7 (s, CH_3); ^{31}P{^{1}H}: δ = 11.5 (s). *sc*-(*RR,SS*)-**4c**$^+$ PF_6^-: ^{1}H (TMS as ref.): δ = 7.64–7.36 (m, 3 C_6H_5), 5.69 (s, C_5H_5), 4.37–4.30 (m, OCHH′), 3.64 (ddd, J_{HH} = 8.7, 12.3, J_{HP} = 1.2, =CHCO), 2.84 (ddd, J_{HH} = 5.1, 8.7, J_{HP} = 13.8, =CH_ZH_E), 2.42 (ddd, J_{HH} = 5.1, 12.3, J_{HP} = 5.7, =CH_ZH_E), 1.40 (dd, J_{HH} = 7.2, 7.2, CH_3); ^{13}C{^{1}H} (CD_2Cl_2 as ref.): δ = 175.8 (s, CO), 133.6 (d, J_{CP} = 10.2, *o*-Ph), 133.2 (d, J_{CP} = 2.6, *p*-Ph), 130.3 (d, J_{CP} = 11.2, *m*-Ph), 99.7 (s, C_5H_5), 62.4 (s, OCH_2), 37.8 (d, J_{CP} = 6.9, =CH_2), 36.3 (s, =*C*HCO), 14.7 (s, CH_3)[30]; ^{31}P{^{1}H}: δ = 10.6 (s). *ac*-(*RS,SR*)-**4c**$^+$ PF_6^-: ^{1}H (TMS as ref.): δ = 7.64–7.36 (m, 3 C_6H_5), 5.91 (s, C_5H_5), 3.89 (dq, J_{HH} = 7.2, 10.8, OC*H*H′), 3.82 (ddd, J_{HH} = 2.7, 10.8, J_{HP} = 1.8, =CH_ZH_E), 3.51 (dq, J_{HH} = 7.2, 10.8, OCH*H*′), 3.20 (ddd, J_{HH} = 9.0, 10.8, J_{HP} = 10.8, =CHCO), 0.94 (dd, J_{HH} = 7.2, 7.2, CH_3)[31]; ^{13}C{^{1}H} (CD_2Cl_2 as ref.): δ = 98.6 (s, C_5H_5), 61.8 (s, OCH_2), 45.2 (d, J_{CP} = 5.8, =*C*HCO), 29.6 (s, =CH_2), 13.8 (s, CH_3); ^{31}P{^{1}H}: δ = 4.9 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-H_2C=$CHPh$)]$^+$ PF_6^- (**7**$^+$ PF_6^-): – A) Benzyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2Ph) (**9**[8a]; 0.198 g, 0.312 mmol), CH_2Cl_2 (15 ml), Ph_3C^+ PF_6^- (0.133 g, 0.343

mmol), and ethereal CH_2N_2 (ca. 2.4 mmol) were combined in a procedure analogous to that given for $\mathbf{3}^+$ PF_6^-. A similar workup gave $\mathbf{7}^+$ PF_6^- [0.151 g, 0.191 mmol, 61%, 92:8 (*RS,SR*)/(*RR,SS*)][28]. – B) A Schlenk flask was charged with *ac*-[(η^5-C_5H_5)Re(NO)(PPh$_3$)(=CHPh)]$^+$ PF_6^- ($\mathbf{6}^+$ PF_6^-[8a]; 0.094 g, 0.121 mmol), CH_2Cl_2 (10 ml), and a stir bar and was cooled to −80°C. Then ethereal CH_2N_2 (ca. 0.50 mmol) was added with stirring. The cold bath was allowed to gradually warm. After 10 h, the solution was added to ether (40 ml). The resulting yellow powder was collected by filtration, washed with ether (2 × 3 ml) and dried under oil-pump vacuum to give $\mathbf{7}^+$ PF_6^- [0.032 g, 0.040 mmol, 33%; 6:94 (*RS,SR*)/(*RR,SS*)][28].

Reaction of $\mathbf{6}^+$ PF_6^- *and* $N_2CHCO_2C_2H_5$: Complex **9** (0.198 g, 0.312 mmol), CH_2Cl_2 (5 ml), Ph_3C^+ PF_6^- (0.145 g, 0.374 mmol), and $N_2CHCO_2C_2H_5$ (100 µl, 0.955 mmol) were combined in a procedure analogous to that given for $\mathbf{3}^+$ PF_6^-. A similar workup gave [(η^5-C_5H_5)Re(NO)(PPh$_3$)(η^2-PhHC=CHCO$_2$C$_2$H$_5$)]$^+$ PF_6^- ($\mathbf{8}^+$ PF_6^-; 0.203 g, 0.235 mmol, 75%) as a mixture of several diastereomers that could not be further purified. – IR (thin film): $\tilde{\nu}$ = 1747 cm^{-1} (NO, vs), 1705 (CO, s). – NMR (CD_2Cl_2): ^{1}H (CHDCl$_2$ as ref.): δ = 5.96 (d, J_{HP} = 0.6, C_5H_5, major), 6.06 (d, J_{HP} = 0.6, C_5H_5), 5.91 (d, J_{HP} = 0.9, C_5H_5), 5.82 (d, J_{HP} = 0.6, C_5H_5); ^{31}P{^{1}H}: δ = 4.8 (68%), 3.4 (12%), 12.1 (11%), 17.8 (7%), 19.7 (2%).

[1] [1a] W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 800; *Angew. Chem.* **1978**, *90*, 855. – [1b] M. Putala, D. A. Lemenovskii, *Russ. Chem. Rev.* **1994**, *63*, 197.

[2] Lead 1993–94 references to representative stoichiometric reactions: [2a] J. M. O'Connor, H. Ji, M. Iranpour, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, *115*, 1586. – [2b] R. K. Minhas, J. J. H. Edema, S. Gambarotta, A. Meetsma, *J. Am. Chem. Soc.* **1993**, *115*, 6710. – [2c] R. Réau, R. W. Reed, F. Dahan, G. Bertrand, *Organometallics* **1993**, *12*, 1501. – [2d] F. F. Stewart, W. D. Neilsen, R. E. Ekeland, R. D. Larsen, P. W. Jennings, *Organometallics* **1993**, *12*, 4585.

[3] Reviews and lead 1993–94 references to catalytic reactions: [3a] M. P. Doyle, *Chem. Rev.* **1986**, *86*, 919. – [3b] M. P. Doyle, W. R. Winchester, J. A. A. Hoorn, V. Lynch, S. H. Simonsen, R. Ghosh, *J. Am. Chem. Soc.* **1993**, *115*, 9968. – [3c] D. A. Smith, D. N. Reynolds, K. W. Woo, *J. Am. Chem. Soc.* **1993**, *115*, 2511. – [3d] A. Padwa, D. J. Austin, Y. Gareau, J. M. Kassir, S. L. Xu, *J. Am. Chem. Soc.* **1993**, *115*, 2637. – [3e] H. Nishiyama, Y. Itoh, H. Matsumoto, S.-B. Park, K. Itoh, *J. Am. Chem. Soc.* **1994**, *116*, 2223. – [3f] F. G. West, B. N. Naidu, *J. Am. Chem. Soc.* **1994**, *116*, 8420. – [3g] M. C. Pirrung, A. T. Morehead, Jr., *J. Am. Chem. Soc.* **1994**, *116*, 8991. – [3h] T. Ye, M. A. McKervey, *Chem. Rev.* **1994**, *94*, 1091.

[4] [4a] C. P. Casey, S. H. Bertz, T. J. Burkhardt, *Tetrahedron Lett.* **1973**, 1421. – [4b] See also: F. R. Kreissl, E. O. Fischer, C. G. Kreiter, *J. Organomet. Chem.* **1973**, *57*, C9.

[5] T.-K. Mitsudo, H. Watanabe, K. Watanabe, Y. Watanabe, Y. Takegami, *J. Organomet. Chem.* **1981**, *214*, 87.

[6] J. Wolf, R. Zolk, U. Schubert, H. Werner, *J. Organomet. Chem.* **1988**, *340*, 161.

[7] [7a] W. Tam, G.-Y. Lin, W.-K. Wong, W. A. Kiel, V. K. Wong, J. A. Gladysz, *J. Am. Chem. Soc.* **1982**, *104*, 141. – [7b] J. H. Merrifield, G.-Y. Lin, W. A. Kiel, J. A. Gladysz, *J. Am. Chem. Soc.* **1983**, *105*, 5811. – [7c] A. T. Patton, C. E. Strouse, C. B. Knobler, J. A. Gladysz, *J. Am. Chem. Soc.* **1983**, *105*, 5804.

[8] [8a] W. A. Kiel, G.-Y. Lin, A. G. Constable, F. B. McCormick, C. E. Strouse, O. Eisenstein, J. A. Gladysz, *J. Am. Chem. Soc.* **1982**, *104*, 4865. – [8b] W. A. Kiel, G.-Y. Lin, G. S. Bodner, J. A. Gladysz, *J. Am. Chem. Soc.* **1983**, *105*, 4958. – [8c] W. A. Kiel, W. E. Buhro, J. A. Gladysz, *Organometallics* **1984**, *3*, 879. – [8d] S. Georgiou, J. A. Gladysz, *Tetrahedron* **1986**, *42*, 1109.

[9] C. Roger, G. S. Bodner, W. G. Hatton, J. A. Gladysz, *Organometallics* **1991**, *10*, 3266.

[10] See also: [10a] E. J. O'Connor, M. Kobayashi, H. G. Floss, J. A. Gladysz, *J. Am. Chem. Soc.* **1987**, *109*, 4837. – [10b] G. L. Crocco, K. E. Lee, J. A. Gladysz, *Organometallics* **1990**, *9*, 2819. – [10c] J. J. Kowalczyk, A. M. Arif, J. A. Gladysz, *Chem. Ber.* **1991**, *124*, 729.

[11] [11a] Y. Zhou, J. W. Seyler, W. Weng, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **1993**, *115*, 8509. – [11b] W. Weng, J. A. Ramsden, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **1993**, *115*, 3824.

[12] [12a] G. S. Bodner, T.-S. Peng, A. M. Arif, J. A. Gladysz, *Organometallics* **1990**, *9*, 1191. – [12b] T.-S. Peng, A. M. Arif, J. A. Gladysz, *Helv. Chim. Acta* **1992**, *75*, 442. – [12c] J. Pu, T.-S. Peng, C. L. Mayne, A. M. Arif, J. A. Gladysz, *Organometallics* **1993**, *12*, 2686. – [12d] T.-S. Peng, Y. Wang, A. M. Arif, J. A. Gladysz, *Organometallics* **1993**, *12*, 4535. – [12e] T.-S. Peng, J. Pu, J. A. Gladysz, *Organometallics* **1994**, *13*, 929.

[13] Y. Wang, F. Agbossou, D. M. Dalton, Y. Liu, A. M. Arif, J. A. Gladysz, *Organometallics* **1993**, *12*, 2699.

[14] [14a] In synclinal (*sc*) Re=CHR or Re–(C≒C) conformers of alkylidene or alkene complexes of **I**, the highest priority substituents on the rhenium center (η^5-C_5H_5) and the alkylidene carbon atom (R > H) or C≒C centroid (=*C*HR > =*C*H$_2$) define (60 ± 30)° torsion angles. In anticlinal (*ac*) conformers, the highest priority substituents define (120 ± 30)° torsion angles. The torsion angles in idealized structures **III** and **VIIIc** are 45°, whereas those in **IV** and **Xc** are 135°. – [14b] The (*R*)/(*S*) nomenclature follows conventions described earlier[12e]. – [14c] All isomer ratios are normalized to 100, and error limits on each integer are ±2; e.g., 42:58 ≡ (42 ± 2):(58 ± 2). – [14d] In ligands with more than one potential binding site (e.g., C=C or O=C), the hapticity is designated prior to the binding site.

[15] F. Agbossou, E. J. O'Connor, C. M. Garner, N. Quirós Méndez, J. M. Fernández, A. T. Patton, J. A. Ramsden, J. A. Gladysz, *Inorg. Synth.* **1992**, *29*, 211.

[16] [16a] T. Hudlicky, F. J. Koszyk, T. M. Kutchan, J. P. Sheth, *J. Org. Chem.* **1980**, *45*, 5020, footnote 40. – [16b] F. G. West, K. W. Glaeske, B. N. Naidu, *Synthesis* **1993**, 977, footnote 16.

[17] The *ac*/*sc* ratio was determined from the integrals of the H_c resonance and the overlapping H_a and H_d resonances (the H_b resonance overlapped with some organic impurities and could not be accurately integrated). The H_a integral is a measure of *ac*-$\mathbf{3}^+$-d_2 PF_6^-. The H_d integral is a measure of *sc*-$\mathbf{3}^+$-d_2 PF_6^-, and must equal that of H_c. Hence, the $H_c/(H_a + H_d)$ integral ratio gives the mole fraction of *sc*-$\mathbf{3}^+$-d_2 PF_6^-.

[18] Y. Wang, Ph. D. Thesis, University of Utah, **1994**, Ch. 3.

[19] [19a] The (*RS,SR*)/(*RR,SS*) ratios were 82:18, 89:11, and 96:4 after 19, 42, and 135 h, respectively. – [19b] The *ac*-(*RS,SR*)/*sc*-(*RS,SR*)/*sc* (*RR,SS*) ratios were 7:81:12 and 7:86:7 after 19 and 230 h, respectively. – [19c] The (*RS,SR*)/(*RR,SS*) ratios were 42:58, 64:36, and 93:7 after 4, 10, and 31 h, respectively.

[20] J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, **1982**, p. 66. The $\Delta G^{\neq}$ calculation utilized eq. 6.5c and a Δδ value of 741 Hz (^{31}P).

[21] Nonetheless, we believe that the *ac*/*sc* rotamers of (*RS,SR*)-$\mathbf{4c}^+$ PF_6^- readily interconvert at room temperature. The absence of coalescence in variable-temperature NMR spectra may be due in part to a negative $\Delta S^{\neq}$ value.

[22] With π complexes of **I** and aromatic aldehydes, hexafluorophosphates give slightly higher (*RS,SR*)/(*RR,SS*) ratios than tetrafluoroborates: B. J. Boone, D. P. Klein, J. W. Seyler, N. Quirós Méndez, A. M. Arif, J. A. Gladysz, *J. Chem. Soc., Chem. Commun.*, in press.

[23] J. M. Fernández, J. A. Gladysz, *Organometallics* **1989**, *8*, 207.

[24] [24a] W. E. Buhro, S. Georgiou, J. M. Fernández, A. T. Patton, C. E. Strouse, J. A. Gladysz, *Organometallics* **1986**, *5*, 956. – [24b] C. M. Garner, N. Quirós Méndez, J. J. Kowalczyk, J. M. Fernández, K. Emerson, R. D. Larsen, J. A. Gladysz, *J. Am. Chem. Soc.* **1990**, *112*, 5146.

[25] J. I. Seeman, *Chem. Rev.* **1983**, *83*, 83.

[26] F. Mari, P. M. Lahti, W. E. McEwen, *J. Am. Chem. Soc.* **1992**, *114*, 813, and references therein.

[27] NMR data were recorded with Varian 300-MHz spectrometers, and all coupling constants (*J*) are in Hz. The vinylic protons H_Z and H_E are defined with reference to the =CHR substituent.

[28] The IR and NMR (^{1}H, ^{31}P) spectra were identical with those of authentic samples described in ref.[7b] and/or ref.[12a].

[29] These assignments and the *J* values were verified by homonuclear decoupling experiments. The $H_2C=CH_2$ ^{1}H resonances of $\mathbf{3}^+$ PF_6^- were multiplets.

[30] The *i*-PPh$_3$ ^{13}C resonance was obscured.

[31] Partial data; the $=CH_ZH_E$ ^{1}H resonance was obscured.

[32] The OCH_2 and =CH ^{1}H resonances overlapped and could not be assigned.

[405/94]