A Crystallographic Map of Chiral Recognition in π Complexes of Aromatic Aldehydes and a Chiral Transition Metal Lewis Acid: Enantioface Binding Selectivities in Solution Correlate to Distances between Metal and Carbon Stereocentres in the Solid State

Brian J. Boone, Darryl P. Klein, N. Quirós Méndez, Jeffery W. Seyler, A. M. Arif and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

The title claim is established with five π-aromatic aldehyde complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHAr)]^+ X^-$; electronegative aryl substituents give shorter rhenium–carbon bond lengths and higher binding selectivities, providing the first easily conceptualized mechanism for an electronic effect upon chiral recognition.

Most types of bonding interactions between two chiral or prochiral species offer the potential for 'chiral recognition'—the selective formation of one of two possible diastereoisomeric adducts.[1] Steric effects can obviously play a major role, and have been well documented. Recently, however, significant electronic effects have been discovered in asymmetric catalysis, the origins of which are frequently arcane.[2] Thus, we have sought to study electronic effects in chiral recognition—a subject that has received scant attention.[1a]

The chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ **I** forms diastereoisomeric π-adducts with aromatic aldehydes, as shown in Fig. 1 [(*RS*,*SR*) **II** and (*RR*,*SS*) **III**].[3] These differ in the O=CHAr enantioface bound to rhenium, and rapidly interconvert *via* σ-isomers.[3c,d] The Re–(O=C) conformations maximize overlap of the HOMO of **I** and the O=C π*-acceptor orbital, while directing the larger =CHAr terminus *anti* to the bulky PPh_3 ligand. The (*RR*,*SS*) diastereoisomer, in which the aryl group is *syn* to the cyclopentadienyl ligand and distanced from the smaller nitrosyl ligand, is disfavoured sterically. Thus, high levels of chiral recognition or enantioface binding selectivity are observed.

We previously noted that aromatic aldehydes with electron-withdrawing substituents gave higher (*RS*,*SR*) : (*RR*,*SS*) ratios.[3c] We sought to define the underlying basis for this electronic effect. We thought that distances between the rhenium and carbon stereocentres should decrease in adducts of the more π-acidic aldehydes. This would enhance destabilizing steric interactions between the cyclopentadienyl ligands and aryl groups in the (*RR*,*SS*) diastereoisomers, giving higher (*RS*,*SR*) : (*RR*,*SS*) ratios and chiral recognition.† Hence, correlations to crystallographic rhenium–carbon bond lengths would be expected. In this communication, we report the experimental verification of this chiral recognition mechanism.

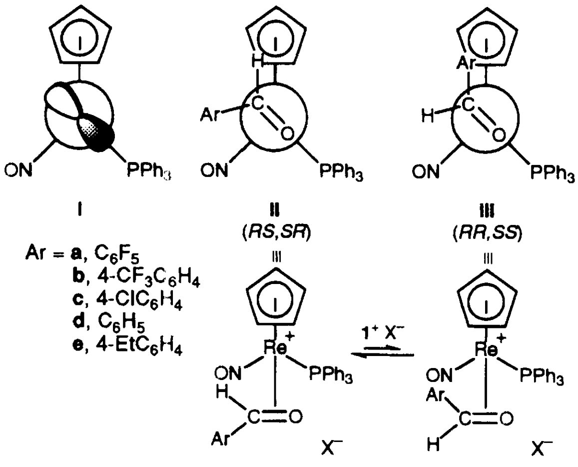

Fig. 1 d-Orbital HOMO of the pyramidal rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ **I** and idealized structures of diastereoisomeric aldehyde complexes **II**, **III**

The pentafluorobenzaldehyde, *p*-trifluorobenzaldehyde, *p*-chlorobenzaldehyde, benzaldehyde and *p*-ethylbenzaldehyde complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CHAr)]^+ X^-$ (**1a–e**$^+$ X^-) were prepared by published procedures,[3] or simple modifications thereof. Crystal structures of the five salts shown in Fig. 2 were determined.‡ Each crystallized as the more stable (*RS*,*SR*) diastereoisomer. As illustrated in Fig. 2, the rhenium–carbon bond lengths decreased from 2.199(6) Å [(*RS*,*SR*)-**1e**$^+$ PF_6^-] to 2.161(9) Å [(*RS*,*SR*)-**1a**$^+$ PF_6^-] as the electronegativities of the aryl substituents increased.

Next, 0.00071 mol dm^{-3} CH_2Cl_2 solutions of the tetrafluoroborate salts **1a–e**$^+BF_4^-$ were prepared (293 K). The (*RS*,*SR*) : (*RR*,*SS*) ratios were determined by ^{31}P NMR at 173 and 183 K.§ Measurements were made on at least four independently prepared samples. The data, including standard deviations, are summarized in Fig. 2.

The rhenium–carbon bond lengths are plotted *vs.* the (*RS*,*SR*) : (*RR*,*SS*) ratios in Fig. 3. As the rhenium–carbon bonds contract from 2.199(6) to 2.161(9) Å, the enantioface binding selectivities increase from 75 : 25 or 79 : 21 (**1e**$^+$ BF_4^-, 183 or 173 K, respectively) to 97 : 3 (**1a**$^+$ BF_4^-). Thus, Fig. 3 can be viewed as a crystallographic map of a chiral recognition event. The (*RS*,*SR*) : (*RR*,*SS*) ratios correspond to ΔG values ranging from 0.5 to 1.2 kcal mol^{-1} (1 cal = 4.184 J). By the commonly employed 'three esd' criterion, the bond lengths in *adjacent* pairs of compounds in Fig. 3 are not statistically different. However, there is a statistically rigorous overall correlation with the (*RS*,*SR*) : (*RR*,*SS*) ratios in solution.¶

Other aspects of aldehyde ligand bonding were probed. First, the crystal structures of (*RS*,*SR*)-**1a–e**$^+$ X^- were overlaid on a stereoscopic viewing screen. The homology was good, and no other factors that should appreciably contribute to chiral recognition could be identified. The positions of the O=C hydrogen and aryl substituents were then interchanged, keeping bond lengths and angles constant. When the resulting (*RR*,*SS*) diastereoisomers were viewed with atoms set at van der Waals radii, spatial overlaps of the aryl groups with the cyclopentadienyl ligands were modest. Thus, the interactions that give rise to the 0.5–1.2 kcal mol^{-1} energy differences in (*RS*,*SR*) : (*RR*,*SS*) diastereoisomers are not visually striking.

The preceding data establish that electronic effects can influence chiral recognition in π-complexes of chiral metal fragments and prochiral aldehydes. In the cases of **1a–e**$^+$ X^-, this is manifested in a key structural parameter—the distance between the rhenium and carbon stereocentres—the variation in which controls binding selectivities. This leads to the general prediction that chiral recognition in metal π-complexes will be enhanced when the π-acidity of the ligand *or* the π-basicity of the metal fragment is increased. To our knowledge, this represents a new approach to the optimization of chiral receptors, which are most commonly initially designed and then modified based upon steric principles.

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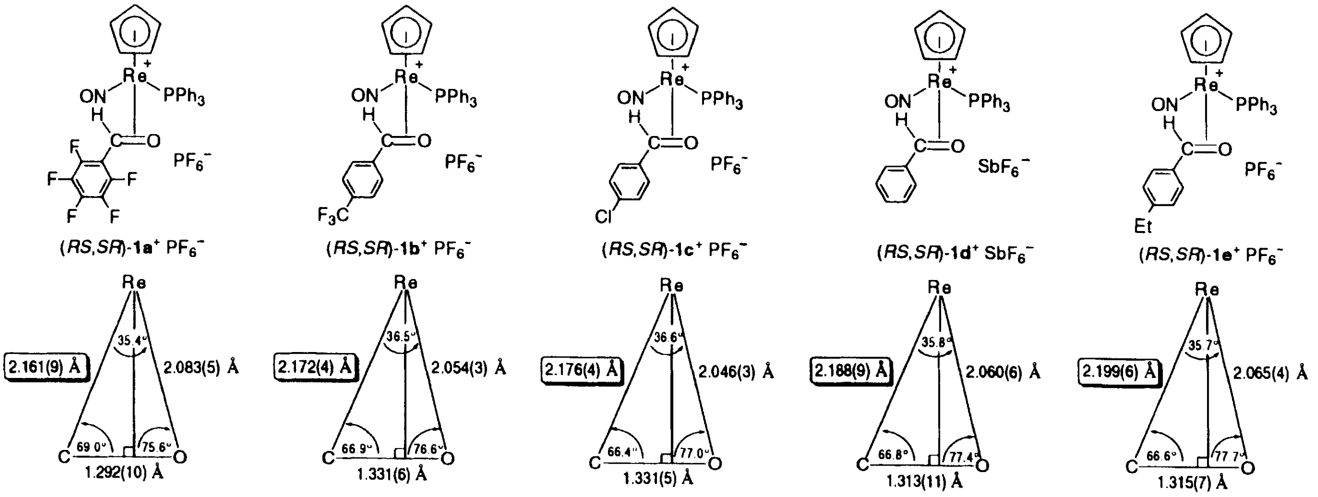
Fig. 2 Views of the Re–O=C planes of crystalline π-aromatic aldehyde complexes (*RS,SR*)-**1a**–**e**$^+X^-$, and enantioface binding selectivities in solution



T/K	(*RS,SR*):(*RR,SS*) Ratios, **1**$^+$ BF_4^- (0.00071 mol dm^{-3} CH_2Cl_2)				
183	96.9(3):3.1(3)	87.9(5):12.1(5)	82.9(5):17.1(5)	77.8(3):22.2(3)	75.0(6) : 25.0(6)
173	96.8(4):3.2(4)	88.7(6):11.3(6)	84.2(5):15.8(5)	79.6(6):20.4(6)	78.6(10):21.4(10)

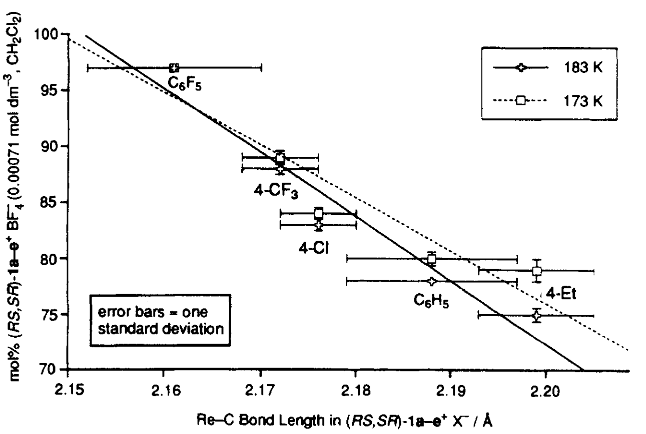


Fig. 3 A crystallographic 'map' of chiral recognition in aromatic aldehyde complexes **1a**–**e**$^+$ X^-

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Footnotes

† The rhenium–carbon bond lengths in **1**$^+$ X^- would not necessarily be equal in (*RS,SR*) and (*RR,SS*) diastereoisomers. However, they should undergo parallel changes as aryl substituents are varied.

‡ *Crystallographic data* (*RS,SR*)-**1a**$^+PF_6^-$/(*RS,SR*)-**1b**$^+PF_6^-$/(*RS,SR*)-**1c**$^+PF_6^-$/(*RS,SR*)-**1d**$^+SbF_6^-$/(*RS,SR*)-**1e**$^+PF_6^-$: $C_{30}H_{21}F_{11}NO_2P_2Re$/$C_{31}H_{25}F_9NO_2P_2Re$/$C_{30}H_{25}ClF_6NO_2P_2Re$/$C_{30}H_{26}F_6NO_2PSbRe$/$C_{32}H_{30}F_6NO_2P_2Re$; M = 884.638/862.684/829.131/885.462/822.740; monoclinic/triclinic/triclinic/monoclinic/monoclinic; space group $P2_1/n$ (no. 14)/$P\bar{1}$ (no. 2)/$P\bar{1}$ (no. 2)/$P2_1/c$ (no. 14)/$P2_1/n$ (no. 14); a/Å 13.775(1)/14.908(2)/10.584(2)/11.790(2)/13.690(1); b/Å 16.247(1)/10.656(1)/14.987(1)/18.160(2)/21.845(2); c/Å 15.196(1)/10.220(1)/9.958(1)/14.357(2)/10.781(1); α/° —/95.38(2)/106.89(1)/—/—; β/° 116.360(3)/74.74(2)/93.55(1)/100.72(1)/106.00(1); γ/° —/93.64(2)/85.67(1)/—/—; V/Å^3 3047.31/1558.29/1505.81/3020.18/3099.00; Z = 4/2/2/4/4; ambient temp.; D_c/g cm^{-3} 1.93/1.84/1.83/1.95/1.76; D_o/g cm^{-3} (CCl_4–CH_2I_2) 1.92/1.83/1.82/1.92/1.74; diffractometer Syntex $P\bar{1}$/Syntex $P\bar{1}$/Enraf-Nonius CAD-4/Syntex $P\bar{1}$/-Enraf-Nonius CAD-4; Radiation (λ/Å) Mo-Kα (0.71073)/Mo-Kα(0.71073)/Cu-Kα(1.54056)/Mo-Kα(0.71073)/Cu-Kα(1.54056); scan type θ–2θ; /° 3.0–48.0/3.0–48.0/4.0–130.0/3.0–46.0/4.0–130.0; reflections measured 5318/5658/5317/4684/5207; total unique data 4998/5458/5023/4366/4447; no. of observations [$I > 3\sigma(I)$] 2994/4508/4729/2677/4202; no. of variables 428/415/389/379/398; goodness of fit 1.15/1.60/1.59/2.55/1.11; R (averaging; I_{obs}, F_{obs}) 0.026, 0.017/—/0.024, 0.017/0.042, 0.023/0.029, 0.018; R 0.034/0.029/0.031/0.036/0.031; R_w 0.044/0.032/0.034/0.042/0.034; Δ/σ (max) 0.006/0.011/0.001/0.006/0.011; $\Delta\rho$ (max, e Å^{-3}) 1.55 (1.22 Å from Re)/0.74 (3.4 Å from Re)/0.87 (0.74 Å from Re)/0.67/0.69. Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied. The structures were solved by standard heavy-atom techniques with the SDP/VAX package [(*RS,SR*)-**1a**$^+$ PF_6^-: weighting scheme type one, isotropic extinction coefficient].[9] The O=CH hydrogens of (*RS,SR*)-**1a**,**e**$^+PF_6^-$, all hydrogens of (*RS,SR*)-**1b**$^+$ PF_6^-, and the *p*-chlorobenzaldehyde hydrogens of (*RS,SR*)-**1c**$^+$ PF_6^- were located. The O=CH hydrogen of (*RS,SR*)-**1a**$^+$ PF_6^- was refined with fixed isotropic parameters. The remaining hydrogen atom positions were calculated and added to the structure factor calculations but were not refined. The methyl group in (*RS,SR*)-**1e**$^+$ PF_6^- was disorded. Distances between fluorine atoms of the anions and non-hydrogen atoms of the cations were all greater than 3.0 Å. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[5] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. The crystal structure of (*RS,SR*)-**1b**$^+PF_6^-$ was reported earlier.[3b] The crystal structure of (*RS,SR*)-**1c**$^+PF_6^-$ was also determined at 148 K. However, bond lengths and angles were essentially identical, and the estimated standard deviations of most did not improve. Optimally, correlations between solution and solid-state phenomena should use as many data points as possible. Over a four-year period, we prepared complexes of **I** and numerous other substituted benzaldehydes (*e.g.* *p*-fluoro, *p*-phenyl, *p*-azido, *p*-chloromethyl, *p*-iodomethyl, *p*-methoxymethyl, *p*-phenoxy, *p*-trimethylsilyl, *p*-dimethylphenylsilyl, *p*-trimethylstannyl, *p*-triphenylstannyl), and conducted an extensive series of crystallizations. However, only the five compounds in Fig. 2 gave material suitable for X-ray analysis.

§ The (*RS,SR*):(*RR,SS*) ratios vary with solvent, concentration, counteranion and temperature, as will be detailed in a forthcoming full paper. Concentrations must be dilute to accommodate the less soluble complexes.

¶ The commonly utilized χ^2 test can be applied to Fig. 3. If, as a simplification, a linear relationship is assumed, the probability that the data are random as opposed to correlated is less than 5%.[6]

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