ELSEVIER

Inorganica Chimica Acta 269 (1998) 167–180

Inorganica Chimica Acta

Additions of carbon nucleophiles to acyclic imine complexes of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$: controlling factors in 1,3-asymmetric induction and syntheses of non-racemic organic amines [1]

Gene A. Stark, J.A. Gladysz *

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

Received 14 May 1997; accepted 30 June 1997

Abstract

Reactions of the racemic or enantiomerically pure benzaldehyde-derived imine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(CH_3)=C(H)C_6H_5)]^+TfO^-$ ($\mathbf{1}^+TfO^-$; 95:5 *E*/*Z* N=C isomers) and RLi (THF, −100°C) give amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}(CH_3)CH(R)C_6H_5)$ (**5**) (R = **a**/CH_3, **b**/$C{\equiv}CSi(CH_2CH_3)_3$, **c**/$CH_2Si(CH_3)_3$) in quantitative NMR yields as 74–72:26–28 mixtures of Re,C configurational diastereomers. These labile adducts and TfOH react to give amine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)CH(R)C_6H_5)]^+TfO^-$ ($\mathbf{6}^+TfO^-$). Reaction of $\mathbf{6a}^+TfO^-$ (prepared from (*R*)-$\mathbf{1}^+TfO^-$) and $Et_4N^+CN^-$ yields the cyanide complex (*R*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (85%, >98% ee) and amine (*R*)-$NH(CH_3)CH(CH_3)C_6H_5$ (81%, 46% ee). Reactions of $\mathbf{1}^+TfO^-$ and CN^- give similar amido complexes (85–84:15–16 Re,C diastereomers), but appear reversible, with additions of CH_3OTf affording $\mathbf{1}^+TfO^-$. Reactions of the acetophenone-derived complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(CH_3)=C(CH_3)C_6H_5)]^+TfO^-$ ($\mathbf{4}^+TfO^-$) with $C_6H_5CH_2MgCl$ and $(CH_3)_3SiCH_2Li$ give 41 and >99% deprotonation to the enamido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}(CH_3)C(C_6H_5)=CH_2)$. Some addition occurs with $C_6H_5CH_2MgCl$, and CN^-. NMR spectra (−100°C) show Re–N= rotamers of $\mathbf{1,4}^+TfO^-$, and mechanisms of 1,3-asymmetric induction are analyzed in detail. © 1998 Elsevier Science S.A.

Keywords: Rhenium complexes; Imine complexes; Chiral complexes

1. Introduction

Additions of carbon nucleophiles to imines or imine derivatives see extensive use in amine and alkaloid syntheses, often for the purpose of generating new carbon stereocenters [1]. Accordingly, there has been intense interest in the development of enantioselective methodologies. Approaches that have received attention include (i) nitrogen-bound chiral auxiliaries [2–4], (ii) chiral ligands that associate with the nucleophile [5] and (iii) chiral catalysts [6]. There have been parallel developments with enantioselective hydrogenations and hydrosilylations of imines, which often provide alternative routes to the same products [7].

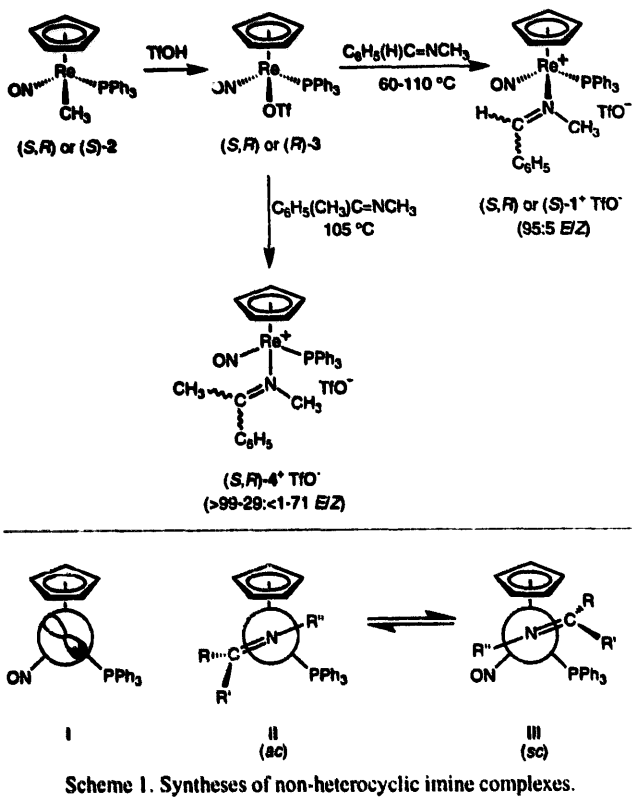
Imines readily bind to transition metals. We have had an ongoing interest in the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**), numerous adducts of which are easily prepared in enantiomerically pure form. In previous papers, we have described an extensive series of σ-imine complexes of **I** [8–13]. These include species derived from free imines [8a], as well as from the elaboration of nitrile [8a], pyrrolidine [9], isoquinoline [10], quinoline [11], pyrrolyl [12] and indolyl [13] ligands. During this work, we found that strong carbon nucleophiles undergo highly diastereoselective additions to the N=C moieties of isoquinoline, quinoline and indolenine complexes of **I** [10,11,13]. In particular, isoquinoline could be efficiently converted to various alkyl, dialkyl and trialkyl hydroisoquinoline derivatives of high enantiomeric purities [10]. We sought to probe analogous addition reactions with substrates where the N=C linkage was not part of a heterocyclic ring.

Accordingly, we returned to the simple non-heterocyclic or 'acyclic' imine complexes of **I** described in our first paper [8a]. In this study, we report (i) diastereoselective additions of carbon nucleophiles to benzaldehyde and acetophenone-derived imine complexes of **I**, (ii) reactions of the resulting neutral amido complexes with electrophiles to give cationic amine complexes, (iii) subsequent displacement reactions

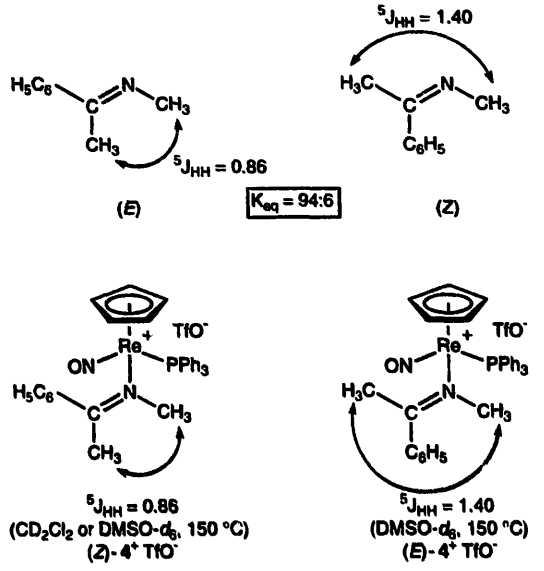
* Corresponding author. Tel.: +1-801-581 4300; fax: +1-801-585 7807.

[1] This paper is dedicated to Professor Dr Wolfgang Beck, whose many seminal publications, including studies of transition metal imine complexes, have inspired numerous projects in our laboratory. One of us also warmly thanks him for his first Weisswurst.

PII S0020-1693(97)05787-3



Scheme 1. Syntheses of non-heterocyclic imine complexes.



Scheme 2. Key data for *E*/*Z* assignments [18].

that give non-racemic chiral amines, (iv) several competing processes, such as imine ligand deprotonation and (v) detailed analyses of the mechanisms of 1,3-asymmetric induction. Complementary investigations of imine complexes of other chiral transition metal Lewis acids have been undertaken in other research groups [4,14–16].

2. Results

2.1. Imine complexes

The racemic and enantiomerically pure aldimine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(CH_3)=C(H)\text{-}C_6H_5)]^+TfO^-$ (1^+TfO^-), (*S*)-1^+TfO^- and (*R*)-1^+TfO^- were prepared by the previously reported routes shown in Scheme 1 [8a] [2]. First, toluene solutions of the methyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**), (*S*)-**2** and (*R*)-**2** (>99% ee) were treated with triflic acid (TfOH) to generate the substitution-labile triflate complexes $(\eta^5\text{-}C_5H_5)\text{-}Re(NO)(PPh_3)(OTf)$ (**3**), (*R*)-**3** and (*S*)-**3**. Then the *N*-methyl imine of benzaldehyde was added, and the samples heated. Workup gave 1^+TfO^-, (*S*)-1^+TfO^- and (*R*)-1^+TfO^- in 79–56% yields as 95:5 mixtures of *E*/*Z* N=C geometric isomers [3]. The *E*-isomer, in which the larger substituents on each N=C terminus are *trans* (rhenium and phenyl), would be expected to be more stable.

The crystal structure of (*E*)-1^+TfO^- has been determined [8a], and isomerically homogeneous samples were sought for addition reactions. Curiously, we were unable to again crystallize 1^+TfO^- or (*S*)-1^+TfO^- as pure *E*-isomers. The hexafluorophosphate and hexafluoroantimonate salts $1^+PF_6^-$, (*S*)-$1^+PF_6^-$ and $1^+SbF_6^-$ were also prepared. In all cases, 95:5 *E*/*Z* mixtures were obtained. Alumina, calcium oxide and silica gel chromatography did not give any separation. Difference NOE experiments had suggested that the isomers did not readily interconvert [8a]. Thus, ^1H NMR spectra were recorded in DMSO-d_6 at elevated temperatures. The *E*/*Z* H_3CN=C and N=C*H* signals (δ 3.79/3.44 and 8.49/8.24, 100°C, 500 MHz) appeared to coalesce between 120 and 150°C. This would correspond to $\Delta G^{\ddagger}$ values of 21.5 and 19.1 kcal mol^{-1} (403 K, *E*→*Z* and *Z*→*E*) [4]. Since some decomposition occurred under these conditions, 2D NMR chemical exchange experiments were also conducted [17b,c]. At appropriate temperatures and mixing times, off-diagonal *E*/*Z* cross peaks were observed.

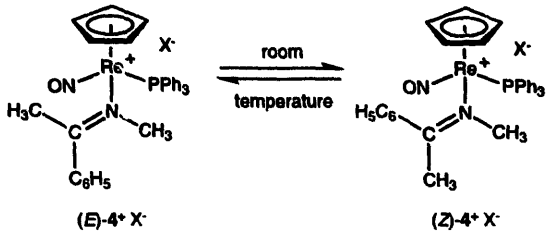
The *E*/*Z* isomers of 1^+TfO^- gave distinct ^{31}P NMR signals. In THF at −80°C [5], resonances appeared at 20.8 and 20.1 ppm (95:5). At −100°C, the *E* resonance was replaced by two new signals (21.1, 20.4 ppm; 78:22). Except for a slight shift, the *Z* resonance was unaffected (19.7 ppm; normalized isomer ratio 73:21:6) [3]. The new resonances coalesced upon warming. These were provisionally ascribed to rotamers about the Re–N= bond, as illustrated by the idealized structures **II** and **III** in Scheme 1 [8a]. The latter is found in crystalline (*E*)-1^+TfO^-, and reactivity data below suggest that it also dominates in solution. The former is found

[2] Abbreviations: $TfO^- = CF_3SO_3^-$; $PPN^+ = [Ph_3PNPPh_3]^+$; BNPPA = 1,1'-binaphthyl-2,2'-diylphosphoric acid.

[3] Diastereomer ratios are normalized to 100, and the error limits on each component are ±2 (95:5≡(95±2):(5±2)).

[4] The $\Delta G^{\ddagger}$ calculation used the H_3CN=C signals, and equation 6.5c in Ref. [17a].

[5] The enantiomerically pure complexes are more soluble than the racemates, and were thus used in the majority of NMR tube experiments.



(*E*)-4⁺X⁻ (*Z*)-4⁺X⁻

		time (h) and *E*/*Z* ratio					
complex	solvent	0	6	12	24	48	96
4⁺ TfO⁻	$CDCl_3$	97:3	75:25	63:37	53:47	50:50	50:50
4⁺ TfO⁻	CD_2Cl_2	99:1	78:22	66:34	58:42	55:45	55:45
4⁺ PF_6^-[a]	CD_2Cl_2	98:2	80:20	69:31	61:39	55:45	55:45

[a]poorly soluble in $CDCl_3$

Scheme 3. Isomerization of 4^+X^-.

in the crystal structure of a benzophenone-derived imine complex [8a]. Rotamers should also be possible with (*Z*)-1^+ TfO^-, in which the rhenium and phenyl N=C substituents are *cis*. Here, the equilibrium concentration of the less stable species may be too small to detect.

For reactivity comparisons below, an imine complex with a disubstituted N=*C* terminus was sought. Thus, as shown in Scheme 1, the triflate complex **3** and the *N*-methyl imine of acetophenone were reacted. Workup gave the new ketimine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(CH_3)=C(CH_3)C_6H_5)]^+TfO^-$ (4^+TfO^-) in 77% yield as a mixture of N=C isomers. The stereochemistry was assigned from the $H_3CN{=}CCH_3$ couplings diagrammed in Scheme 2. The free imine gives a smaller ^5J(HH) value when the methyl groups are *cis* (0.86 versus 1.40 Hz) [18]. In CD_2Cl_2, one isomer of 4^+TfO^- exhibited methyl signals with widths of 2.9–2.8 Hz (half height) and couplings of 0.86 Hz. The other gave broad signals with widths of 17–20 Hz that did not sharpen at low temperature or in CD_3CN. However, spectra recorded in DMSO-d_6 at 150°C showed resolved couplings (0.86 and 1.40 Hz). Hence, these were assigned as (*Z*)-4^+TfO^- and (*E*)-4^+TfO^-, respectively.

In contrast to 1^+TfO^-, crystallization gave the pure *E*-isomer of 4^+TfO^-. Also, the *E*/*Z*-isomers slowly equilibrated in solution. This process was briefly probed. First, the hexafluorophosphate salt $4^+PF_6^-$ was prepared, which also crystallized as the *E*-isomer. Then solutions of (*E*)-4^+X^- were monitored by ^{31}P and ^1H NMR as summarized in Scheme 3. The data establish *E*/*Z* equilibrium ratios of 50:50 ($CDCl_3$) to 55:45 (CD_2Cl_2). Thus, the N=*C* methyl and phenyl groups have comparable effective steric sizes. Similar trends are found in other equilibria involving **I** [19]. Also, the rate is not significantly affected by the counter anion. Hence, pathways involving triflate ion addition to the N=C moiety are excluded. Of the possible remaining mechanisms, the most direct would be N=C bond rotation [20].

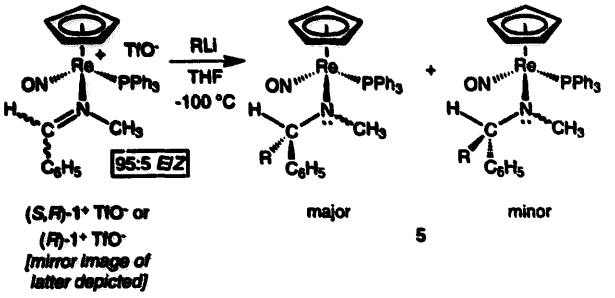
Low temperature ^{31}P NMR spectra of 4^+TfO^- also showed Re–N= rotamers. In CD_2Cl_2 at −20°C, *E*/*Z* resonances appeared at 14.7 and 17.0 ppm. At −80°C, the *E* resonance was replaced by two new signals (15.9, 13.6 ppm; 95:5). The *Z* resonance was essentially unaffected (17.9 ppm). The new resonances coalesced when the probe was warmed. The greater rotamer ratio relative to (*E*)-1^+TfO^- (78:22) presumably reflects the greater size of the N=*C* substituent *cis* to the bulky rhenium (CH_3 versus H). Similar attempts to detect Re–N= rotamers of quinoline and isoquinoline complexes of **I** have been unsuccessful [10,11].

2.2. *Additions of organolithium reagents to* 1^+TfO^-

As shown in Scheme 4, 1^+TfO^- or (*R*)-1^+TfO^- (95:5 *E*/*Z*) and organolithium reagents RLi (1.0 equiv.) were combined in THF at −100°C. The solutions turned deep red, characteristic of amido complexes of **I** [10,11,21]. After 15–30 min, ^{31}P NMR spectra were recorded (−100°C). In all cases, the starting material signal had been replaced by at least two new signals. This, together with other data below, indicated the formation of diastereomeric amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}(CH_3)(CH(R)C_6H_5)$ (**5**). Further details of each addition are as follows.

The reaction of 1^+TfO^- and CH_3Li gave three ^{31}P NMR signals in a 17:74:9 ratio (19.4, 19.2, 14.4 ppm). When the sample was warmed to −80°C, only one signal was detected (19.1 ppm). When the sample was warmed to −50°C, two signals were present in a 74:26 ratio (19.7, 18.9 ppm). All changes were reversible. Thus, the −50°C signals were assigned to Re,C configurational diastereomers of the amido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}(CH_3)CH(CH_3)C_6H_5)$ (**5a**). The additional −100°C signals were provisionally assigned to Re–$\ddot{N}$ rotamers of the minor diastereomer, consistent with the behavior of (*E*)-1^+TfO^- and (*E*)-4^+TfO^- [6]. The sample was warmed as solvent was removed

[6] Note that the amido nitrogen of **5** is also a stereocenter. For a summary of evidence that Re–N rotational barriers are greater than nitrogen inversion barriers, see Ref. [21].



(*S,R*)-**1**$^+$ TfO$^-$ or (*R*)-**1**$^+$ TfO$^-$ [mirror image of latter depicted]

RLi	diastereomer ratio, **5**	^{31}P NMR (ppm, major/minor)
a, CH_3Li	74:26	19.7/18.9[a]
b, $(CH_3CH_2)_3SiC{\equiv}CLi$	72:28	23.2/17.7[b]
c, $(CH_3)_3SiCH_2Li$	73:27	18.7/14.9[c]

[a] −50°C. [b] −100°C. [c] −80°C.

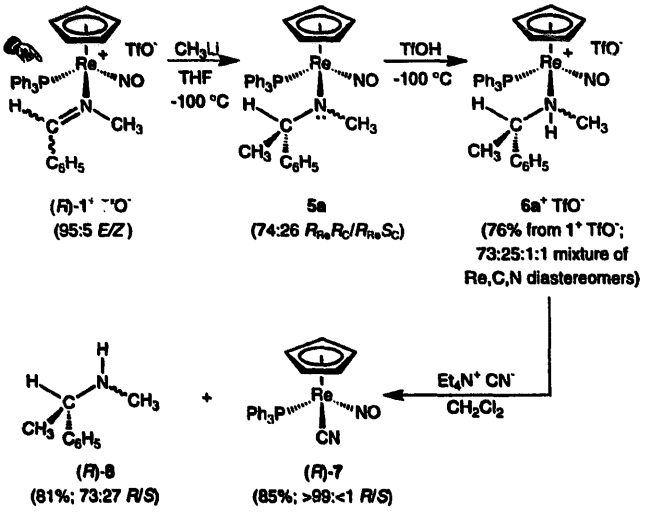
Scheme 4. Additions of organolithium reagents to **1**$^+$TfO$^-$.

by oil pump vacuum, and THF-d_8 was added. Both ^{1}H and ^{31}P NMR spectra showed extensive decomposition, including free PPh_3 (−7.1 ppm).

The reaction of **1**$^+$TfO$^-$ and the svelte nucleophile $(CH_3CH_2)_3SiC{\equiv}CLi$ gave two ^{31}P NMR signals in a 72:28 ratio (23.2, 17.7 ppm). These were assigned to Re,C configurational diastereomers of the amido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\dot{N}(CH_3)CH(C{\equiv}CSi(CH_2CH_3)_3)C_6H_5)$ (**5b**). No other isomers were detected.

The reaction of (*R*)-**1**$^+$TfO$^-$ and the bulkier nucleophile $(CH_3)_3SiCH_2Li$ gave three ^{31}P NMR signals in a 30:38:32 ratio (18.5, 18.3, 15.0 ppm). When the sample was warmed to −80°C, two signals were present in a 73:27 ratio (18.7, 14.9 ppm). This change was reversible. The −80°C signals were assigned to configurational diastereomers of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\dot{N}(CH_3)CH(CH_2Si(CH_3)_3)C_6H_5)$ (**5c**). The additional −100°C signals were assigned to Re–$\dot{N}$ rotamers of the major diastereomer. When the probe was warmed to −60°C, the minor diastereomer slowly epimerized to the major diastereomer. Other amido complexes of **I** also epimerize, but at varying temperatures [10,22]. The mechanism, which involves inversion at rhenium, has been studied in detail [22]. When the probe was warmed to −40°C, only the major diastereomer remained (19.1 ppm). No other species were detected.

As summarized in Scheme 4, the preceding additions afforded similar mixtures of diastereomers, with the 'downfield' species dominating. This suggested analogous approach trajectories. In order to aid stereochemical assignments, chemically and configurationally more stable derivatives were sought. Reactions of amido complexes of **I** and TfOH have previously been shown to give cationic amine complexes, which have excellent thermal stability and rhenium stereocenters that are no longer labile [22,23]. A slight complication in the case of complex **5** is that protonation preserves the nitrogen stereocenter, but now in a non-labile



(*R*)-**1**$^+$ TfO$^-$ (95:5 *E/Z*) — **5a** (74:26 $R_{Re}R_C/R_{Re}S_C$) — **6a**$^+$ TfO$^-$ (76% from **1**$^+$ TfO$^-$; 73:25:1:1 mixture of Re,C,N diastereomers)

(*R*)-**8** (81%; 73:27 *R/S*) — (*R*)-**7** (85%; >99:<1 *R/S*)

Scheme 5. Synthesis of a non-racemic amine.

form [7]. Thus, four Re,C,N configurational diastereomers are possible.

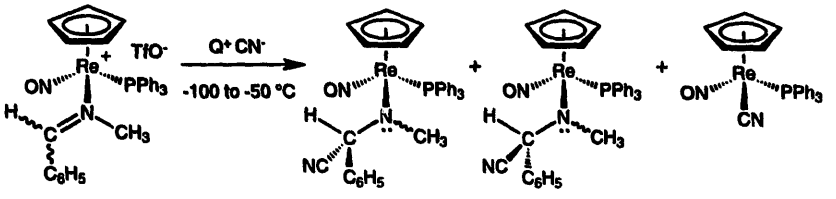
Accordingly, **5a** was generated from (*R*)-**1**$^+$TfO$^-$ and CH_3Li in an NMR tube. Then TfOH (2.0 equiv.) was added at −100°C. A ^{31}P NMR spectrum (−100°C) showed four signals in a 4:3:72:21 ratio (20.0, 17.1, 15.4, 12.0 ppm), which were assigned to diastereomers of the amine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)CH(CH_3)C_6H_5)]^+TfO^-$ (**6a**$^+$TfO$^-$). As shown in Scheme 5, an analogous preparative reaction gave analytically pure **6a**$^+$TfO$^-$ in 76% yield as a 73:25:1:1 diastereomer mixture. The spectroscopic properties of **6a**$^+$TfO$^-$ were similar to those of other amine complexes of **I** [23].

A reaction of racemic **5b** and TfOH in an NMR tube gave three ^{31}P NMR signals (17.3, 16.2, and 14.2 ppm; 71:20:9), corresponding to diastereomers of the amine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)CH(C{\equiv}CSi(CH_2CH_3)_3)\text{-}C_6H_5)]^+TfO^-$ (**6b**$^+$TfO$^-$). A sample of **5c** was generated from (*R*)-**1**$^+$TfO$^-$ and then kept at −40°C to allow epimerization to the more stable diastereomer. Subsequent addition of TfOH gave $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)\text{-}CH(CH_2Si(CH_3)_3)C_6H_5)]^+TfO^-$ (**6c**$^+$TfO$^-$) as a 41:59 mixture of diastereomers (15.2, 11.8 ppm), presumably differing in configuration at nitrogen.

2.3. Synthesis of a non-racemic amine

Previous studies have shown that amine complexes of **I** and cyanide ion react to give free amines and the cyanide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**7**) in quantitative spectroscopic yields [10,22,23]. Importantly, configuration is retained at rhenium, as well as at any carbon stereocenters. Furthermore, **7** is easily recycled to the methyl complex **2** (Scheme 1) with retention at rhenium [10]. Accordingly, we sought to detach the amine ligand from the

[7] This issue could be avoided by the *N*-methylation of **5**, which would remove the nitrogen stereocenter. However, reactions of amido complexes of **I** and CH_3OTf in THF generally give polymeric material.



(S)-1⁺ TfO⁻ (95:5 E/Z)

solvent	Q^+	diastereomer ratio, 9	^{31}P NMR (ppm, major/minor)
THF	PPN^+	85:15	18.0/21.1
CH_2Cl_2	PPN^+	84:16	17.9/20.4
THF	Et_4N^+	85:15	18.0/21.1
CH_2Cl_2	Et_4N^+	84:16	17.9/20.3

Scheme 6. Addition of cyanide ion to 1^+TfO^-.

non-racemic sample of $\mathbf{6a}^+TfO^-$ shown in Scheme 5, and establish configuration.

Thus, $\mathbf{6a}^+TfO^-$ and $Et_4N^+CN^-$ (1.0 equiv.) were combined in CH_2Cl_2. Workup gave the non-racemic cyanide complex **7** in 85% yield as a >99:<1 *R/S* mixture [23,24], as assayed both polarimetrically and with a chiral NMR shift reagent. Hence, there is no loss of configuration at rhenium at any step in the reaction sequence. The non-racemic amine $NH(CH_3)CH(CH_3)C_6H_5$ (**8**), which is commercially available, was isolated in 81% yield. A chiral NMR shift reagent indicated a 73:27 mixture of enantiomers, consistent with the diastereomer ratio of the amido complex precursor **5a**. Polarimetry indicated a dextrorotatory sample, showing the *R* configuration to be dominant. Analogous carbon configurations were assigned to the major diastereomers of amido complexes **5b** and **c** [8].

2.4. Additions of cyanide ion to 1^+TfO^-

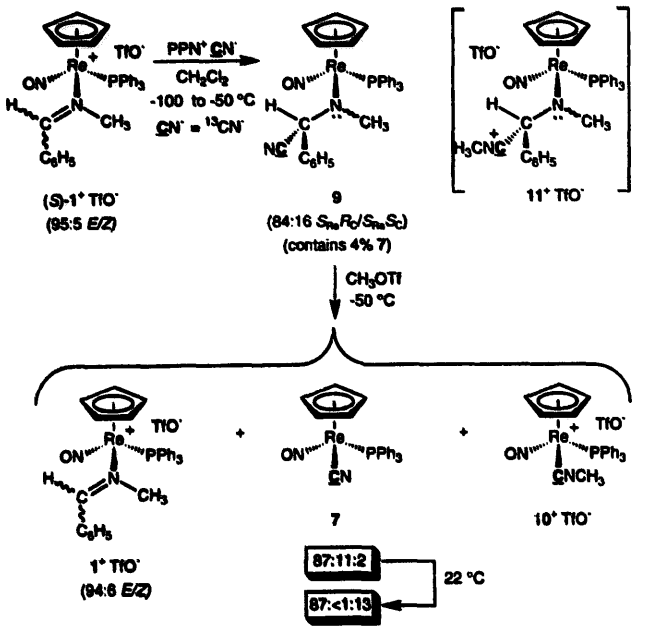
There has been much recent interest in enantioselective versions of the Strecker synthesis of amino acids, one step of which entails the addition of cyanide ion to imines [3,6c]. In earlier studies, we found that cyanide ion readily added to aldehyde and ketone complexes of **I**. Subsequent reactions gave protected cyanohydrins of high enantiomeric purities [25]. Thus, we set out to examine analogous additions to 1^+TfO^-.

As shown in Scheme 6, (*S*)-1^+TfO^- (95:5 *E/Z*) and PPN^+CN^- (1.0 equiv.) (see footnotes 1 and 4) were combined in an NMR tube in THF at −100°C. Reaction was slow, but complete after 15 min at −50°C. A ^{31}P NMR spectrum of the red solution showed two major new resonances (18.0, 21.1 ppm; 85:15) that were assigned to Re,C configurational diastereomers of the cyanide-substituted amido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}(CH_3)CH(CN)C_6H_5)$ (**9**). The cyanide complex **7** also formed in 4% yield (19.1 ppm), as confirmed by spiking with an authentic sample. A similar reaction of (*S*)-1^+TfO^- and PPN^+CN^- in CH_2Cl_2 gave **9** as a 84:16 diastereomer mixture, and 6% of **7** (18.1 ppm). Comparable results were obtained with $Et_4N^+CN^-$ (Scheme 6).

The configuration of the major diastereomer of **9** was presumed to be analogous to those of amido complexes **5** (see footnote 7). However, the upfield/downfield pattern of the ^{31}P NMR chemical shifts differed. An IR spectrum of a cold solution gave a ν(NO) band close to that of the dimethylamido complex of **I** (1633 versus 1634 cm^{-1}) [21]. A sample was prepared in CD_2Cl_2, and a ^1H NMR spectrum (−50°C) showed $N(CH_3)CH$ signals at δ 5.78 and 2.22/2.69 (85:15). The solution was warmed to room temperature. After 1 h, a ^1H NMR spectrum showed a 12:2:86 mixture of the two diastereomers of **9** and cyanide complex **7** (δ 5.61, 5.50, 5.28; C_5H_5), as well as free $C_6H_5(H)C{=}NCH_3$. Hence, **9** is unstable with respect to **7** and the free imine.

As shown in Scheme 7, a 96:4 mixture of **9** and **7** was generated with ^{13}C-labeled cyanide ion. Then CH_3OTf was added (1.5 equiv., −50°C). The solution turned orange, and a ^{31}P NMR spectrum showed that **9** had been consumed. The imine complex 1^+TfO^- (19.0, 17.9 ppm, 94:6 *E/Z*), cyanide complex **7** (18.1 ppm, d, $^2J(PC) = 11.6$ Hz), and the known methyl isocyanide complex $\mathbf{10}^+TfO^-$ (15.1 ppm, d, $^2J(PC) = 10.1$ Hz) [10] had formed in a 87:11:2 ratio. The sample was warmed to room temperature. After 2 h, only 1^+TfO^- (17.9, 16.4 ppm; 94:6 *E/Z*) and $\mathbf{10}^+TfO^-$ (14.3 ppm) remained (87:13). A possible explanation would be that the cyanide ion reversibly adds to (*S*)-1^+TfO^-, and is preferentially methylated. Reversible addition would also nicely account for the thermal decomposition products of **9**.

[8] Absolute configurations are specified by conventions described previously [8a]. Note that ($S_{Re}S_C$)-**5a** has rhenium and carbon configurations identical with those of ($S_{Re}R_C$)-**5b,c,9** (major addition product diastereomers from (*S*)-1^+TfO^-).



Scheme 7. Attempted methylation of cyanide addition product 9.

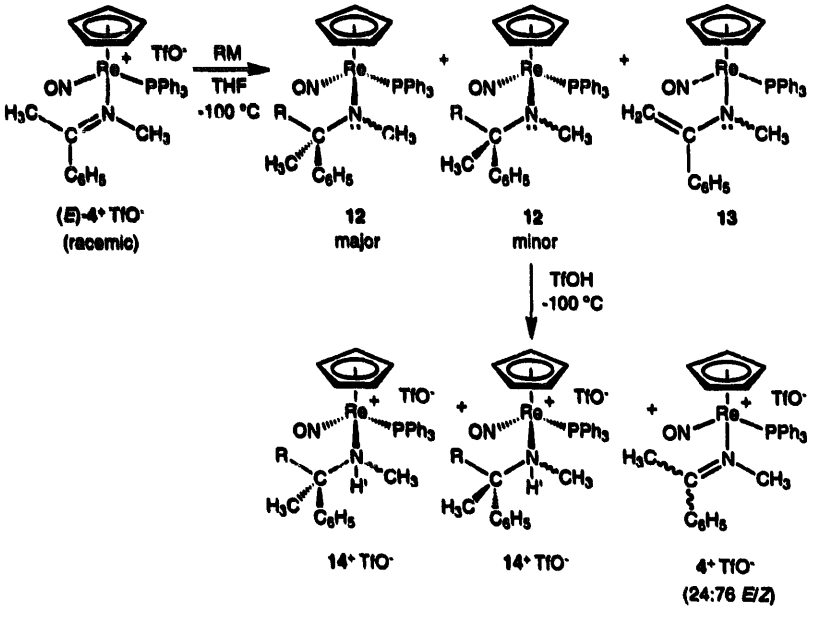
Conceivably, the cyanide nitrogen in 9 might be methylated to give 11^+TfO^- (Scheme 7), which could then fragment to 1^+TfO^- and free methyl isocyanide. However, when reactions were conducted in CD_2Cl_2, ^1H NMR spectra showed only acetonitrile (δ 1.97; no singlets 2.1–3.0), presumably derived from free cyanide ion.

A similar reaction of 9 and TfOH (1.0 equiv.) was conducted in THF at −50°C. A ^{31}P NMR spectrum showed that 9 was consumed, and three new signals in a 15:73:12 ratio (20.4, 16.0, 15.7 ppm). The chemical shifts were distinct from those obtained in the methylation experiments, and consistent with diastereomeric amine complexes. However, given the multitude of problems in the preceding reactions, further chemistry was not pursued.

2.5. Reactions of 4^+TfO^-

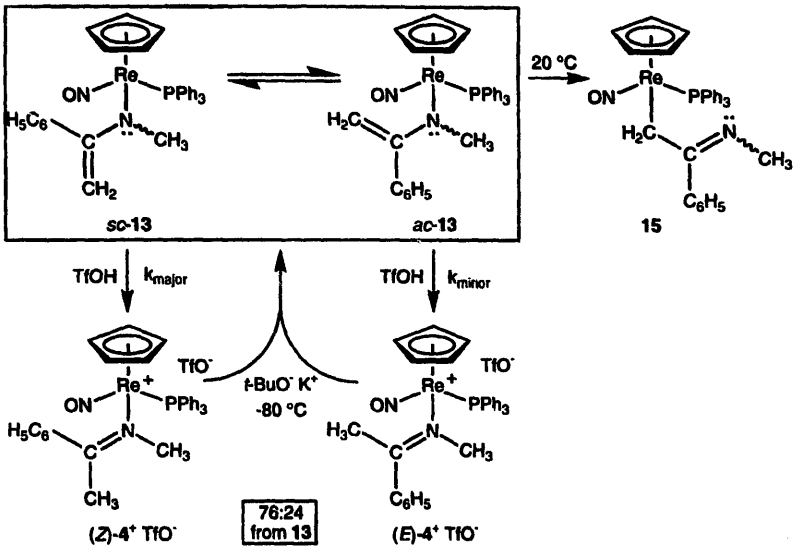
We sought to study similar additions to the ketimine complex 4^+TfO^-. We had hoped for improved diastereoselectivities, since in contrast to 1^+TfO^-, 4^+TfO^- can be accessed as a single N=C geometric isomer. However, 4^+TfO^- also contains protons α to the imine carbon. In earlier work, we found that such protons can be abstracted by t-BuO^-K^+, giving neutral enamido (N(R")C=CRR') complexes [10b,26]. In some cases, strong nucleophiles or even cyanide ion gave competing deprotonation. When enamido complexes are treated with TfOH, cationic imine complexes again form [10,11].

As shown in Scheme 8, (*E*)-4^+TfO^- and $C_6H_5CH_2MgCl$ (1.0 equiv.) were combined in THF at −100°C. After 15 min, a ^{31}P NMR spectrum (−100°C) showed five signals in a 40:2:1:55:2 ratio (19.4, 18.7, 18.3, 17.0, −8.1 ppm). The last was attributed to traces of free PPh_3. The first was assigned to the deprotonation product, enamido complex (η^5-C_5H_5)Re(NO)(PPh_3)(N(CH$_3$)C(C_6H_5)=CH_2) (13), as supported below. The other three signals were ascribed to isomers of the addition product (η^5-C_5H_5)Re(NO)-



RM	product ratio, 12/12/13
a, $C_6H_5CH_2MgCl$	56:3:41 ≡ (95:5):70
b, $(CH_3)_3SiCH_2Li$	<1:<1:>99

Scheme 8. Reactions of carbon nucleophiles and 4^+TfO^-.



Scheme 9. Reactions of enamido complex **13**.

$(PPh_3)(\ddot{N}(CH_3)CH(CH_2C_6H_5)C_6H_5)$ (**12**). Accordingly, upon warming to −50°C, reversible coalescence to two signals occurred (17.8, 17.5 ppm, 5:95; 59:41 **12**/**13**). The −50°C signals were assigned to Re,C configurational diastereomers of **12**. The additional −100°C signals were assigned, by analogy with similar cases above, to Re–$\ddot{N}$ rotamers.

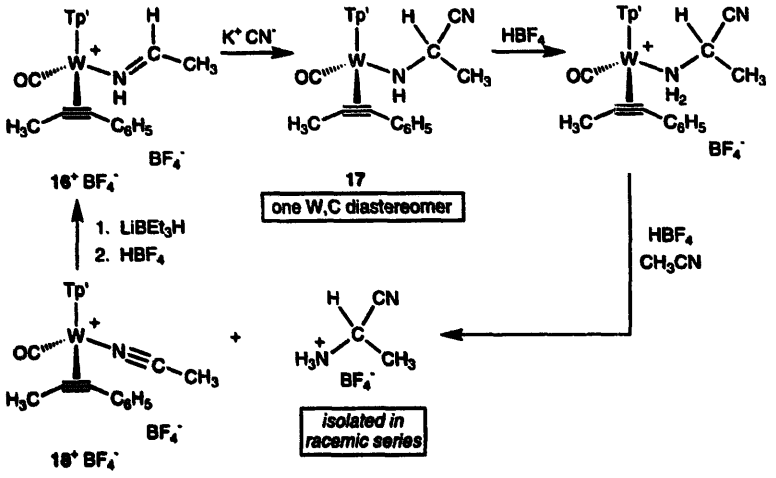
The preceding sample was treated with TfOH (2.0 equiv., −100°C). A ^{31}P NMR spectrum showed that **13** had been protonated back to the imine complex **4**$^+$TfO$^-$. As analyzed below, a 24:76 *E*/*Z* mixture was obtained (19.6, 17.2 ppm). Similarly, **12** had been protonated to the new amine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)CH(CH_2C_6H_5)\text{-}C_6H_5)]^+TfO^-$ (**14**$^+$TfO$^-$). At least two Re,C,N configurational diastereomers were present (16.5, 18.7 ppm; 89:11). Workup gave a mixture of **4**$^+$TfO$^-$ and diastereomerically pure **14**$^+$TfO$^-$ that was characterized by ^1H NMR. The relative configurations of the rhenium and carbon stereocenters in Scheme 8 were assigned as described in Section 3.

A similar reaction was conducted with (*E*)-**4**$^+$TfO$^-$ and the bulkier and more basic nucleophile $(CH_3)_3SiCH_2Li$ (Scheme 8). A ^{31}P NMR spectrum (−100°C) showed the clean formation of enamido complex **13** (19.4 ppm). Addition of TfOH as above gave the imine complex **4**$^+$TfO$^-$ as a 24:76 *E*/*Z* mixture (Schemes 8 and 9), which was isolated and characterized by IR and ^1H NMR. In view of this result, reactions with alkyl lithium reagents were not further investigated. However, additional characterization of **13** was sought.

Thus, as shown in Scheme 9, **4**$^+$TfO$^-$ and solid t-BuO$^-$K$^+$ (1.0 equiv.) were combined at −80°C in THF. The solvent was removed below room temperature. A ^{31}P NMR spectrum (THF-d_8, ambient temperature) showed **13** and eight minor products (78:8:4:3:3:2:1:1:1). A ^{13}C NMR spectrum gave a NC=C signal at 174.3 ppm, and a phosphorus-coupled NCH_3 signal at 57.4 ppm ($^3J(CP) = 6$ Hz). The NCH_3 ^1H NMR signal showed long range coupling to a =CH proton ($^5J(HH) = 1.6$ Hz). A similar reaction was conducted in an NMR tube with a THF solution of t-BuO$^-$K$^+$. A ^{31}P NMR spectrum (−80°C) showed a 95:5 mixture of **13** and a second species, **15** (19.8, 23.3 ppm). The sample was worked up at room temperature, and only **15** remained.

The NMR and IR data clearly showed **15** to be the β-imino alkyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C(C_6H_5)=\ddot{N}CH_3)$, derived from a formal 1,3-shift of rhenium as shown in Scheme 9. In particular, the ^1H NMR spectrum gave two signals for the diastereotopic ReCHH′ protons, both of which were coupled to phosphorus. The ^{13}C NMR spectrum showed a diagnostic upfield $ReCH_2$ signal (−12.6 ppm), and a downfield C=N signal (182.8 ppm). The IR spectrum gave a ν(C=N) band at 1599 cm^{-1} (m). A second set of NMR signals was also detected (~4%), and tentatively assigned to a C=N geometric isomer. Analogous linkage isomerizations of related oxygenated ligands (e.g., OCH=CHR and CHRC(H)=O) are well documented [27]. However, such 1,3-shifts have not been observed with other enamido complexes of **I**, even when kept at 55°C [10b].

Finally, (*E*)-**4**$^+$TfO$^-$ and $Et_4N^+CN^-$ (1.0 equiv.) were combined in CH_2Cl_2 at −100°C. The sample was kept at −50°C for 15 min. A ^{31}P NMR spectrum showed unreacted (*E*)-**4**$^+$TfO$^-$ (34%), and three new signals in a 58:9:33 ratio (19.1, 18.9, 18.8 ppm). The probe was warmed to room temperature. A ^{31}P NMR spectrum showed only the new signals, but now in a 2:92:6 ratio (20.2, 18.9, 18.5 ppm). An IR spectrum confirmed that the major product was cyanide complex **7** (ν(C≡N)/ν(NO) 2096/1687 cm^{-1} (s/vs)), consistent with the thermal decomposition of addition product **9** described above. However, the dominant species at −50°C is likely enamido complex **13**, suggesting yet another reversible equilibrium.



Scheme 10. Related transformations of non-racemic chiral tungsten complexes (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate).

3. Discussion

3.1. Merits of methodology

The above reactions of carbon nucleophiles with acyclic imine complexes of **I** illustrate several practical drawbacks that will preclude significant use in enantioselective syntheses of chiral amines. These include (i) complications in obtaining isomericaly pure N=C adducts, (ii) often modest diastereoselectivities, (iii) potentially epimerizable addition products, and (iv) competing deprotonations. The first problem is avoided with heterocyclic imines, which possess a fixed N=C stereochemistry. Importantly, when N=C isomers of Lewis acid adducts are separable, as with $\mathbf{4}^+\mathrm{TfO}^-$, there is the opportunity for better stereocontrol than in catalytic methodologies, which would be expected to generate *E/Z* mixtures. However, the feasibility of such separations is difficult to predict in advance.

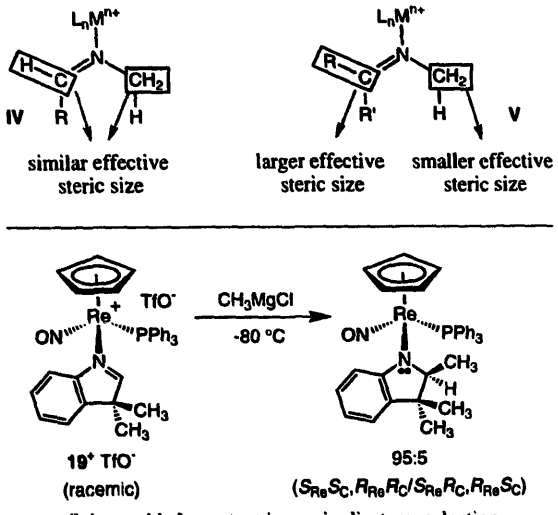
Nonetheless, the preceding data provide a variety of insights regarding mechanisms of 1,3-asymmetric induction in additions to chiral Lewis acid adducts of imines. Thus, diastereoselectivities are analyzed in the following section. Curiously, deprotonation is not a significant problem in reactions of nucleophiles with aldehyde or ketone complexes of **I** [25]. The proportion of addition products might increase with milder carbon nucleophiles, such as copper or zinc reagents. However, the rhenium fragment **I** is a strong π donor, with the d orbital HOMO shown in Scheme 1. Although **I** forms isolable or detectable complexes with numerous weak σ donor ligands, it does not appear to strongly activate unsaturated ligands towards nucleophilic addition.

In this context, data that have been detailed elsewhere are relevant [28]. For example, palladium Lewis acids catalyze additions of allyl stannanes to imines at 20–50°C [29]. However, no reaction occurs when $Bu_3SnCH_2CH{=}CH_2$ and $\mathbf{1}^+\mathrm{TfO}^-$ are combined in THF at 60°C (21 h). Similarly, ytterbium Lewis acids catalyze aza Diels-Alder reactions of imines [30], and numerous cycloadditions have been reported with stoichiometric amounts of Lewis acids [2d]. However, the imine complex [8a] $[(\eta^5\text{-}C_5H_5)\mathrm{Re}(\mathrm{NO})(\mathrm{PPh_3})(\eta^1\text{-}\mathrm{N(H)}{=}\mathrm{C(H)}C_6H_5)]^+\mathrm{TfO}^-$ does not react with 2,3-dimethyl-1,3-butadiene or Danishefsky's diene in refluxing THF (24 h). Hence, imine complexes of more Lewis acidic transition metal fragments should allow a broader range of chemistry, and merit attention for future research.

Templeton and co-workers have developed an extensive chemistry of imine complexes of a chiral tungsten Lewis acid [4]. Highly diastereoselective hydride and cyanide additions have been reported, and some particularly important results are depicted in Scheme 10. The reaction of cyanide and the non-racemic imine complex $\mathbf{16}^+\mathrm{BF_4}^-$ gives a single W,C diastereomer of amido complex **17**. A two step sequence then affords a free α-amino nitrile, and the acetonitrile complex $\mathbf{18}^+\mathrm{BF_4}^-$ with retention of configuration. The latter can be recycled to $\mathbf{16}^+\mathrm{BF_4}^-$ without racemization. All steps proceed in high yields, and without the complications found with **I**. Hence, this system holds greater promise for practical enantioselective syntheses of amines. Only a few other additions to chiral transition metal imine complexes appear to have been investigated [14]. However, as noted above, there is an extensive literature involving other types of nitrogen-bound chiral auxiliaries [1–3,15].

3.2. Mechanism of diastereoselection

In contrast to η^1 aldehyde or ketone ligands, imine ligands bear two substituents on the coordinated atom. In aldehyde or ketone complexes, the equilibrium distribution of M–Ö= rotamers will be a function of the relative sizes of the =CRR' moiety and oxygen lone pair. Thus, there should be a strong preference for the conformation that directs the much larger =CRR' group into the least congested interstice. However, in imine complexes the equilibrium distribution of M–N(R")= rotamers will be a function of the relative sizes of



Scheme 11. Important issues in diastereoselection.

the =CRR′ and R″ moieties. These can vary, thereby complicating the development of general methodologies.

Low temperature NMR spectra of (*E*)-**1**$^+$TfO$^-$ and (*E*)-**4**$^+$TfO$^-$ show 78:22 and 95:5 mixtures of Re–N= rotamers, respectively. Scheme 4 and 8 establish a close correlation of these ratios and diastereoselectivities, irrespective of the bulk of the RLi or RMgX nucleophile. Thus, we sought to assign rotamer structures. The idealized geometries in Scheme 1 (**II**, **III**) follow from steric and electronic factors that have been extensively analyzed earlier, and crystallographic data [8a]. Importantly, the interstice between the small nitrosyl and medium sized cyclopentadienyl ligands is the most spacious, and can best accommodate the largest imine nitrogen substituent.

In (*E*)-*N*-methyl aldimine complexes such as (*E*)-**1**$^+$TfO$^-$, the =C*H*R hydrogen is directed towards the metal fragment. Thus, as sketched in **IV** in Scheme 11, it is difficult to predict whether the =CHR or CH_3 nitrogen substituent will have the greater effective steric size. With (*E*)-**1**$^+$TfO$^-$, however, the addition stereochemistry, coupled with precedent for related systems, provide valuable clues. Importantly, previous studies have shown that nucleophiles preferentially attack ketone complexes of **I** from a direction *anti* to the bulky PPh_3 ligand [25]. Analogous trajectories have been documented with isoquinoline and quinoline complexes of **I** [10,11], and many other species [9].

If nucleophiles similarly attack (*E*)-**1**$^+$TfO$^-$ *anti* to the PPh_3 ligand, diastereoselection will be a function of two transition states derived from different Re–N= rotamers, as illustrated by **VI** and **VII** in Scheme 12 (top). The former gives the major diastereomers in Scheme 4, and the latter gives the minor diastereomers. Thus, **VI** must be the dominant transition state, in accord with the Re–N= conformation in crystalline (*E*)-**1**$^+$TfO$^-$ [8a]. These data strongly suggest that the Re–N= rotamer in **VI** is the more stable, and that the CH_3 nitrogen substituent has the greater size. Next consider the plausible scenario that additions of RM reagents are faster than Re–N= bond rotation. NMR experiments show that cyanide ion additions (Scheme 6) are much slower. Hence, the higher diastereoselectivities (85–84:15–16 versus 74–72:26–28) would reflect the opposite Curtin-Hammett limit, in which product ratios are determined by transition state energies [32].

In *N*-methyl ketimine complexes such as (*E*)-**4**$^+$TfO$^-$, a non-hydrogen N=*C* substituent is *cis* to the metal fragment. With reference to (*E*)-**1**$^+$TfO$^-$, the *cis* substituent would destabilize the Re–N= rotamer in **VI** (more congested interstice) to a greater extent than **VII** (less congested interstice). Thus, the rotamer that compromises 95% of (*E*)-**4**$^+$TfO$^-$ must correspond to that in **IX** (Scheme 12, bottom), in agreement with a crystal structure of a related ketimine complex [8a]. Configurations have been assigned to the diastereomeric addition products **12** (Schemes 8 and 12) accordingly. Hence, as sketched in **V** in Scheme 11, a disubstituted =CRR′ nitrogen substituent has a distinctly greater size than a CH_3 nitrogen substituent. This should be general for all metal fragments.

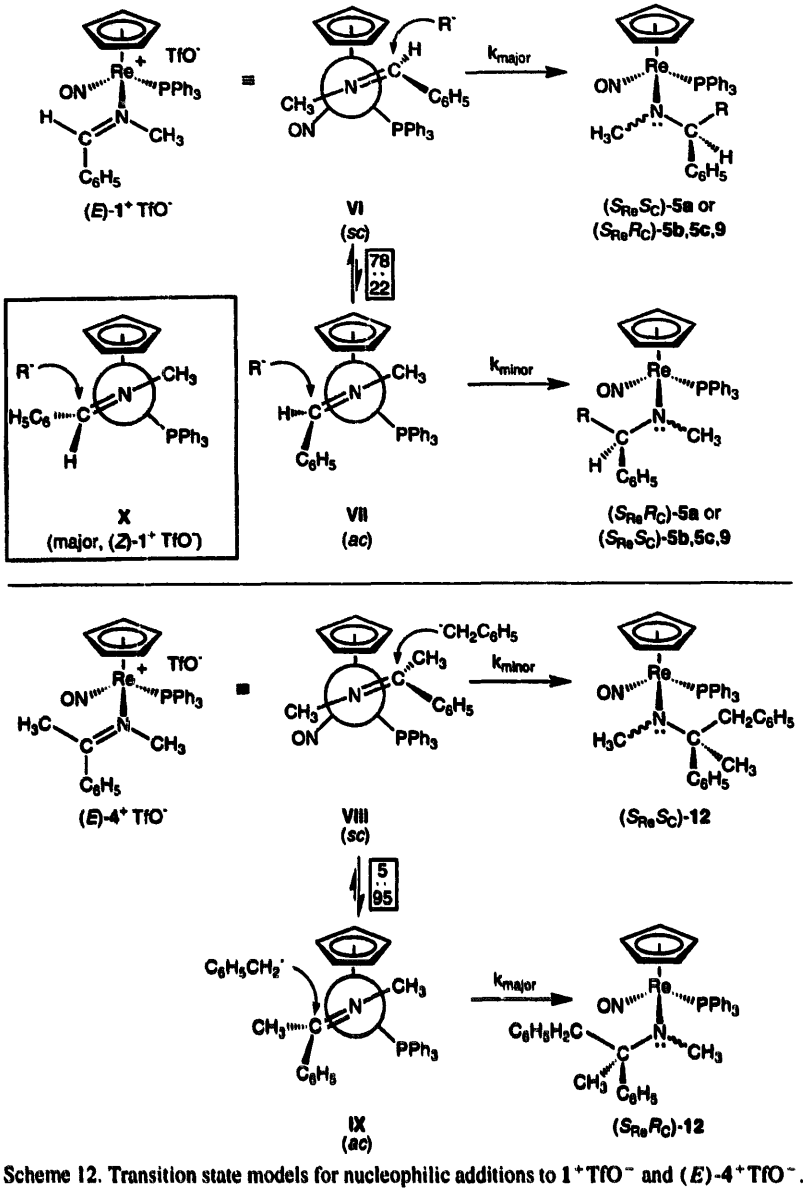
In (*Z*)-*N*-methyl aldimine complexes such as (*Z*)-**1**$^+$TfO$^-$, a non-hydrogen N=*C* substituent is also *cis* to the metal fragment. Thus, (*Z*)-**1**$^+$TfO$^-$ should favor the Re–N= rotamer in **X**. This leads to the interesting corollary that both geometric isomers of **1**$^+$TfO$^-$ should preferentially give the same addition product diastereomer. Such synergies can occur when the dominant M–N= rotamer switches with a change of *E*/*Z* stereochemistry. These analyses are also easily extended to cyclic imine ligands. For example, the indolenine complex **19**$^+$TfO$^-$ in Scheme 11 undergoes highly diastereoselective addition of CH_3MgCl [13]. Here, an *ortho* CH moiety of the *N*-aryl group should generate much greater steric interactions than the small N=C*H* hydrogen. Hence, there should be a highly biased population of Re–N= rotamers, similar to those in **VI** (major) and **VII** (minor).

A final point of stereochemistry concerns the protonation of enamido complex **13**. As shown in Scheme 9, one N–C= rotamer will give (*Z*)-**4**$^+$TfO$^-$, and the other (*E*)-**4**$^+$TfO$^-$, irrespective of the Re-conformation or direction of electrophilic attack. Hence, the rotamer with the rhenium *syn* to the phenyl substituent and *anti* to the larger $=CH_2$ substituent (*sc*-**13**) is slightly more reactive.

4. Conclusions

The above data show that the efficacy of 1,3-asymmetric induction in adducts of chiral Lewis acids and acyclic imines can be a function of rotamer populations about the Lewis acid–nitrogen bond. As exemplified in Scheme 11, it will be difficult to achieve biased rotamer equilibria with some classes of imines. For *N*-methyl aldimine complexes with thermodynamically preferred *cis* *M*N=C*H* linkages (**IV**), our results suggest that M–N= rotamer ratios will usually be low. However, bulky *N*-alkyl groups such as t-butyl might give

[9] For related examples of 1,3-asymmetric induction involving C_β electrophilic attack upon vinyl complexes of **I**, see Ref. [31].



Scheme 12. Transition state models for nucleophilic additions to 1^+TfO^- and (E)-4^+TfO^-.

higher ratios. In the case of rhenium Lewis acid **I**, rotamers analogous to that in **VI** should be much more favored. Importantly, there would also be an effect upon *E*/*Z* N=C equilibria, with the *E*-isomers (t-butyl and =C*H*R *cis*) destabilized.

By definition, *N*-methyl ketimine complexes have *cis* *M*N=C*R* linkages. Our results suggest that M–N= rotamer ratios will usually be higher, enhancing prospects for efficient asymmetric induction — provided that only one N=C isomer is present. Larger *N*-alkyl groups would now lower rotamer ratios. Similar generalizations are possible with cyclic imines. For example, substitution of the N=C*H* hydrogen in indolenine complex 19^+TfO^- (Scheme 11) by a methyl group should give imine nitrogen substituents of similar effective steric sizes. This would decrease rotamer ratios, and likely addition diastereoselectivities as well.

With regard to the chiral rhenium Lewis acid **I**, some of the preceding strategies might lead to higher diastereoselectivities. Other positive attributes of **I** include the many routes to imine adducts that have been developed, the ease with which they can be obtained in enantiomerically pure form, and the simple amine detachment/recycling protocol [8–13]. However, problems arising from the moderate Lewis acidity (which facilitates cyanide ion dissociation) and competing deprotonations are likely to remain. Regardless, the above data will allow a much higher level of design in developing new enantioselective approaches to amines from chiral transition metal imine complexes. Additional studies with more Lewis acidic chiral rhenium fragments are in progress [28].

5. Experimental

5.1. General data

Instrumental protocols and solvent and reagent purifications were identical to those in earlier papers [8a], and addi-

tional details are given elsewhere [28]. RLi and RMgCl solutions were standardized [33]. NMR spectra were recorded at ambient probe temperature and referenced as follows unless noted: ^{1}H (δ), $Si(CH_3)_4$ (0.00), CD_2HCN (1.93), $CDHCl_2$ (5.32), THF-d_7 (3.58, 1.73), CD_2HSOCD_3 (2.50); ^{13}C (ppm), $CDCl_3$ (77.0), CD_3CN (1.3), THF-d_8 (67.4, 25.3); ^{31}P (ppm), external 85% H_3PO_4 (0.00); ^{19}F (ppm), $CFCl_3$ (0.00). All coupling constants (J) are in Hz.

5.2. Syntheses

5.2.1. [(η^5-C_5H_5)Re(NO)(PPh_3)(η^1-N(CH_3)=C(H)-C_6H_5)]$^+X^-$ (**1**$^+X^-$)

5.2.1.1. Method A

A flask was charged with (*S*)-**1**$^+$TfO$^-$ (0.473 g, 0.584 mmol, 95:5 *E*/*Z*) [8a], $NH_4^+PF_6^-$ (0.952 g, 5.84 mmol), and acetone (40 ml). The mixture was stirred for 0.5 h, and solvent was removed by rotary evaporation. Then CH_2Cl_2 (200 ml) was added, and the mixture was filtered through silica gel. Hexane (100 ml) was added to the filtrate. The yellow–orange powder was collected on a frit, washed with pentane, and dried by oil pump vacuum to give (*S*)-**1**$^+PF_6^-$ (0.302 g, 0.375 mmol, 64%, 95:5 *E*/*Z*) [10]. A portion was crystallized (acetone/hexane) to give orange prisms (95:5 *E*/*Z*). IR (cm^{-1}, KBr/CH_2Cl_2): ν(NO) 1702/1701 (vs), ν(PF) 837/847 (s). ^{1}H NMR (CD_2Cl_2): 8.25/8.19 (d/br s, ^4J(HH) = 1.7, *E*/*Z* CH), 7.63–7.39 (m, 11H of 4Ph), 7.36–7.24 (m, 6H of 4Ph), 7.21–7.13 (m, 1H of 4Ph), 6.96–6.90 (m, 2H of 4Ph), 5.58/5.45 (2s, *E*/*Z* C_5H_5), 3.79/3.44 (2d, ^4J(HH) = 1.7/1.2, *E*/*Z* CH_3). ^{19}F NMR: −72.8 (d, ^1J(PF) = 711). ^{31}P{^{1}H} NMR: 17.8/16.3 (2s, *E*/*Z*).

5.2.1.2. Method B

Complex **1**$^+$TfO$^-$ (0.171 g, 0.211 mmol, 95:5 *E*/*Z*) [8a], $Na^+SbF_6^-$ (0.109 g, 0.422 mmol), and acetone (180 ml) were combined in a procedure analogous to Method A to give **1**$^+SbF_6^-$ as an orange–yellow powder (0.131 g, 0.146 mmol, 69%, 95:5 *E*/*Z*). A portion was crystallized (acetone/hexane) to give orange prisms (95:5 *E*/*Z*). IR (cm^{-1}, CH_2Cl_2): ν(NO) 1701 (vs). ^{1}H NMR (CD_2Cl_2): 8.25/8.19 (d/br s, ^4J(HH) = 1.7, *E*/*Z* CH), 7.63–7.39 (m, 11H of 4Ph), 7.36–7.24 (m, 6H of 4Ph), 7.21–7.13 (m, 1H of 4Ph), 6.96–6.90 (m, 2H of 4Ph), 5.56/5.44 (2s, *E*/*Z* C_5H_5), 3.78/3.43 (2d, ^4J(HH) = 1.7/1.2, *E*/*Z* CH_3). ^{31}P{^{1}H} NMR: 17.6/16.2 (2s, *E*/*Z*).

5.2.2. [(η^5-C_5H_5)Re(NO)(PPh_3)(η^1-N(CH_3)=C(CH_3)-C_6H_5)]$^+X^-$ (**4**$^+X^-$)

5.2.2.1. Method A

A Schlenk flask was charged with (η^5-C_5H_5)-Re(NO)(PPh_3)(CH_3) (**2** [34]) (1.00 g, 1.80 mmol) and toluene (50 ml) and cooled to −45°C (CH_3CN/CO_2). Then TfOH (0.159 ml, 1.80 mmol) was added with stirring to generate (η^5-C_5H_5)Re(NO)(PPh_3)(OTf) (**3**) [35]. After 10 min, $C_6H_5(CH_3)C{=}NCH_3$ (1.30 ml, 8.99 mmol) [36] was added and the flask was placed in a 105°C oil bath. An orange powder began to form. After 15 h, the mixture was allowed to cool to room temperature. The powder was collected on a frit, washed with hexane (2×30 ml), and dried by oil pump vacuum to give **4**$^+$TfO$^-$ (0.780 g, 0.945 mmol, 53%, 61:39 *E*/*Z*). The filtrate and washings were concentrated (50 ml), and hexane (100 ml) was added. A second crop of **4**$^+$TfO$^-$ was similarly collected (0.353 g, 0.427 mmol, 24%, 29:71 *E*/*Z*), for a combined yield of 77%. A portion of the first crop was crystallized (acetone /hexane) to give orange prisms of (*E*)-**4**$^+$TfO$^-$, m.p. 213–215°C decomp. *Anal.* Calc. for $C_{32}H_{31}F_3N_2O_4PReS$: C, 47.23; H, 3.84. Found: C, 47.48 H, 3.90%. IR (cm^{-1}, KBr): ν(NO) 1689 (vs). ^{1}H NMR (CD_3CN): 7.62–7.32 (m, 16H of 4Ph), 7.17–6.86 (m, 4H of 4Ph), 5.63/5.51 (2s, *E*/*Z* C_5H_5), 3.10, 2.81 (2 br s, *E* $H_3CN{=}CCH_3$), 3.04, 2.34 (2q, ^5J(HH) = 0.86, *Z* $H_3CN{=}CCH_3$). ^{13}C{^{1}H} NMR: 186.5/186.1 (2s, *E*/*Z* C=N), 133.0 (d, ^2J(PC) = 10.4, *E* *o*-PPh), 132.5/132.0 (2d, ^1J(PC) = 54.5, *E*/*Z* i-PPh), 131.4/131.3 (2d, ^4J(PC) = 2.1, *E*/*Z* *p*-PPh), 129.4/129.2 (2d, ^3J(PC) = 10.9/10.4, *E*/*Z* *m*-PPh), 137.2/143.8, 129.7/128.7, 128.8/126.7, 126.1 (7s, *E*/*Z* *CPh*), 93.0/93.1 (2s, *E*/*Z* C_5H_5), 58.7/57.1 (2d, ^3J(CP) = 2.6/3.1, *E*/*Z* NCH_3), 34.5/25.4 (2s, *E*/*Z* CCH_3). ^{19}F NMR: −78.7 (s). ^{31}P{^{1}H}NMR: 15.6/17.5 (2s, *E*/*Z*). ^{1}H NMR (DMSO-d_6, 150°C, partial): 5.85/5.68 (2s, *E*/*Z* C_5H_5), 3.22, 2.70 (q and s, ^5J(HH) = 1.40 and $w_{1/2}$ = 3.5, *E* $H_3CN{=}CCH_3$), 3.21, 2.47 (2q, ^5J(HH) = 0.86, *Z* $H_3CN{=}CCH_3$).

5.2.2.2. Method B

A flask was charged with **4**$^+$TfO$^-$ (0.113 g, 0.137 mmol, 61:39 *E*/*Z*), $NH_4^+PF_6^-$ (0.220 g, 1.37 mmol), and acetone (100 ml). The mixture was stirred for 0.5 h, and solvent was removed by rotary evaporation. Then CH_2Cl_2 was added, and the mixture was filtered through Celite. Hexane (200 ml) was added to the filtrate. The yellow–orange powder was collected on a frit, washed with pentane, and dried by oil pump vacuum to give **4**$^+PF_6^-$ (0.091 g, 0.11 mmol, 81%, 61:39 *E*/*Z*) [10]. A portion was crystallized (acetone/hexane) to give orange prisms (>99–98:<1–2 *E*/*Z*). IR (cm^{-1}, CH_2Cl_2): ν(NO) 1701 (vs), ν(PF) 847 (s). ^{1}H NMR (CD_2Cl_2): 7.64–7.35 (m, 8H of 4Ph), 7.42–7.19 (m, 10H of 4Ph), 6.84–6.76 (m, 2H of 4Ph), 5.60/5.46 (2s, *E*/*Z* C_5H_5), 3.17, 2.84 (2 br s, *E* $H_3CN{=}CCH_3$), 3.13, 2.37 (2q, ^5J(HH) = 0.86, *Z* $H_3CN{=}CCH_3$). ^{19}F NMR: −72.9 (d, ^1J(PF) = 710). ^{31}P{^{1}H} NMR: 14.6/16.9 (2s, *E*/*Z* PPh_3), −144.0 (sep, ^1J(PF) = −710, PF_6^-). ^{1}H NMR (CD_2Cl_2, −80°C, partial, *E*): 5.50/5.46 (2s, *ac*/*sc* C_5H_5, 95/5), 3.00/3.87 (2s, *ac*/*sc* CH_3), 2.97/1.93 (2s, *ac*/*sc* CH_3). ^{31}P{^{1}H} NMR: 15.9/13.6 (2s, *ac*/*sc* 95/5). ^{1}H NMR (partial, *Z*): 5.40 (s, C_5H_5), 2.96/2.27 (2s, $H_3CN{=}CCH_3$). ^{31}P{^{1}H} NMR: 17.9 (s).

[10] The ^{19}F NMR and IR spectra showed TfO^-/PF_6^- metathesis to be complete.

5.2.3. $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}(CH_3)CH(R)C_6H_5)$ (5)

The following procedure is representative. A Schlenk flask was charged with 1^+TfO^- (0.205 g, 0.253 mmol, 95:5 *E/Z*) [8a] and THF (15 ml) and cooled to −100°C (CH_3CH_2OH/N_2). Then $(CH_3CH_2)_3SiC{\equiv}CLi$ (0.904 ml, 0.253 mmol, 0.28 M in diethyl ether) [37] was added dropwise with stirring to generate $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-$(\ddot{N}(CH_3)CH(C{\equiv}CSi(CH_2CH_3)_3)C_6H_5)$ (**5b**). An aliquot was transferred by cannula to an NMR tube, which was placed in a −100°C NMR probe (data: see text and Scheme 4).

5.2.4. $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)CH(CH_3)$-$C_6H_5)]^+TfO^-$ ($6a^+TfO^-$)

A Schlenk flask was charged with (*R*)-1^+TfO^- (0.681 g, 0.839 mmol, 95:5 *E/Z*) [8a] and THF (100 ml) and cooled to −100°C. Then CH_3Li (0.750 ml, 0.840 mmol, 1.1 M in diethyl ether) [11] was added dropwise with stirring to generate **5a**. After 0.5 h, TfOH (0.111 ml, 1.26 mmol) was added and the cold bath was removed. After 1 h, solvent was removed by oil pump vacuum. The residue was dissolved in CH_2Cl_2 and charcoal was added. The mixture was stirred (0.5 h) and filtered through Celite. The solvent was concentrated (2 ml) by rotary evaporation, and hexane/diethyl ether (150 ml, 50:50 (vol./vol.)) was added. The orange powder was collected on a frit, washed with hexane, and dried by oil pump vacuum to give $\mathbf{6a}^+TfO^-$ as a 73:25:1:1 mixture of Re,C,N configurational diastereomers (0.529 g, 0.639 mmol, 76%) [12]. *Anal.* Calc. for $C_{33}H_{33}F_3N_2O_4PReS$: C, 47.88; H, 4.02. Found: C, 47.79; H, 4.01%. IR (cm^{-1}, CH_2Cl_2): ν(NO) 1685 (vs). ^1H NMR ($CDCl_3$): 7.60–7.20 (m, 4Ph), 5.62/6.15 (2 dq, 71:26, J = 7/6, 7/6, NH), 5.50/5.47/5.15/5.09 (4s, 1:1:73:25, C_5H_5), 4.10/4.01 (2 dq, 71:26, J = 7/6, 7/6, CH), 2.86/2.69 (2d, 71:26, J = 5.3/5.3, NCH_3) 1.43/1.58 (2d, 71:26, J = 6.8/6.7, CCH_3). $^{31}P\{^1H\}$ NMR: 19.6/17.5/14.9/14.1 (4s, 1:1:72:26).

5.2.5. $NH(CH_3)CH(CH_3)C_6H_5$ (8)

A Schlenk flask was charged with $\mathbf{6a}^+TfO^-$ (0.114 g, 0.138 mmol) that had been prepared as described above, CH_2Cl_2 (10 ml), and $Et_4N^+CN^-$ (0.022 g, 0.14 mmol). The solution was stirred for 1 h, and the solvent was removed by oil pump vacuum. The residue was dissolved in benzene (20 ml) and washed with 15% aqueous KOH (20 ml). The KOH was extracted with benzene (3×20 ml). The combined benzene fractions were washed with water (20 ml) and brine (20 ml) and dried over K_2CO_3. Solvent was removed by rotary evaporation, and diethyl ether (50 ml) and hexane (50 ml) were added. The yellow powder was collected by filtration, washed with pentane, and dried by oil pump vacuum to give (*R*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ ((*R*)-**7**) (0.071 g, 0.12 mmol, 85%, >98% ee by (+)-Eu(hfc)$_3$), $[\alpha]_{589}^{24}$ −176±4° (*c* 1.06 mg/ml, CH_2Cl_2) [23,24]. Solvent was removed from the filtrate. The colorless oil was dried by oil pump vacuum to give (*R*)-**8** (0.015 g, 0.11 mmol, 81%; 46% ee, 0.2 equiv. of (-)-BNPPA) (see footnote 1) [38], $[\alpha]_{589}^{24}$ +20±4° (*c* 1.8 mg/ml, $CHCl_3$) [13]. Both (*R*)-**7** and (*R*)-**8** were pure by ^1H NMR ($CDCl_3$).

5.2.6. $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}(CH_3)CH(CN)C_6H_5)$ (9)

5.2.6.1. Method A

An NMR tube was charged with (*S*)-1^+TfO^- (0.020 g, 0.025 mmol, 95:5 *E/Z*) and PPN^+CN^- (0.016 g, 0.028 mmol) [39] and cooled to −100°C. Then CH_2Cl_2 (0.8 ml) was added. After 0.5 h, the tube was placed in a −100°C NMR probe, and $^{31}P\{^1H\}$ NMR spectra were recorded as the probe was warmed to −50°C. Then HOTf (0.004 ml, 0.05 mmol) was added, and the probe warmed further (data: see text). IR (cm^{-1}, CH_2Cl_2): ν(NO) 1633 (vs).

5.2.6.2. Method B

Complex (*S*)-1^+TfO^- (0.030 g, 0.037 mmol, 95:5 *E/Z*), $Et_4N^+CN^-$ (0.006 g, 0.04 mmol), and CD_2Cl_2 (0.8 ml) were combined as in the previous procedure. After 0.5 h, the tube was placed in a −50°C NMR probe, and spectra were recorded (partial data): ^1H NMR: 7.67–7.07 (m, 4Ph), 5.78 (s, CH), 5.41/5.40 (2s, 85:15, C_5H_5), 2.22/2.69 (2s, 85:15, NCH_3). $^{31}P\{^1H\}$ NMR: 17.9/20.3 (2s, 85:15). The sample was further warmed (data: see text).

5.2.7. Reaction of 4^+TfO^- and $C_6H_5CH_2MgCl$

A Schlenk flask was charged with 4^+TfO^- (0.109 g, 0.133 mmol, >99:<1 *E/Z*) and THF (20 ml) and cooled to −100°C. Then $C_6H_5CH_2MgCl$ (0.146 ml, 0.133 mmol, 0.91 M in THF) was added dropwise with stirring. An aliquot was transferred by cannula to an NMR tube, which was placed in a −100°C probe (data: see text). After 2 h, TfOH (0.023 ml, 0.27 mmol) was added, and a second aliquot was similarly assayed. The cold bath was removed. After 1 h, solvent was removed by oil pump vacuum. The residue was dissolved in CH_2Cl_2 (40 ml) and charcoal was added. The mixture was stirred (0.5 h) and filtered through Celite. The filtrate was concentrated (5 ml), and hexane (100 ml) was added. The yellow powder was collected on a frit, washed with pentane, and dried by oil pump vacuum to give a mixture of 4^+TfO^- (0.033 g, 0.041 mmol, 30%, 51:49 *E/Z*, 79 mol% by $^1H/^{31}P$ NMR) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)CH$-$(CH_2C_6H_5)C_6H_5)]^+TfO^-$ (**14**$^+TfO^-$, 0.009 g, 0.01 mmol, 7%, >98% diastereomer purity). ^1H NMR for **14**$^+TfO^-$ ($CDCl_3$, partial): 8.39 (br s, NH), 5.23 (s, C_5H_5), 3.52 (d, ^2J(HH) = 12.5, CH*H*′), 3.28 (d, ^2J(HH) = 12.5, CH*H*′), 2.43 (br s, NCH_3), 1.78 (s, CCH_3). $^{31}P\{^1H\}$ NMR: 18.0 (s).

[11] NMR experiments with CH_3Li that contained LiBr showed additional products after TfOH addition.

[12] Traces of 1^+TfO^- were detectable by NMR.

[13] Commercial samples of (*R*)-**8** (Aldrich) have [α] values of +70°.

5.2.8. (η^5-C_5H_5)Re(NO)(PPh_3)($\ddot{N}(CH_3)C(C_6H_5)=CH_2$) (13)

A Schlenk flask was charged with 4^+TfO^- (0.073 g, 0.088 mmol, >99:<1 *E/Z*) and THF (25 ml) and cooled to −80°C (acetone/CO_2). Then t-BuO^-K^+ (0.010 g, 0.088 mmol) was added. The cold bath was removed, and an oil pump vacuum applied. The residue was kept under vacuum (1 h) and extracted with THF-d_8. The sample was transferred by cannula to an NMR tube (additional data: see text). IR (cm^{-1}, THF-d_8): ν(NO) 1655 (vs). ^1H NMR (THF-d_8): 7.55–7.32 (m, 17H of 4Ph, $=CH_2$), 7.29–7.15 (m, 4H of 4Ph), 7.07–7.00 (m, 1H of 4Ph), 4.90 (s, C_5H_5), 2.97 (d, ^5J(HH) = 1.6, CH_3). $^{13}C\{^1H\}$ NMR: 174.3 (s, =CN), 149.3, 134.8, 129.6, 127.8, 126.8 (5s, C*Ph*, $=CH_2$), 134.9 (d, ^1J(CP) = 48.3, i-PPh), 134.9 (d, ^2J(CP) = 10.6, *o*-PPh), 131.1 (d, ^4J(CP) = 2.0, *p*-PPh), 129.4 (d, ^3J(CP) = 10.1, *m*-PPh), 93.1 (s, C_5H_5), 57.4 (d, ^3J(CP) = 6, NCH_3). $^{31}P\{^1H\}$ NMR: 19.1 (s).

5.2.9. (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C(C_6H_5)=\ddot{N}CH_3$) (15)

An NMR tube was charged with $4^+PF_6^-$ (0.020 g, 0.024 mmol, 52:48 *E/Z*) and THF (0.8 ml) and cooled to −80°C. Then t-BuO^-K^+ (0.024 ml, 0.024 mmol, 1.0 M in THF) was added. The tube was placed in a −80°C NMR probe (data: see text), and then removed and allowed to warm. After 2 h, the sample was transferred to a Schlenk flask, and an oil pump vacuum applied. The residue was kept under vacuum (3 h) and dissolved in THF-d_8. The sample was transferred by cannula to an NMR tube. IR (cm^{-1}, THF-d_8): ν(NO) 1649 (vs), ν(C=N) 1599 (m). ^1H NMR (THF-d_8): 7.76–7.71 (m, 2H of 4Ph), 7.49–7.37 (m, 15H of 4Ph), 7.31–7.14 (m, 3H of 4Ph), 4.61/4.91 (2s, 96:4, C_5H_5), 3.10 (dd, ^2J(HH) = 11, ^3J(HP) = 6, ReC*H*H′), 2.72 (dd, ^2J(HH) = 11, ^3J(HP) = 4, ReCH*H*′), 2.99/2.82 (2s, 96:4, $2CH_3$). $^{13}C\{^1H\}$ NMR: 182.8 (s, C=N), 145.0, 128.7, 128.3, 127.9 (4s, C*Ph*), 137.2 (d, ^1J(CP) = 51.4, i-PPh), 134.7 (d, ^2J(CP) = 10.6, *o*-PPh), 131.2 (d, ^4J(CP) = 2.5, *p*-PPh), 129.4 (d, ^3J(CP) = 10.6, *m*-PPh), 90.9/91.1 (2s, 96:4, C_5H_5), 39.2/30.8 (2s, 96:4, CH_3), −12.6 (s, CH_2). $^{31}P\{^1H\}$ NMR: 23.7/26.1 (2s, 96:4).

Acknowledgements

We thank the NIH for financial support, Dr D.A. Knight for exploratory experiments, and Dr C.L. Mayne for the 2D NMR data.

References

[1] (a) R.A. Volkmann, in B.M. Trost, I. Fleming and S.L. Schreiber (eds.), Comprehensive Organic Synthesis, Vol. 1, Pergamon, New York, 1991, Ch. 1.12; (b) D. Enders and U. Reinhold, Tetrahedron: Asymmetry, 8 (1997) 1895.

[2] Lead references to an extensive literature: (a) M.J. Lucero and K.N. Houk, J. Am. Chem. Soc., 119 (1997) 826; (b) D. Enders, R. Locktman and G. Raabe, SYNLETT, (1996) 126, and earlier papers cited in Ref. 7; (c) A.B. Smith, III, K.M. Yager and C.M. Taylor, J. Am. Chem. Soc., 117 (1995) 10879; (d) K. Ishihara, M. Miyata, K. Hattori, T. Tada and H. Yamamoto, J. Am. Chem. Soc., 116 (1994) 10520; (e) T. Basile, A. Bocoum, D. Savoia and A. Umani-Ronchi, J. Org. Chem., 59 (1994) 7766.

[3] Lead reference for cyanide ion additions: F.A. Davis, P.S. Portonovo, R.E. Reddy and Y. Chiu, J. Org. Chem., 61 (1996) 440.

[4] Studies with chiral tungsten Lewis acids: (a) S.G. Feng and J.L. Templeton, Organometallics, 11 (1992) 1295; (b) J.L. Caldarelli, P.S. White and J.L. Templeton, J. Am. Chem. Soc., 114 (1992) 10097; (c) T.B. Gunnoe, P.S. White and J.L. Templeton, J. Am. Chem. Soc., 118 (1996) 6916; (d) L.W. Francisco, P.S. White and J.L. Templeton, Organometallics, 15 (1996) 5127.

[5] (a) Review: S.E. Denmark and O.J.-C. Nicaise, J. Chem. Soc., Chem. Commun., (1996) 999; (b) H. Fujieda, M. Kanai, T. Kambara, A. Iida and K. Tomioka, J. Am. Chem. Soc., 119 (1997) 2060; (c) M. Nakamura, A. Hirai and E. Nakamura, J. Am. Chem. Soc., 118 (1996) 8489.

[6] (a) Y. Yamamoto, Y. Kubota, Y. Honda, H. Fukui, N. Asao and H. Nemoto, J. Am. Chem. Soc., 116 (1994) 3161; (b) H. Sasai, S. Arai, Y. Tahara and M. Shibasaki, J. Org. Chem., 60 (1995) 6656; (c) M.S. Iyer, K.M. Gigstad, N.D. Namdev and M.A. Lipton, J. Am. Chem. Soc., 118 (1996) 4910.

[7] Lead references: (a) A.H. Hoveyda and J.P. Morken, Angew. Chem., Int. Ed. Engl., 35 (1996) 1262; (b) X. Verdaguer, U.E.W. Lange, M.T. Reding and S.L. Buchwald, J. Am. Chem. Soc., 118 (1996) 6784; (c) N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya and R.J. Noyori, J. Am. Chem. Soc., 118 (1996) 4916; (d) R. Sablong, J.A. Osborn and J.W. Faller, J. Organomet. Chem., 527 (1997) 65.

[8] (a) D.A. Knight, M.A. Dewey, G.A. Stark, B.K. Bennett, A.M. Arif and J.A. Gladysz, Organometallics, 12 (1993) 4523; (b) G.A. Stark and J.A. Gladysz, Inorg. Chem., 35 (1996) 5509.

[9] W.R. Cantrell, Jr., G.B. Richter-Addo and J.A. Gladysz, J. Organomet. Chem., 472 (1994) 195.

[10] (a) G.B. Richter-Addo, D.A. Knight, M.A. Dewey, A.M. Arif and J.A. Gladysz, J. Am. Chem. Soc., 115 (1993) 11863; (b) G.A. Stark, M.A. Dewey, G.B. Richter-Addo, D.A. Knight, A.M. Arif and J.A. Gladysz, in H. Werner and J. Sundermeyer (eds.), Stereoselective Reactions of Metal-Activated Molecules, Vieweg, Braunschweig, Germany, 1995, p. 51.

[11] G.A. Stark, A.M. Arif and J.A. Gladysz, Organometallics, 13 (1994) 4523.

[12] T.J. Johnson, L.J. Alvey, M. Brady, C.L. Mayne, A.M. Arif and J.A. Gladysz, Chemistry — A European Journal, 1 (1995) 294.

[13] T.J. Johnson, A.M. Arif and J.A. Gladysz, Organometallics, 13 (1994) 3182.

[14] For additions to N=C moieties that are part of a chelate, see: (a) L. Bendahl, A. Hammershøi, D.K. Jensen, E. Kaifer, A.M. Sargeson and A.C. Willis, J. Chem. Soc., Chem. Commun., (1996) 1649; (b) G.C. Martin, J.M. Boncella and E.J. Wucherer, Organometallics, 10 (1991) 2804.

[15] For additions to non-ligating N=C moieties in chiral transition metal complexes, see: D.M. David, L.A.P. Kane-Maguire and S.G. Pyne, J. Chem. Soc., Dalton Trans., (1994) 289, and Refs. therein.

[16] For other non-racemic complexes of acyclic imines and chiral transition metal Lewis acids, see: (a) J.W. Faller, Y. Ma, C.J. Smart and M.J. DiVerdi, J. Organomet. Chem., 420 (1991) 237; (b) A. Togni, G. Rist, G. Rihs and A. Schweiger, J. Am. Chem. Soc., 115 (1993) 1908; (c) D.A. Gately and J.R. Norton, J. Am. Chem. Soc., 118 (1996) 3479.

[17] (a) J. Sandström, Dynamic NMR Spectroscopy, Academic Press, New York, 1982; (b) R.R. Ernst, G. Bodenhausen and A. Wokaun, Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Clarendon Press, Oxford, 1987, Ch. 9; (c) J. Pu, T.-S.

Peng, C.L. Mayne, A.M. Arif and J.A. Gladysz, Organometallics, 12 (1993) 2686.
[18] (a) R.A. Abramovitch and E.P. Kyba, J. Am. Chem. Soc., 96 (1974) 480; (b) D.A. Nelson and R.L. Atkins, Tetrahedron Lett., 51 (1967) 5197.
[19] J.A. Gladysz and B.J. Boone, Angew. Chem., Int. Ed. Engl., 36 (1997) 550.
[20] (a) R. Knorr, J. Ruhdorfer, J. Mehlstäubl, P. Böhrer and D.S. Stephenson, Chem. Ber., 126 (1993) 747; (b) H.-O. Kalinowski and H. Kessler, Top. Stereochem., 7 (1973) 295.
[21] M.A. Dewey, D.A. Knight, A.M. Arif and J.A. Gladysz, Chem. Ber., 125 (1992) 815.
[22] M.A. Dewey, G.A. Stark and J.A. Gladysz, Organometallics, 15 (1996) 4798.
[23] M.A. Dewey, D.A. Knight, D.P. Klein, A.M. Arif and J.A. Gladysz, Inorg. Chem., 30 (1991) 4995.
[24] J.M. Fernández and J.A. Gladysz, Organometallics, 8 (1989) 207.
[25] D.M. Dalton, C.M. Garner, J.M. Fernández and J.A. Gladysz, J. Org. Chem., 56 (1991) 6823.
[26] (a) L.J. Alvey, University of Utah, Salt Lake City, unpublished results; (b) M.A. Dewey, Ph.D. Dissertation, University of Utah, Salt Lake City, 1991, Ch. 5.
[27] J.F. Hartwig, R.G. Bergman and R.A. Andersen, Organometallics, 10 (1991) 3326, and Refs. therein.
[28] G.A. Stark, Ph.D. Dissertation, University of Utah, Salt Lake City, 1997.
[29] (a) H. Nakamura, H. Iwama and Y. Yamamoto, J. Am. Chem. Soc., 118 (1996) 6641; J. Chem. Soc., Chem. Commun., (1996) 1459; (b) see also: S. Kobayashi and S. Nagayama, J. Org. Chem., 62 (1997) 232.
[30] H. Ishitani and S. Kobayashi, Tetrahedron Lett., 37 (1996) 7357, and Refs. therein.
[31] G.S. Bodner, D.E. Smith, W.G. Hatton, P.C. Heah, S. Georgiou, A.L. Rheingold, S.J. Geib, J.P. Hutchinson and J.A. Gladysz, J. Am. Chem. Soc., 109 (1987) 7688.
[32] J.I. Seeman, Chem. Rev., 83 (1983) 83.
[33] (a) M.R. Winkle, J.M. Lansinger and R.C. Ronald, J. Chem. Soc., Chem. Commun., (1980) 87; (b) S.C. Watson and J.F. Eastham, J. Organomet. Chem., 9 (1967) 165.
[34] (a) F. Agbossou, E.J. O'Connor, C.M. Garner, N. Quirós Méndez, J.M. Fernández, A.T. Patton, J.A. Ramsden and J.A. Gladysz, Inorg. Synth., 29 (1992) 211; (b) improved PPh_3 substitution step: Y. Zhou, M.A. Dewey and J.A. Gladysz, Organometallics, 12 (1993) 3918.
[35] J.H. Merrifield, J.M. Fernández, W.E. Buhro and J.A. Gladysz, Inorg. Chem., 23 (1984) 4022.
[36] E.P. Kyba, Org. Prep. Proced., 2 (1970) 149.
[37] W.D. Wulff, P.-C. Tang, K.-S. Chan, J.S. McCallum, D.C. Yang and S.R. Gilbertson, Tetrahedron, 41 (1985) 5813.
[38] M.J. Shapiro, A.E. Archinal and M.A. Jarema, J. Org. Chem., 54 (1989) 5826.
[39] A. Martinsen and J. Songstad, Acta Chem. Scand., 31 (1977) 645.