Configurational Equilibria in Amido and Lithioamido Complexes of Formulas $(\eta^5\text{-}C_5H_5)Re(NO)(PAr_3)(\ddot{N}HCHRR')$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PAr_3)(\ddot{N}LiR'')$: Epimerization Occurs at Rhenium via Phosphine Dissociation

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The diastereomerically and enantiomerically pure amido complex (*SR*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}HCH(CH_3)Ph)$ ((*SR*)-**5**) converts to (*RR*)-**5** (inversion at rhenium, retention at carbon) in THF-d_8 at 49.4 °C with $k_1 = 2.34 \times 10^{-4}$ s^{-1} and $k_{-1} = 0.90 \times 10^{-4}$ s^{-1}. Similarly, (*SS*)-**5** converts to (*RS*)-**5** with $k_1 = 0.90 \times 10^{-4}$ s^{-1} and $k_{-1} = 2.30 \times 10^{-4}$ s^{-1}. Both epimerizations give equilibrium ratios (*RR*/*SR* or *SS*/*RS*) of 70:30. Reactions with HOTf yield $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_2CH(CH_3)Ph)]^+TfO^-$, and subsequent additions of $Et_4N^+CN^-$ afford $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ and $NH_2CH(CH_3)Ph$ (all steps with retention at rhenium and carbon). Enantiomeric purities and absolute configurations are assayed by chiral NMR shift reagents and (−)-menthyl chloroformate derivatives, respectively, establishing configurations of epimerized **5**. Reaction of (*SR*)-**5** and P(*p*-tol)$_3$ in THF-d_8 at 49.4 °C gives $(\eta^5\text{-}C_5H_5)Re(NO)(P(p\text{-tol})_3)(\ddot{N}HCH(CH_3)Ph)$ (50:50 (t_0) → 66:34 (t_∞) *RR*/*SR*) with $k = 4.6 \times 10^{-4}$ s^{-1}, twice that for the conversion of (*SR*)-**5** to (*RR*)-**5**. Rate data for the latter at 32.3−59.1 °C give $\Delta H^\ddagger = 26$ kcal/mol and $\Delta S^\ddagger = 6$ eu. These results are best modeled by mechanisms involving initial and rate determining PPh_3 dissociation, with anchimeric assistance by the amido lone pair, to give an intermediate that is trigonal planar at rhenium and combines with PAr_3 without significant diastereoselectivity. Reactions of *n*-BuLi with **5** and related complexes give $\ddot{N}LiR$ species from which PPh_3 is lost at lower temperatures, and are presumed to be much less configurationally stable.

The most common types of "chiral-at-metal" complexes[1] contain four different ligands. Although there are usually important geometric distinctions, such metal centers resemble the classical "asymmetric carbon", ***C***ABCD. Chiral-at-metal complexes are seeing increasing use in enantioselective organic synthesis.[1−5] As such, the characterization of configurational processes—racemization when the metal is the only stereocenter or epimerization when there are additional stereocenters—is of fundamental importance.

We have had an ongoing interest in enantioselective and diastereoselective transformations mediated by the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**).[4−12] Adducts of many types of neutral and anionic Lewis bases are easily prepared in enantiomerically pure form.[4,5,13] With neutral Lewis bases, remarkable configurational stabilities have been observed.[14,15] No racemization has ever been detected, including many

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compounds that have been kept for extended periods at elevated temperatures.[15] Most anionic Lewis bases give adducts of similar configurational stabilities.[16] However, with amido and alkoxide ligands, the rhenium can racemize or epimerize.[17] Depending upon the conditions and ligand, temperatures range from 50 °C to below 20 °C.

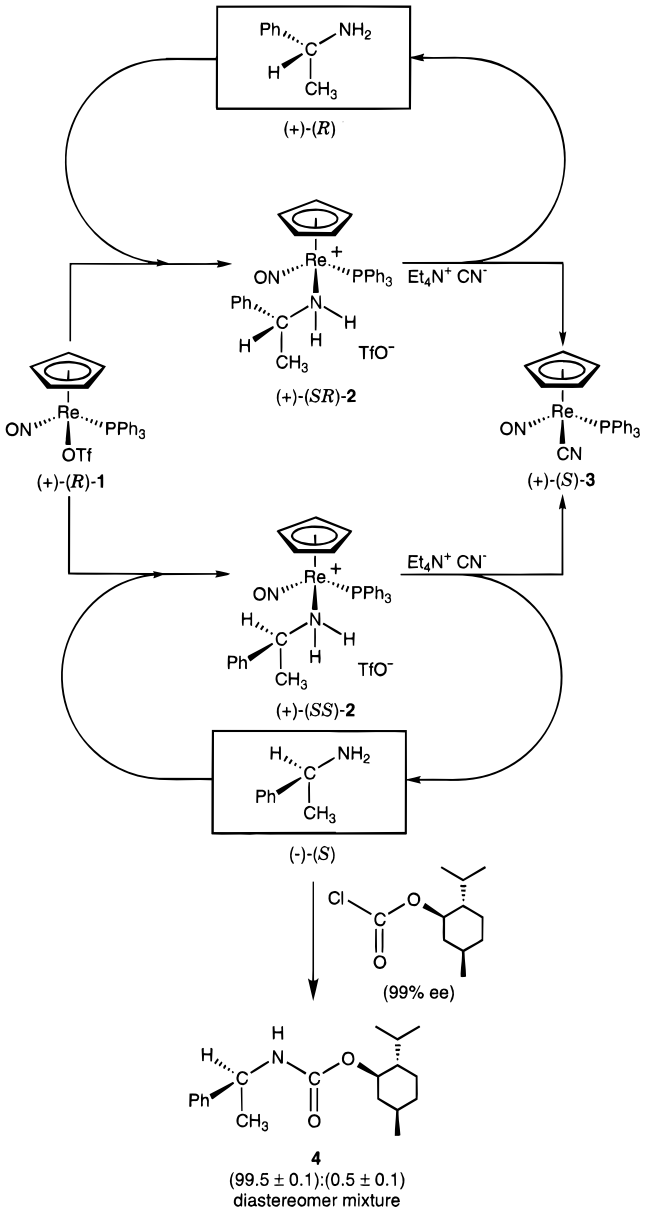
We have sought to develop applications of **I** in the enantioselective synthesis of chiral organonitrogen compounds. Toward this end, we have published an extensive series of papers involving adducts of **I** and various neutral and anionic nitrogen donor ligands.[6−12] These have contained several incidental observations of configurationally labile amido complexes.[10,12] In this paper, we present a detailed mechanistic study of a representative epimerization. We also describe the generation of adducts of **I** and *lithio*amido ligands, −N̈LiR. This rare type of complex[18] can be viewed as a strong "chiral base" and could have many potential applications in enantioselective syntheses. A portion of this work has been communicated,[8a] and a companion paper on the epimerization of related alkoxide complexes has appeared.[17]

Results

Syntheses of Amine Complexes. It has been previously shown that the triflate complex (η^5-C_5H_5)-Re(NO)(PPh_3)(OTf) (**1**) and amines react to give the corresponding cationic amine complexes in high yields.[7] Thus, racemic **1** was generated in toluene as previously described[16] and treated with racemic α-methylbenzylamine (5.0 equiv) as shown for the scalemic educts in Scheme 1. The new amine complex [(η^5-C_5H_5)Re(NO)-(PPh_3)($NH_2CH(CH_3)C_6H_5$)]$^+$TfO$^-$ (**2**) precipitated and was isolated in 81% yield as a mixture of Re/C configurational diastereomers. When this reaction was monitored by ^{1}H NMR under homogeneous conditions in CD_2Cl_2, **2** cleanly formed as a (52 ± 2):(48 ± 2)[19] mixture of diastereomers. Data below establish that the α-methylbenzylamine ligand does not readily exchange with free α-methylbenzylamine. Hence, there is very little or no kinetic selectivity.

Several factors prompted the use of an amine with an α-carbon stereocenter. First, epimerization was initially detected in complexes with ReN*C*HRR′ linkages, where inversion could in principle occur at either rhenium or carbon. Both processes operate with related alkoxide complexes.[17] Second, diastereomer interconversion is often easier to monitor than enantiomer interconversion. Also, each enantiomer of α-methylbenzylamine is commercially available. Accordingly, we sought to synthesize each diastereomer of **2** in enantiomerically pure form. As shown in Scheme 1, (−)-(*S*)-α-methylbenzylamine and the scalemic triflate complex (+)-(*R*)-**1**[16,20] were reacted. Workup gave (+)-(*SS*)-**2** in 84% yield and ≥98% de.[19] An analogous reaction of the opposite enantiomer, (+)-(*R*)-α-methylbenzylamine, gave the opposite diastereomer, (+)-(*SR*)-**2**, in 80% yield and ≥98% de.

Scheme 1. Synthesis and Substitution Reactions of Amine Complexes 2



The amine complexes (+)-(*SR*)-**2** and (+)-(*SS*)-**2** were characterized by microanalysis, polarimetry, and IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, as summarized in the Experimental Section. Both gave similar optical rotations ([α]$^{25}_{589}$ 374 ± 6 and 395 ± 5°),[21] indicating a dominating contribution by the rhenium stereocenter. The IR ν_{NO} values and ^{31}P NMR chemical shifts were comparable to those of other primary amine complexes of **I**.[7] The configurations at rhenium, which correspond

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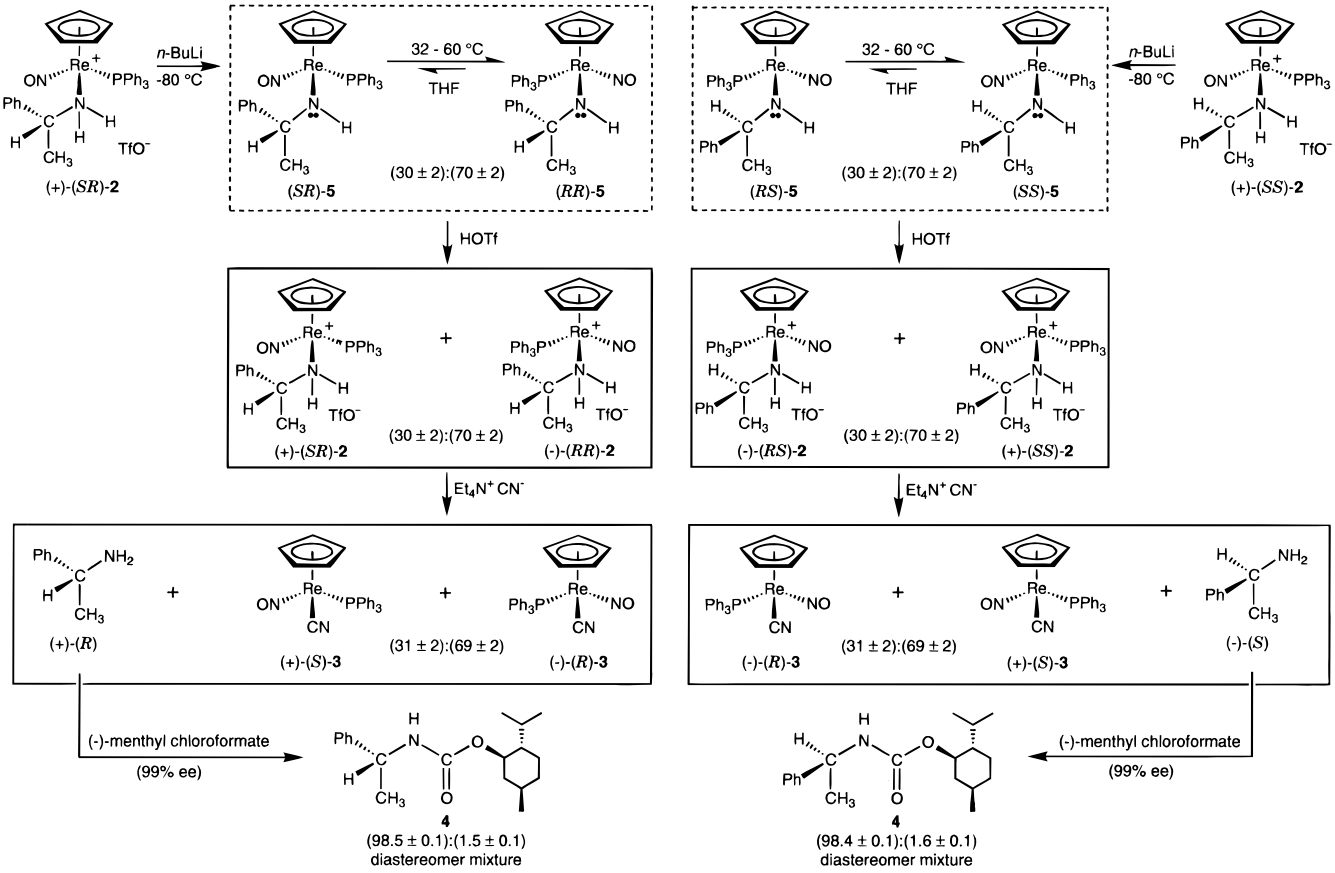
(19) All diastereomer and enantiomer ratios are normalized to 100. For NMR determinations, error limits on each component are generally ±2. When no signal can be detected for a second, independently prepared isomer, a ≥99:≤1 ratio is assumed.

(20) Rhenium configurations follow from conventions described earlier[7,10,14b] and are specified prior to carbon configurations. Serendipitously, *R*/*S* designations also track the *relative* configurations for all compounds in this paper.

(21) All [α] values were recorded in CH_2Cl_2 in thermostated cells utilizing procedures described earlier: Dewey, M. A.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2390.

Scheme 2. Generation and Epimerization of Amido Complexes 5



to retention, were assigned by analogy to many other substitution reactions of **1**.[5,7,16] A CD_2Cl_2 solution of (+)-(*SR*)-**2** was treated with excess (−)-(*S*)-α-methylbenzylamine. After 10 h, a ^{1}H NMR spectrum showed that no (+)-(*SS*)-**2** had formed. Hence, in the absence of an extraordinary thermodynamic bias, there is no exchange of free and coordinated α-methylbenzylamine by any mechanism.

Substitution and Deprotonation of Amine Complexes. For reasons noted above, means of assaying both the rhenium and carbon configurations of **2** were required. It has been previously shown that amines and related ligands can be displaced from **I** by the cyanide salt $Et_4N^+CN^-$ and with retention at rhenium.[5,7,10] Accordingly, (+)-(*SR*)- and (+)-(*SS*)-**2** were separately treated with $Et_4N^+CN^-$ in CH_2Cl_2 as shown in Scheme 1. Column chromatography gave the cyanide complex (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CN) ((+)-(*S*)-**3**)[7] in 71 and 67% yields.[22] Importantly, both the optical rotations ($[\alpha]_{589}^{25}$ 183 ± 3°; lit. 179 ± 4°)[7,21] and ^{1}H NMR spectra in the presence of the chiral shift reagent (+)-Eu(hfc)$_3$ showed enantiomeric purities of ≥98% ee (≥99:≤1 *S*/*R*).[19] This bounds the enantiomeric purities of (+)-(*SR*)- and (+)-(*SS*)-**2** as ≥98% ee.

Further chromatography of the latter reaction gave (−)-(*S*)-α-methylbenzylamine.[22] The sample was derivatized with (−)-menthyl chloroformate (99% ee) to give the urethane **4** depicted in Scheme 1.[23] Subsequent capillary GC analysis reproducibly indicated a (99.5 ± 0.1):(0.5 ± 0.1) mixture of diastereomers (99.0% de). Hence, as would be expected, scalemic α-methylbenzylamine can be bound to and detached from **I** with little or no racemization.

Primary and secondary amine complexes of **I** are readily *N*-deprotonated by *n*-BuLi to the corresponding neutral amido complexes.[8b] Thus, (+)-(*SR*)-**2** and (+)-(*SS*)-**2** were separately dissolved in THF at −80 °C. As shown in Scheme 2, 1.0 equiv of *n*-BuLi was added, and the yellow-orange solutions immediately turned red. The amido complexes (*SR*)-(η^5-C_5H_5)Re(NO)(PPh_3)(ÑHCH(CH$_3$)Ph) ((*SR*)-**5**) and (*SS*)-**5** formed cleanly, as assayed by ^{31}P NMR. The solvent was replaced by THF-d_8, and ^{1}H and ^{13}C NMR spectra were recorded at −20 °C. Each product was ≥98% de, and configurations were assigned with the assumption that *N*-deprotonation should proceed with retention at rhenium and carbon. All spectroscopic data were similar to those of amido complexes reported previously,[8b] and are summarized in the Experimental Section. The ^{13}C NMR spectra showed weak CF_3 signals from the byproduct lithium triflate.

Epimerization of Amido Complexes. When NMR spectra of (*SR*)-**5** or (*SS*)-**5** were recorded at room temperature, trace amounts of the opposite diastereomer slowly appeared. Thus, a THF-d_8 solution of (*SR*)-**5** was kept at 60 °C. Epimerization occurred over the course of 2.5 h to give a (30 ± 2):(70 ± 2)[19] mixture of diastereomers, as assayed by integration of the cyclopentadienyl ^{1}H NMR signals. The *new* diastereomer predominated. An identical experiment was conducted with (*SS*)-**5**. Epimerization occurred to give a (70 ± 2):(30 ± 2)[19] mixture of diastereomers, with the *original* diastereomer predominating. This establishes that (*SS*)-**5** and (*RR*)-**5** are slightly more stable than (*SR*)-**5** and (*RS*)-**5**, with a K_{eq} of 2.3 at 60 °C. Hence, the pyramidal rhenium fragment **I** exhibits a moderate

(22) The preparative yield of this spectroscopically quantitative transformation was not optimized.
(23) Westley, J. W.; Halpern, B. *J. Org. Chem.* **1968**, *33*, 3978.

Table 1. Rates of Disappearance of Amido Complexes (*SR*)-5 and (*SS*)-5 in THF-d_8

entry	complex/additive	temp (°C)[a]	10^4k_1 (s^{-1})	10^4k_{-1} (s^{-1})
1	(*SR*)-**5**[b]	32.3	0.23 ± 0.02	0.082 ± 0.008
2		40.4	0.77 ± 0.04	0.27 ± 0.03
3		49.4	2.34 ± 0.12	0.90 ± 0.09
4		59.1	7.9 ± 0.4	3.9 ± 0.4
5	(*SR*)-**5**[b] + 10PPh_3 (0.98 M)	49.4	2.50 ± 0.23	0.95 ± 0.21
6	(*SS*)-**5**[b]	49.4	0.90 ± 0.19	2.30 ± 0.49
7	(*SR*)-**5**[c] + 19P(*p*-tol)$_3$ (0.96 M)	49.4	4.6 ± 0.6	

[a] ±1 C. [b] Epimerization rates. [c] Substitution rates.

thermodynamic preference or degree of chiral recognition for binding one carbon configuration of the −ṄHCH(CH$_3$)Ph moiety.

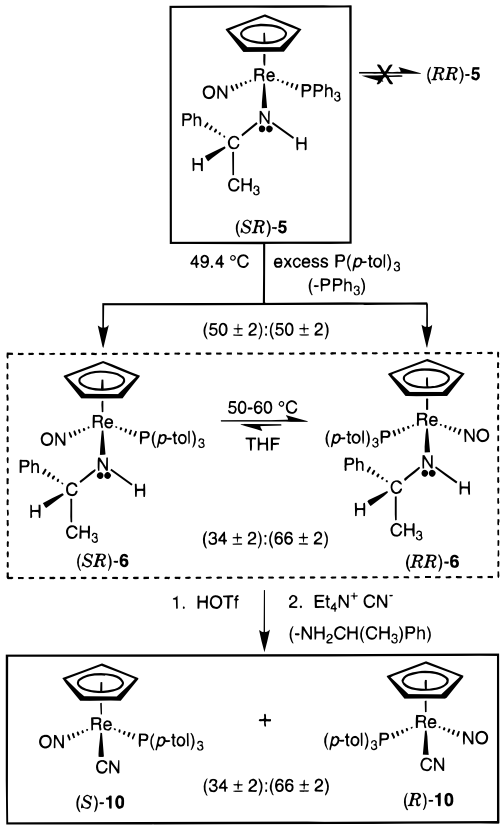
The site of epimerization was assayed next. As shown in Scheme 2, the sample obtained from (*SR*)-**5** was treated with HOTf. The amine complex **2** formed as a (30 ± 2):(70 ± 2) mixture of diastereomers, as assayed by ^{31}P NMR. Then, as described for diastereomerically pure **2** above (Scheme 1), $Et_4N^+CN^-$ was added. Workup gave the cyanide complex **3** and α-methylbenzylamine in 65% and 53% yields, respectively.[22] Analyses of the former indicated enantiomeric purities of 39 ± 2% ee ((+)-Eu(hfc)$_3$) and 37 ± 2% ee ($[\alpha]^{25}_{589}$ −67 ± 1°)—corresponding to an enantiomer ratio of (31 ± 2):(69 ± 2). The close agreement with the diastereomer ratio of epimerized (*SR*)-**5** requires that inversion has occurred at rhenium.

Accordingly, both probes of enantiomeric purity showed the major enantiomer to be (−)-(*R*)-**3**, in which the rhenium configuration is *opposite* to that of (*SR*)-**5**. As a check, the α-methylbenzylamine was treated with (−)-menthyl chloroformate (99% ee) and the resulting urethane **4** analyzed as described above. As indicated in Scheme 2, **4** was a (98.5 ± 0.1):(1.5 ± 0.1) mixture of diastereomers (97.0% de), with the major component derived from (+)-(*R*)-α-methylbenzylamine. Hence, there is little or no inversion at carbon, and (*SR*)-**5** epimerizes to give virtually exclusively (*RR*)-**5**.

The epimerized sample obtained from (*SS*)-**5** (Scheme 2) was similarly reacted. Workup gave the cyanide complex (+)-(*S*)-**3** in 60% yield, for which analyses indicated enantiomeric purities of 39 ± 2% ee ((+)-Eu(hfc)$_3$) and 38 ± 2% ee ($[\alpha]^{25}_{589}$ 68 ± 1°) or a (69 ± 2):(31 ± 2) *S*/*R* enantiomer ratio. The α-methylbenzylamine was converted to the urethane **4**, which was a (98.4 ± 0.1):(1.6 ± 0.1) mixture of diastereomers (96.8% de) with the major component derived from (−)-(*S*)-α-methylbenzylamine. These data show that (*SS*)-**5** undergoes inversion at rhenium to give (*RS*)-**5** but remains as the dominant isomer at equilibrium.

Additional mechanistic information was sought. Thus, the rates of epimerization of (*SR*)-**5** and (*SS*)-**5** were measured in THF-d_8 at 49.4 °C. The approach to equilibrium was followed by integration of the cyclopentadienyl ^{1}H NMR signals. Standard data treatments gave the rate constants in entries 1 and 6 of Table 1.[24] As expected, the k_1 value of each reaction matched the k_{-1} value of the other. The effect of added PPh_3 was also probed (entry 5). No appreciable difference was found, suggesting that PPh_3 dissociation is unlikely prior to the rate-determining step. Rates of epimerization of (*SR*)-**5** were also measured at additional temperatures (entries 2−4) and used to calculate activation parameters as described below.

Scheme 3. Epimerization of (*SR*)-5 in the Presence of Excess P(*p*-tol)$_3$

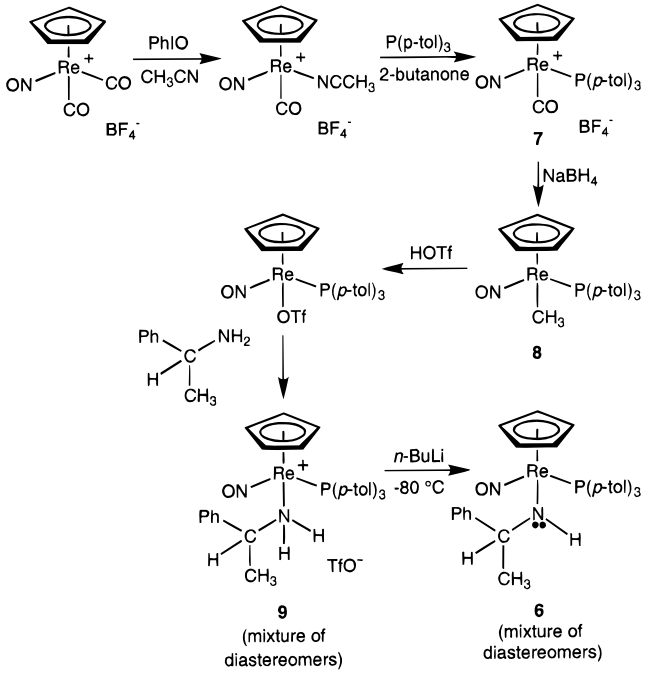


Phosphine Substitution. Phosphine dissociation plays a key role in the racemization or epimerization of other chiral-at-metal complexes.[1] We sought to probe this possibility—particularly as an initial, rate-determining step—with **5**. As shown in Scheme 3, (*SR*)-**5** and excess P(*p*-tol)$_3$ were combined in THF-d_8 at 49.4 °C. Importantly, no epimerization to (*RR*)-**5** was detected by NMR. Rather, the substitution product (η^5-C_5H_5)Re(NO)(P(*p*-tol)$_3$)(ṄHCH(CH$_3$)Ph) (**6**) cleanly formed. At low conversion (<1$t_{1/2}$), **6** was a (50 ± 2):(50 ± 2) mixture of diastereomers. With time, **6** equilibrated to a (34 ± 2):(66 ± 2) mixture. By analogy to **5**, the less stable and more stable diastereomers were presumed to be (*SR*)-**6** and (*RR*)-**6**, derived from inversion at rhenium and retention at carbon.

To confirm the preceding structural assignment, P(*p*-tol)$_3$-substituted complexes were independently pre-

(24) (a) Capellos, C.; Bielski, B. H. J. *Kinetic Systems*; Wiley: New York, 1972; Chapter 4 or 8. (b) The linearity of $\ln([C]_{eq} - [C]_t)$ or $\ln([(RR)\text{-}\mathbf{5}]_{eq} - [(RR)\text{-}\mathbf{5}]_t)$ vs time plots used in data reduction is sensitive to the value of $[C]_{eq}$ or K_{eq} and provides a check on the latter. Thus, the normalized equilibrium ratios[19] were adjusted by up to ±2 (the experimental error) to optimize linearity. (c) Error limits on rate constants represent the standard deviations on the slopes of ln([C]) or $\ln([C]_{eq} - [C]_t)$ vs time plots. (d) Standard deviations for $\Delta H^‡$ and $\Delta S^‡$ values were estimated according to: Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1964; pp 378−379.

Scheme 4. Syntheses of Authentic Samples of P(*p*-tol)$_3$ Complexes

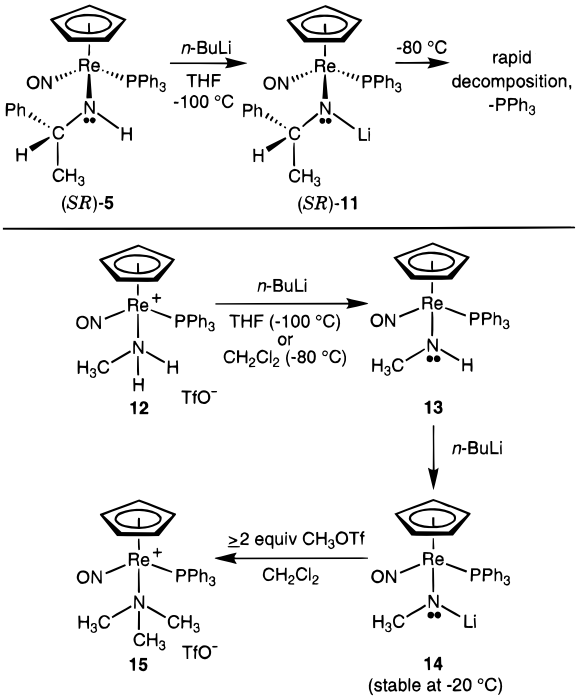


pared. First, the racemic carbonyl and methyl complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(P(p\text{-tol})_3)(CO)]^+BF_4^-$ (**7**) and $(\eta^5\text{-}C_5H_5)Re(NO)(P(p\text{-tol})_3)(CH_3)$ (**8**) were synthesized analogously to the PPh_3-substituted homologs,[13] as summarized pictorially in Scheme 4 and detailed in the Experimental Section. Then **8** and HOTf were combined to generate the triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(P(p\text{-tol})_3)(OTf)$. This solution was treated with α-methylbenzylamine, giving the amine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(P(p\text{-tol})_3)(NH_2CH(CH_3)Ph)]^+TfO^-$ (**9**) as a mixture of diastereomers. Complexes **7**−**9** were characterized by microanalysis and IR and NMR spectroscopy, as summarized in the Experimental Section. Finally, **9** and *n*-BuLi were reacted to give an authentic sample of **6**, which was worked up analogously to **5** and characterized by ^1H and ^{31}P NMR. The ^{31}P NMR signals of the P(*p*-tol)$_3$ complexes were consistently ca. 3 ppm upfield from the PPh_3 analogs.

The reaction of (*SR*)-**5** and P(*p*-tol)$_3$ was repeated on a preparative scale in THF at 60 °C. As shown in Scheme 3, the resulting **6** was treated with HOTf and then $Et_4N^+CN^-$. Workup gave the new cyanide complex (*R*)-$(\eta^5\text{-}C_5H_5)Re(NO)(P(p\text{-tol})_3)(CN)$ ((*R*)-**10**) in 34% yield[22] following crystallization. Complex (*R*)-**10** was characterized by microanalysis and IR and NMR spectroscopy. A ^1H NMR spectrum in the presence of (+)-Eu(hfc)$_3$ gave baseline separation of the cyclopentadienyl and methyl resonances. In accord with the configurational assignment made above, the upfield/downfield pattern was the same as that of the sample of **3** derived from (*SR*)-**5** in Scheme 2. Integration indicated an enantiomeric purity of 32 ± 2% ee, corresponding to a (34 ± 2):(66 ± 2) *S*/*R* enantiomer ratio and identical with the equilibrium diastereomer ratio of the precursor **6**.

Finally, the rate of reaction of (*SR*)-**5** and excess P(*p*-tol)$_3$ in THF-d_8 at 49.4 °C was measured under conditions analogous to the other experiments in Table 1.[24a,c] As shown in entry 7, **6** formed with a rate constant approximately twice that for the conversion of (*SR*)-**5** to (*RR*)-**5** (entry 3). The significance of this relationship will be analyzed below.

Scheme 5. Generation and Trapping of Lithioamido Complexes



Generation of Lithioamido Complexes. We thought that lithiated amido complexes of the type $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}LiR)$ would be exceptionally strong non-nucleophilic bases and might see use as chiral analogs of dialkylamides such as $LiN(CH(CH_3)_2)_2$ (LDA). Many valuable enantioselective transformations that utilize strong chiral bases have recently been developed.[25] However, the electropositive Re$\ddot{N}Li$ substituent should render the nitrogen an even stronger π donor. This would, in view of the epimerization mechanism proposed below, further labilize the rhenium stereocenter. Thus, we sought to generate such species and probe their chemical and/or configurational stabilities.

Accordingly, (*SR*)-**5** was generated in THF in a NMR tube as described above and treated with slightly greater than 1.0 equiv of *n*-BuLi at −100 °C (Scheme 5). The solution turned a slightly deeper red, and a ^{31}P NMR spectrum was recorded (−100 °C). The (*SR*)-**5** was consumed (28.6 ppm at −100 °C), and one major new species had formed (**11**; 30.4 ppm, 80%). This was provisionally assigned as the lithioamido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}LiCH(CH_3)Ph)$. Free PPh_3 (−8.0 ppm, 10%) and a series of weak resonances at 28.5−31.5 ppm were also present. The probe was warmed to −80 °C and then −50 °C. The sample turned black, and the relative concentration of PPh_3 increased.

Similar results were obtained starting with the isopropylamine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_2CH(CH_3)_2)]^+TfO^-$.[7a] In an initial experiment, the addition of 1.0 equiv of *n*-BuLi cleanly formed the new amido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}HCH(CH_3)_2)$ (29.3 ppm, −100 °C). In a second experiment, the addition of 2.0 equiv of *n*-BuLi gave another new species (32.6 ppm, 96%) that was presumed to be the lithioamido complex

(25) Lead references to a now-extensive literature: (a) Cox, P. J.; Simpkins, N. S. *Tetrahedron Asymm.* **1991**, *2*, 1. (b) Hoppe, I.; Marsch, M.; Harms, K.; Boche, G.; Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2158. (c) Cowton, E. L. M.; Gibson, S. E.; Schneider, M. J.; Smith, M. H. *J. Chem. Soc., Chem. Commun.* **1996**, 839. (d) Park, Y. S.; Boys, M. L.; Beak, P. *J. Am. Chem. Soc.* **1996**, *118*, 3757.

(η^5-C_5H_5)Re(NO)(PPh_3)(N̈LiCH(CH_3)$_2$). Some PPh_3 was again present (4%), and the relative concentration gradually increased as the probe was warmed from −100 °C.

Next, as shown in Scheme 5, the methylamine complex [(η^5-C_5H_5)Re(NO)(PPh_3)(NH_2CH_3)]$^+$TfO$^-$ (**12**)[7a] was similarly reacted. When **12** and 1.5 equiv of *n*-BuLi were combined at −100 °C, a ^{31}P NMR spectrum showed a mixture of the previously characterized amido complex (η^5-C_5H_5)Re(NO)(PPh_3)(N̈HCH$_3$) (**13**; 29.1 ppm)[8b] and a new species (**14**; 31.1 ppm). Then another 0.5 equiv of *n*-BuLi was added. A ^{31}P NMR spectrum showed the quantitative formation of **14**, which was assigned as the lithioamido complex (η^5-C_5H_5)Re(NO)(PPh_3)(N̈LiCH$_3$). The probe was slowly warmed. No appreciable decomposition was observed at temperatures up to −20 °C. At 0 °C, PPh_3 began to form (−5.0 ppm; 5% in first spectrum).

An analogous sequence in CH_2Cl_2 at −80 °C also gave **13** (27.7 ppm) and then **14** (28.1 ppm; 78%). However, small amounts of PPh_3 (8%) and two other byproducts (19.7, 18.3 ppm; 6%, 8%) formed concurrently. Their relative concentrations increased somewhat as the sample was warmed to −50 and −20 °C. These observations are consistent with the greater reactivity of CH_2Cl_2 toward strongly basic and/or nucleophilic species. To further support the assignments, trapping experiments were attempted. Thus, a CH_2Cl_2 solution of **14** was similarly generated and treated with CH_3-OTf (2.2 equiv; reactive toward THF). Workup gave the known trimethylamine complex [(η^5-C_5H_5)Re(NO)(PPh_3)-(N(CH_3)$_3$)]$^+$TfO$^-$ (**15**)[7a] in 69% yield. It was also thought that the P(*p*-tol)$_3$ analog of **14** might be more stable. Thus, a THF solution of **14** was warmed in the presence of 20 equiv of P(*p*-tol)$_3$. However, no NMR evidence for substitution was observed, suggesting that PPh_3 loss initiates an irreversible decomposition cascade.

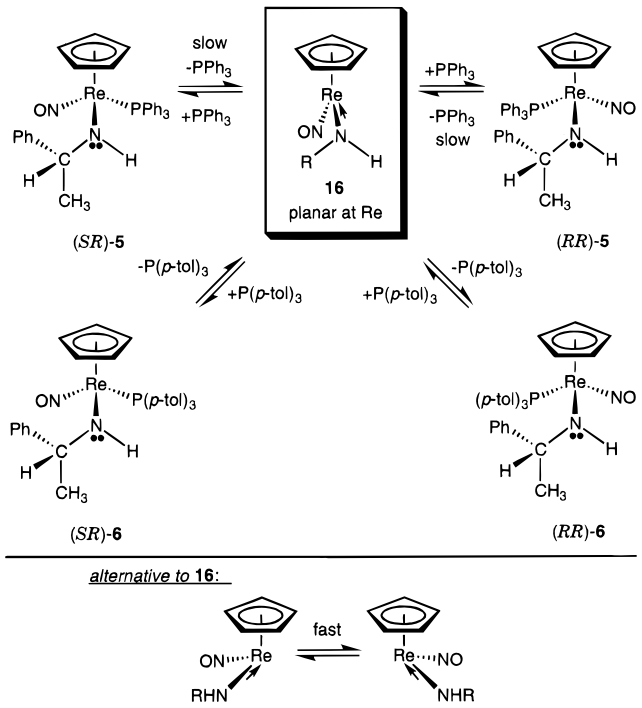
Discussion

Mechanism of Reaction of 5. We propose, on the basis of data presented above, that the epimerization and substitution processes in Schemes 2 and 3 involve a common initial step—rate-determining PPh_3 dissociation to give an unsaturated intermediate of empirical formula (η^5-C_5H_5)Re(NO)(NHCH(CH_3)Ph) (**16**)—as illustrated in Scheme 6. The corroborating evidence is as follows.

First, consider the finding that the rate of PPh_3 ligand substitution is *twice* as fast as the rate of epimerization (entries 7 vs 3, Table 1). Since the former reaction is conducted with a large excess of P(*p*-tol)$_3$, nearly every PPh_3 dissociation should lead to substitution. In the absence of P(*p*-tol)$_3$, the unsaturated intermediate **16**, which is chiral by virtue of the carbon stereocenter, recombines with PPh_3 to give **5**. If this occurs without significant diastereoselectivity, giving *S* and *R* rhenium configurations equally, then epimerization will occur at *half* the rate of PPh_3 substitution.

Several supporting observations deserve emphasis. First, the closely related alkoxide complexes (η^5-C_5R_5)-Re(NO)(PPh_3)(OR′) also undergo substitution by P(*p*-tol)$_3$.[17] Extensive rate experiments have rigorously established a dissociative mechanism. Second, as shown in Scheme 7, the dimethylamido complex (η^5-C_5H_5)Re-(NO)(PPh_3)(N̈(CH_3)$_2$) decomposes slowly at room temperature or over the course of a few minutes in refluxing

Scheme 6. Proposed Epimerization and Substitution Mechanisms



THF-d_8 to PPh_3 and the dimeric compound **17**.[8b] The most probable mechanism would involve an initial PPh_3 dissociation. Third, the reaction of (*SR*)-**5** and P(*p*-tol)$_3$ initially gives a 50:50 mixture of diastereomeric substitution products (*SR*)-**6** and (*RR*)-**6** (Scheme 3). This verifies that there is no detectable diastereoselectivity in the reaction of **16** and simple triarylphosphines.

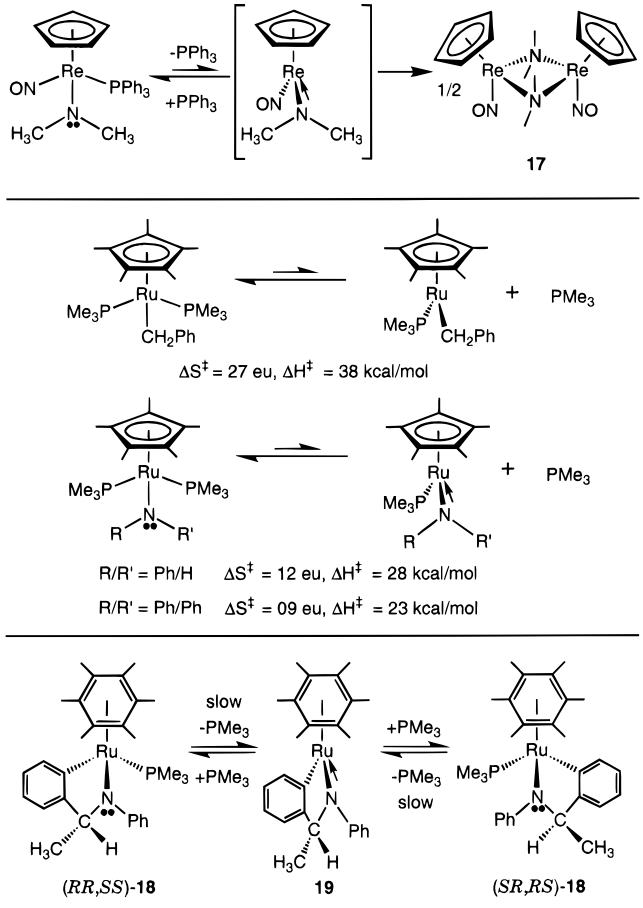
Accordingly, the rates of epimerization in entries 1−4 of Table 1 were multiplied by 2 to give rates associated with a fundamental molecular step—PPh_3 dissociation. The adjusted rate constants were used in Eyring plots. These gave $\Delta H^{\ddagger} = 26 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = 6 \pm 3$ eu for PPh_3 dissociation from the less stable diastereomer (*SR*)-**5** and $\Delta H^{\ddagger} = 28 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = 11 \pm 3$ eu for PPh_3 dissociation from the more stable diastereomer (*RR*)-**5**.[24d] Curiously, these $\Delta S^{\ddagger}$ values are lower than usual for ligand dissociations.

In this context, Brynzda and Bercaw have conducted an extensive study of PMe_3 dissociation from related d^6 ruthenium complexes of the type (η^5-C_5Me_5)Ru(PMe_3)$_2$-(X).[26] Selected data are illustrated in Scheme 7. Amido and hydroxy complexes gave much faster rates than alkyl complexes, and $\Delta S^{\ddagger}$ values decreased upon going from benzyl (27 eu) to hydroxy (19 eu) to N̈HPh (12 eu) or N̈Ph$_2$ (9 eu). Hence, anchimeric assistance in the form of π donation by the amido or hydroxy ligand lone pairs[27] was proposed. This would provide a bond-*making* contribution to the transition state, reducing $\Delta S^{\ddagger}$ values. Similarly, alkyl complexes of the rhenium Lewis acid **I** do not undergo any significant degree of phosphine exchange at temperatures up to 100 °C. Anchimeric assistance also avoids 16-valence-electron

(26) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379.

(27) See the following lead papers and references cited therein: (a) Bickford, C. C.; Johnson, T. J.; Davidson, E. R.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1080. (b) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476. (c) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488.

Scheme 7. Other Relevant Phosphine Dissociation Reactions



intermediates, which are of exceptionally high energy for rhenium.[14c,15,28]

Consequently, the unsaturated intermediate **16** in Scheme 6 and ruthenium analogs in Scheme 7 are represented with three-electron bonds to the amido ligands. A closely allied issue concerns the geometry at rhenium. Brunner has reported that the chiral d^6 manganese complex (η^5-C_5H_5)Mn(NO)(PPh_3)(COPh), which lacks ligand-based stereocenters, undergoes dissociative phosphine substitution with retention of configuration.[1,29] This requires a pyramidal metal geometry or otherwise chiral intermediate. There is also theoretical evidence that d^6, 16-valence-electron (η^5-C_5H_5)M(L)(L′) fragments should have pyramidal ground states.[30]

However, as illustrated by Scheme 3 and our companion studies with alkoxide complexes of **I**,[17] we have repeatedly been unable to effect phosphine substitution with any degree of retention of configuration—even when large excesses of new phosphines are employed. Brunner has also reported many complexes of formulas (η^5-C_5H_5)M(ZO)(PA_2B)(X) (M/ZO = Mn/NO, Fe/CO) that undergo phosphine exchange only with loss of metal configuration.[1,31] Furthermore, Tilley and Caulton have crystallized unsaturated ruthenium complexes of the types (η^5-C_5Me_5)Ru(PR_3)(X) (R/X = $CH(CH_3)_2$/Cl, C_6H_{11}/OCH_2CF_3, C_6H_{11}/$OSiPh_3$), which are closely related to **16**.[27c,32] They find nearly planar ruthenium geometries and short ruthenium−X distances suggestive of multiple bonding. Hence, we favor a trigonal planar geometry for **16**. Alternatively, **16** could still be slightly pyramidalized but have an extremely small inversion barrier, as shown by the tête-bêche at the bottom of Scheme 6.

Finally, it is worth noting that the crystal structure of phenylamido complex (η^5-C_5H_5)Re(NO)(PPh_3)(N̈HC_6H_5) exhibits a significantly above average deviation from idealized octahedral geometry, as compared to over 100 adducts of **I** that have been structurally characterized to date.[8b] In particular, the compressed P−Re−N̈H bond angle of 86.2(2)° and bloated ON−Re−N̈H bond angle of 103.5(3)° (P−Re−NO 93.3(2)°) may reflect some incipient π donation from the amido lone pair in the ground state. However, the amido nitrogen remains slightly pyramidalized (sum of bond angles = 345.5°). Even more marked distortions occur in alkoxide complexes of **I**.[4c]

Related Processes. Numerous phenomena related to those described above have been observed by other researchers. Of these, the most relevant is Boncella's finding that the d^6 ruthenium amido complex (η^6-C_6Me_6)(RuN̈(Ph)$CH(CH_3)C_6H_4$)(PMe_3) (**18**)[33] shown in Scheme 7 epimerizes from the *RR*,*SS* to the *SR*,*RS* diastereomer in C_6D_6 at room temperature ($K_{eq} \geq 50$). As with (*SR*)-**5**, added phosphine did not affect the epimerization rate, and phosphine substitution occurred at a somewhat faster rate. The k_{obs} values gave $\Delta H^{\ddagger} = 25 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = 2.6 \pm 0.5$ eu. These data strongly suggest that epimerization involves the unsaturated intermediate **19** (Scheme 7) and a mechanism essentially identical to that of **5** (Scheme 6). Also, phosphine substitution mechanisms have been studied for many amido complexes besides the ruthenium systems in Scheme 7.[34]

We have probed the site of epimerization in *en*amido complexes of **I**.[10c] As shown in Scheme 8, the enantiomerically pure isoquinoline complex (+)-(*R*)-**20** was treated with $TMSCH_2Li$ to give the addition product **21** as a 94:6 mixture of diastereomers. Further elaboration and detachment of the enamido ligand showed that these had identical rhenium and opposite carbon configurations (*RR* and *RS*), as would be expected.[10a,c] Upon warming, (*RR*)-**21** epimerized at a rate similar to that of (*SR*)-**5** but to a much more biased equilibrium mixture (5:95). Since the sample is not diastereomerically pure, analysis of the product isomers is slightly more involved than in Schemes 2 and 3, and details regarding the calculated values in Scheme 8 are given elsewhere.[10c] Regardless, a four-step sequence gave the cyanide complex (+)-(*S*)-**3** in 86% ee, corresponding to a 7:93 *R*/*S* enantiomer ratio (calculated: 10:90 or (4.7

(28) Casey, C. P.; Vosejpka, P. C.; Underiner, T. L.; Slough, G. A.; Gavney, J. A., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 6680.

(29) (a) Brunner, H.; Aclasis, J.; Langer, M.; Steger, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 810. (b) Brunner, H.; Langer, M. *J. Organomet. Chem.* **1975**, *87*, 223. (c) Brunner, H.; Steger, W. *J. Organomet. Chem.* **1976**, *120*, 239. (d) Brunner, H.; Aclasis, J. A. *J. Organomet. Chem.* **1976**, *104*, 347.

(30) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

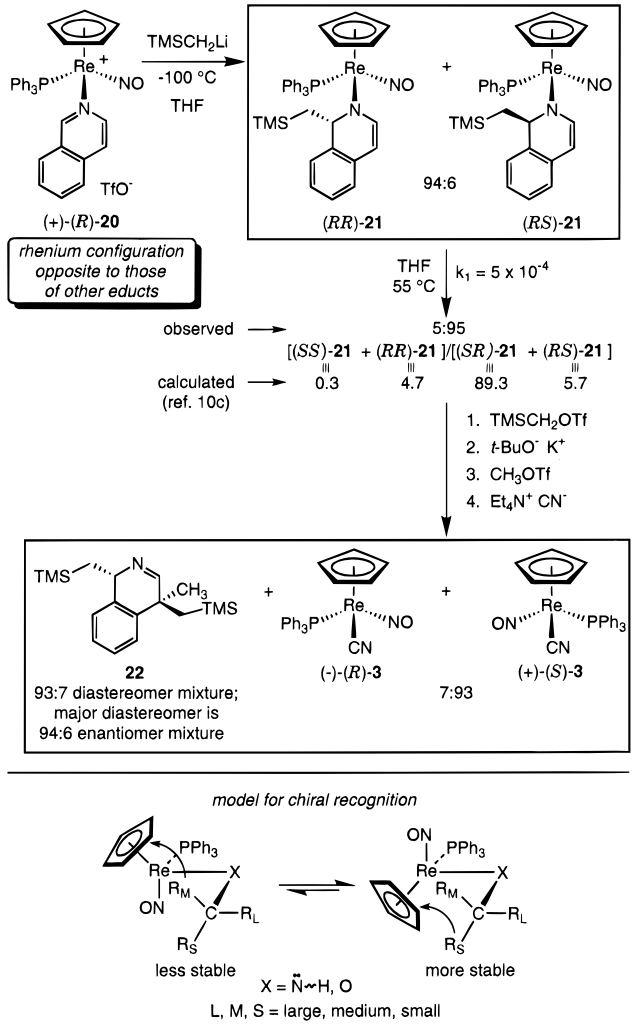
(31) (a) Brunner, H.; Schindler, H.-D. *Chem. Ber.* **1971**, *104*, 2467. (b) Brunner, H.; Schindler, H.-D. *Z. Naturforsch.* **1971**, *26b*, 1220. (c) Brunner, H.; Rackl, F. *J. Organomet. Chem.* **1976**, *118*, C19. (d) Brunner, H.; Fisch, K.; Jones, P. G.; Salbeck J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1521.

(32) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278.

(33) Martin, G. C.; Boncella, J. M. *Organometallics* **1991**, *10*, 2804.

(34) The most germane involves the chiral (but racemic) d^6 iridium complex (η^5-C_5Me_5)Ir(PPh_3)(CH_3)(N̈HPh). The PPh_3 ligand is readily displaced by PPh_2CH_3 at 10 °C, and initial cyclopentadienyl ligand slippage has been proposed: Glueck, D. S.; Bergman, R. G. *Organometallics* **1991**, *10*, 1479.

Scheme 8. Additional Equilibrium Data and Analyses



+ 5.7):(0.3 + 89.3)) and inversion at rhenium. The configuration of the organic product **22** was not assayed, but the high isomeric purity (86% de and 88% ee following distillation at 190 °C) is consistent only with retention at carbon.

The alkoxide complexes (η^5-C_5R_5)Re(NO)(PPh_3)(OCHRR′) epimerize by a mechanism analogous to that of **5**.[17] Although exact comparisons are difficult, rates are generally slightly faster. However, we have occasionally encountered amido complexes, such as (η^5-C_5H_5)Re(NO)(PPh_3)(N̈(CH_3)CH(CH_2TMS)Ph),[12b] that epimerize distinctly below room temperature. Also, alkoxide complexes epimerize at carbon at slightly higher temperatures. The key step in this process is a β-hydride elimination of the alkoxide ligand in the unsaturated intermediate (η^5-C_5R_5)Re(NO)(OCHRR′). There is ample precedent for a β-hydride elimination of the amido ligand in **16**.[35] However, no significant degree of carbon epimerization has been detected in an amido complex of **I** to date. Conditions more forcing than refluxing THF remain to be explored.

Curiously, the alkoxide analog of **5**, (η^5-C_5H_5)Re(NO)(PPh_3)(OCH(CH_3)Ph), gives a slightly higher equilibrium mixture of diastereomers ((82−83):(18−17), C_6D_6, 65 °C). However, the sense of "chiral recognition" is the same, and a model that rationalizes the thermodynamic bias in both cases is sketched at the bottom of Scheme 8 and discussed in detail elsewhere.[10a,17] In brief, if *anti* conformations are maintained along the Ph_3P−Re−X−C−R_L backbones, which contain the bulkiest rhenium and carbon substituents (R_L = Ph), then one diastereomer will experience a unique and destabilizing steric interaction between the cyclopentadienyl ligand and the second largest carbon substituent (R_M = CH_3).

Phosphido and thioalkoxide ligands are weaker π donors than amido or alkoxide ligands.[26,27] Accordingly, phosphido and thioalkoxide complexes of **I** exhibit excellent configurational stabilities.[4b,5,36] However, the triflate complex (η^5-C_5H_5)Re(NO)(PPh_3)(OTf) (**1**) and chloride complex (η^5-C_5H_5)Re(NO)(PPh_3)(Cl) racemize at room temperature with the solvent rate trend CH_2Cl_2 ≫ benzene.[16] The chloride complex may involve a mechanism analogous to that in Scheme 6. However, the triflate ligand is a very poor π donor, so a new mechanism is likely operative with **1**. Since fluoride ligands are strong π donors,[27] it is probable that (η^5-C_5H_5)Re(NO)(PPh_3)(F)[37] is also configurationally labile.

The lithioamido complexes (η^5-C_5H_5)Re(NO)(PPh_3)(N̈LiR) (Scheme 5) lose PPh_3 at much lower temperatures than any of the preceding compounds. Since no PPh_3/P(*p*-tol)$_3$ exchange is detected with the *N*-methyl complex **14**, thermal decomposition is probably faster than racemization or epimerization. Thus, no attempts were made to assay configurational stabilities. Regardless, **14** is significantly more stable than α-branched *N*-alkyl analogs such as **11**. This may reflect a simple steric effect, as bulkier alkoxide complexes of **I** appear to epimerize at slightly faster rates. In our opinion, other chiral lithioamido complexes in which the metal is not a stereocenter remain attractive candidates for exploratory enantioselective syntheses.[25]

Finally, this paper marks the conclusion of our efforts to characterize the structural, configurational, dynamic, and related physical properties of adducts of **I** and organonitrogen donor ligands.[7−9] Studies directed at enantioselective organic syntheses[10−11] remain in progress and will be reported in due course.[12b]

Experimental Section

General Data. Instrumental protocols and solvent and reagent purifications were identical to those in earlier papers,[9a,c] and additional details for much of the following may be found elsewhere.[12] Solvents not specified previously were used as received. Reagents new to this study were obtained from Aldrich or Alfa and treated as follows: (±)-α-methylbenzylamine, (+)-(*R*)-α-methylbenzylamine (97.1% ee), (−)-(*S*)-α-methylbenzylamine (95.8% ee), distilled from CaH_2 and checked for enantiomeric purity;[23] (−)-menthyl chloroformate (99% ee), distilled; P(*p*-tol)$_3$ and $NaBH_4$, used as received. GC was conducted on a Hewlett-Packard 5890 chromatograph with a 25 m × 0.2 mm SE-54 capillary column. Solvents were removed by rotary evaporation unless noted.

[(η^5-C_5H_5)Re(NO)(PPh_3)($NH_2CH(CH_3)Ph$)]$^+$TfO$^-$ (2). A. A Schlenk flask was charged with racemic (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (0.209 g, 0.374 mmol)[13] and toluene (10 mL) and cooled to −45 °C (acetonitrile/CO_2). Then HOTf (0.0331 mL,

(35) (a) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781. (b) For leading references and comparisons of β-hydride eliminations in coordinatively unsaturated iridium amido, alkoxide, and alkyl complexes, see: Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7010.

(36) Zwick, B. D.; Dewey, M. A.; Knight, D. A.; Buhro, W. E.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 2673 and references therein.

(37) Agbossou, S. K.; Roger, C.; Igau, A.; Gladysz, J. A. *Inorg. Chem.* **1992**, *31*, 419.

0.374 mmol) was added with stirring to generate (η^5-C_5H_5)-Re(NO)(PPh_3)(OTf) (**1**).[16] After 5 min, (±)-α-methylbenzylamine (0.241 mL, 1.87 mmol) was added with stirring. The cold bath was removed, and some product precipitated as the mixture warmed. After 2 h, hexane (50 mL) was added with stirring to complete precipitation. The yellow powder was collected by filtration, washed with hexane, and dried by oil pump vacuum to give **2** (0.246 g, 0.303 mmol, 81%), mp 201−203 °C. Anal. Calcd for $C_{31}H_{32}F_3N_2O_4PReS$: C, 47.23; H, 3.84. Found: C, 47.32; H, 3.84.

B. Complex (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (0.198 g, 0.355 mmol),[13,20] toluene (2 mL), HOTf (0.0313 mL, 0.355 mmol), and (−)-(*S*)-α-methylbenzylamine (0.229 mL, 1.78 mmol) were combined in a procedure analogous to method A. A similar workup (ether (50 mL) and hexane (50 mL) were used to complete precipitation) gave (+)-(*SS*)-**2** as a yellow powder (0.243 g, 0.298 mmol, 84%), mp 200−201 °C, $[\alpha]_{589}^{25}$ 374 ± 5° (*c* 0.512 mg/mL).[21,38] Anal. Found: C, 47.06; H, 3.88. IR (cm^{-1}, KBr): ν_{NO} 1678 vs.

C. Complex (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (0.204 g, 0.366 mmol), toluene (2 mL), HOTf (0.0323 mL, 0.366 mmol), and (+)-(*R*)-α-methylbenzylamine (0.235 mL, 1.83 mmol) were combined and worked up in a procedure analogous to method B. This gave (+)-(*SR*)-**2** as a yellow powder (0.238 g, 0.293 mmol, 80%), mp 222−223 °C, $[\alpha]_{589}^{25}$ 397 ± 5° (*c* 0.584 mg/mL).[21,38] Anal. Found: C, 47.33; H, 3.87. IR (cm^{-1}, KBr): ν_{NO} 1692 vs.

NMR for (+)-(*SS*)-**2** ($CDCl_3$):[39] ^{1}H 7.65−7.50 (m, 9H of $4C_6H_5$), 7.45−7.30 (m, 6H of $4C_6H_5$), 7.27−7.15 (m, 5H of $4C_6H_5$), 5.70 (br dd, *J* = 11.7, 11.5, NH), 4.89 (s, C_5H_5), 4.43 (br d, *J* = 11.7, NH′), 3.73 (dq, *J* = 6.5, 11.5, CH), 1.28 (d, *J* = 6.5, CH_3); $^{13}C\{^1H\}$ 140.7 (s, *i*-CPh), 133.8 (d, *J* = 11.0, *o*-PPh), 131.8 (s, *p*-PPh), 131.6 (d, *J* = 55.0, *i*-PPh), 129.7 (d, *J* = 10.9, *m*-PPh), 129.1 (s, *o*-CPh), 129.0 (s, *p*-CPh), 128.4 (s, *m*-CPh), 120.8 (q, J_{CF} = 319.8, CF_3), 91.3 (s, C_5H_5), 65.5 (s, CH), 25.1 (s, CH_3); $^{31}P\{^1H\}$ 23.1 (s).

NMR for (+)-(*SR*)-**2** ($CDCl_3$):[39] ^{1}H 7.55−7.44 (m, 9H of $4C_6H_5$), 7.38−7.32 (m, 2H of $4C_6H_5$), 7.36−7.27 (m, 6H of $4C_6H_5$), 7.21−7.15 (m, 3H of $4C_6H_5$), 6.02 (br dd, *J* = 12.0, 6.0, NH), 5.38 (s, C_5H_5), 4.02 (br d, *J* = 12.0, NH′), 3.95 (dq, *J* = 6.6, 6.0, CH), 1.45 (d, *J* = 6.6, CH_3); $^{13}C\{^1H\}$ 141.5 (s, *i*-CPh), 133.6 (d, *J* = 11.0, *o*-PPh), 131.6 (s, *p*-PPh), 131.4 (d, *J* = 54.9, *i*-PPh), 129.5 (d, *J* = 10.8, *m*-PPh), 128.9 (s, *o*-CPh), 128.5 (s, *m*-CPh), 127.3 (s, *p*-CPh), 120.5 (q, J_{CF} = 319.8, CF_3), 91.3 (s, C_5H_5), 66.1 (d, *J* = 2.4, CH), 22.0 (s, CH_3); $^{31}P\{^1H\}$ 21.5 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(N̈HCH(CH_3)Ph) (5). The following is representative. A Schlenk flask was charged with (+)-(*SR*)-**2** (0.049 g, 0.061 mmol) and THF (2 mL) and cooled to −80 °C (acetone/CO_2). Then *n*-BuLi (0.035 mL, 0.061 mmol, 1.73 M in cyclohexane) was added with stirring. After 15 min, the cold bath was removed and an oil pump vacuum applied. The resulting residue was vacuum dried (1 h), cooled to −80 °C, and extracted with THF-d_8 (0.6 mL). The mixture was allowed to warm only enough to dissolve the product. The extract was transferred by cannula to a 5 mm NMR tube, and spectra were recorded at −20 °C. Except for traces of a LiOTf CF_3 resonance, only (*SR*)-**5** was present.

NMR for (*SS*)-**5** (THF-d_8, −20 °C):[39] ^{1}H 8.09−7.64 (m, 15H of $4C_6H_5$), 7.63−7.23 (m, 5H of $4C_6H_5$), 5.06 (s, C_5H_5), 4.10 (dq, *J* = 6.7, 8.0, CH), 1.14 (d, *J* = 8.0, NH), 1.12 (d, *J* = 6.7, CH_3); $^{13}C\{^1H\}$ 153.1 (s, *i*-CPh), 135.5 (d, *J* = 51.3, *i*-PPh), 135.1 (d, *J* = 10.7, *o*-PPh), 131.2 (s, *p*-PPh), 129.1 (d, *J* = 10.2, *m*-PPh), 128.4 (s, *m*-CPh), 126.7 (s, *o*-CPh), 126.0 (s, *p*-CPh), 92.6 (s, C_5H_5), 74.0 (d, *J* = 4.5, CH), 29.0 (s, CH_3); $^{31}P\{^1H\}$ 28.1 (s). IR (cm^{-1}, KBr): ν_{NO} 1629 vs.

NMR for (*SR*)-**5**, (THF-d_8, −20 °C):[39] ^{1}H 7.45−7.27 (m, 15H of $4C_6H_5$), 7.17−7.11 (m, 4H of $4C_6H_5$), 7.07−6.99 (m, 1H of $4C_6H_5$), 5.16 (s, C_5H_5), 3.97 (dq, *J* = 6.5, 9.8, CH), 1.09 (d, *J* = 6.5, CH_3), 1.04 (br d, *J* = 9.8, NH); $^{13}C\{^1H\}$ 152.5 (s, *i*-CPh), 135.6 (d, *J* = 50.6, *i*-PPh), 135.0 (d, *J* = 10.7, *o*-PPh), 130.9 (s, *p*-PPh), 129.1 (d, *J* = 10.2, *m*-PPh), 128.4 (s, *m*-CPh), 127.5 (s, *o*-CPh), 125.8 (s, *p*-CPh), 92.8 (s, C_5H_5), 72.9 (d, *J* = 4.6, CH), 28.1 (s, CH_3); $^{31}P\{^1H\}$ 27.4 (s). IR (cm^{-1}, KBr): ν_{NO} 1624 vs.

Epimerization of (*SS*)-5. Complex (+)-(*SS*)-**2** (0.900 g, 1.11 mmol), THF (25 mL), and *n*-BuLi (0.640 mL, 1.11 mmol, 1.73 M in cyclohexane) were combined in a procedure analogous to that given for (*SR*)-**5** above. The THF extract of (*SS*)-**5** was kept in a 60 °C oil bath for 2.5 h and cooled to −80 °C. Then HOTf (0.0979 mL, 1.11 mmol) was added with stirring to give **2** as a mixture of diastereomers. Solid $Et_4N^+CN^-$ (0.207 g, 1.33 mmol) was added. After 0.5 h, the solvent was removed by oil pump vacuum and the residue extracted with CH_2Cl_2 (30 mL). The extract was washed with H_2O (3 × 25 mL) and 0.1 M NaOH (3 × 10 mL). The combined aqueous layers were saturated with NaCl and washed with ether until the ether was clear (5 × 20 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and concentrated to a residue that was extracted with a THF/CH_2Cl_2 mixture (10/2 mL). The extract was chromatographed on a 2 cm silica gel column (13 g of Merck 230−400 mesh, THF).

A yellow band was taken to dryness, and the residue extracted with CH_2Cl_2 (10 mL). The extract was stored over charcoal (4 h) and filtered through Celite. The filtrate was concentrated to ca. 7 mL, and hexane (50 mL) was slowly added with stirring. The resulting yellow precipitate was collected by filtration, washed with hexane, and dried by oil pump vacuum to give (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CN) ((+)-(*S*)-**3**; 0.378 g, 0.666 mmol, 60%),[7] $[\alpha]_{589}^{25}$ 68 ± 1° (*c* 1.06 mg/mL).[21] Spectroscopic properties were identical to those of an authentic sample. Enantiomeric purity: [α], 38 ± 2% ee; (+)-Eu(hfc)$_3$, 39 ± 2% ee.

The column was further eluted, and TLC showed fractions containing α-methylbenzylamine. These were taken to dryness, and the yellow oil was distilled (20 Torr, 90 °C; Kugelrohr, CO_2(s) condenser). GC showed the colorless oil to be pure α-methylbenzylamine (0.047 g, 0.39 mmol, 35%). A portion (0.020 g, 0.16 mmol) was transferred to a flask, and CH_2Cl_2 (2.5 mL), pyridine (0.040 mL, 0.48 mmol), and (−)-menthyl chloroformate (0.039 mL, 0.18 mmol) were sequentially added with stirring. After 45 min, GC showed the resulting urethane **4** (Scheme 3) to be a (98.4 ± 0.1):(1.6 ± 0.1) diastereomer mixture, with the major component identical to an authentic sample prepared from (−)-(*S*)-α-methylbenzylamine.[23]

Epimerization of (*SR*)-5. Complex (+)-(*SR*)-**2** (0.972 g, 1.20 mmol), THF (25 mL), *n*-BuLi (0.691 g, 1.20 mmol, 1.73 M in cyclohexane), HOTf (0.106 mL, 1.20 mmol), and $Et_4N^+CN^-$ (0.224 g, 1.44 mmol) were combined in a procedure analogous to that for the epimerization of (*SS*)-**5**. A similar workup gave (−)-(*R*)-**3** (0.443 g, 0.780 mmol, 65%; $[\alpha]_{589}^{25}$ −67 ± 1° (*c* 0.936 mg/mL)) (enantiomeric purity: [α], 37 ± 2% ee; (+)-Eu(hfc)$_3$, 39 ± 2%) and α-methylbenzylamine (0.077 g, 0.64 mmol, 53%). The latter was converted to the urethane **4**, which by GC was a (98.5 ± 0.1):(1.5 ± 0.1) diastereomer mixture, with the major component identical to an authentic sample prepared from (+)-(*R*)-α-methylbenzylamine.[23]

Sequential Reaction of (*SR*)-5 with P(*p*-tol)$_3$, HOTf, and $Et_4N^+CN^-$. Complex (+)-(*SR*)-**2** (0.192 g, 0.236 mmol), THF (6 mL), and *n*-BuLi (0.137 mL, 0.236 mmol, 1.73 M in cyclohexane) were combined in a procedure analogous to that given for (*SR*)-**5**. The cold bath was removed, and P(*p*-tol)$_3$ (2.64 g, 8.69 mmol) was added when the sample reached room temperature. The solution was kept in a 60 °C oil bath for 2.5 h and cooled to −20 °C. Data on the product (η^5-C_5H_5)Re(NO)(P(*p*-tol)$_3$)(N̈H_2CH(CH_3)Ph) (**6**) are given in the text and an independent synthesis below. Next, HOTf (0.0209

(38) The reactions of these compounds with $Et_4N^+CN^-$ (text and Scheme 1) were conducted analogously to those described in the epimerization experiments.

(39) NMR spectra were recorded at ambient probe temperature unless noted, and referenced as follows: ^{1}H (δ), $Si(CH_3)_4$ (0.00), THF-d_7 (1.73), CHD_2CN (1.93), or $CHDCl_2$ (5.32); ^{13}C (ppm), $CDCl_3$ (77.0), THF-d_8 (67.4), CD_3CN (1.3), or CD_2Cl_2 (53.8); ^{31}P (ppm), external 85% H_3PO_4 (0.00). All coupling constants represent J_{HH} (^{1}H) or J_{CP} (^{13}C) values unless noted and are in Hz. For samples that are mixtures of diastereomers, paired resonances are separated by slashes (/).

mL, 0.236 mmol) was added with stirring. After 12 h at −20 °C, most of the excess P(*p*-tol)$_3$ had crystallized as colorless cubes containing a small amount of PPh_3. The supernatant was decanted, and data on the product [(η^5-C_5H_5)Re(NO)(P(*p*-tol)$_3$)($NH_2CH(CH_3)C_6H_5$)]$^+TfO^-$ (**9**) are given in an independent synthesis below. Then $Et_4N^+CN^-$ (0.0442 g, 0.283 mmol) was added with stirring. After 0.5 h, the solvent was removed and the residue extracted with CH_2Cl_2 (10 mL). The extract was chromatographed on a 2 cm silica gel column (15 g of Merck 230−400 mesh, 50:50 v/v acetone/hexane). The remaining P(*p*-tol)$_3$ eluted first, and solvent was removed from a yellow band that followed. The residue was extracted with CH_2Cl_2 (10 mL), and a layer of hexane (60 mL) was added. After 3 days, the resulting yellow microcrystals were collected by filtration and dried under a N_2 flow to give (η^5-C_5H_5)Re(NO)(P(*p*-tol)$_3$)(CN)·0.5CH_2Cl_2 (**10**·0.5CH_2Cl_2) (0.025 g, 0.080 mmol, 34%),[22] mp 228−230 °C. Anal. Calcd for $C_{27}H_{26}N_2OPRe\cdot0.5CH_2Cl_2$: C, 50.49; H, 4.16; Cl, 5.42. Found: C, 50.48; H, 4.20; Cl, 5.50. IR (cm^{-1}, KBr): ν_{NO} 1655 vs, ν_{CN} 2097 vs. Enantiomeric purity: (+)-Eu(hfc)$_3$, 32 ± 2% ee.

NMR ($CDCl_3$):[39] ^{1}H 7.42−7.33 (m, 6H of $3C_6H_4$), 7.24−7.18 (m, 6H of $3C_6H_4$), 5.23 (s, C_5H_5), 2.37 (s, $3CH_3$); ^{13}C{^{1}H} 140.9 (s, *p*-PAr), 133.4 (d, J = 11.1, *o*-PAr), 131.6 (d, J = 57.9, *i*-PAr), 129.3 (d, J = 11.1, *m*-PAr), 120.5 (d, J = 11.9, CN), 90.3 (s, C_5H_5), 21.4 (s, CH_3); ^{31}P{^{1}H} 14.2 (s).

[(η^5-C_5H_5)Re(NO)(P(*p*-tol)$_3$)(CO)]$^+BF_4^-$ (7). A Schlenk flask was charged with [(η^5-C_5H_5)Re(NO)(CO)$_2$]$^+BF_4^-$ (5.00 g, 11.8 mmol)[13] and CH_3CN (50 mL) and cooled to 0 °C. Freshly prepared iodosobenzene (2.6 g, 12 mmol)[40] was added, and the suspension was stirred for 3.5 h as it warmed to room temperature. The solvent was removed, and the oily brown residue was extracted with acetone. The extract was filtered through a short silica gel plug, and solvent was removed to give crude [(η^5-C_5H_5)Re(NO)(CO)($NCCH_3$)]$^+BF_4^-$ as a brown oil.[13] The oil was extracted with 2-butanone (50 mL), and P(*p*-tol)$_3$ (7.18 g, 23.6 mmol) was added. The solution was refluxed for 24 h and concentrated to ca. 15 mL. Ether (150 mL) was slowly added with stirring, giving an oil and some powder. This mixture was triturated in ether until a yellow powder formed. The powder was collected by filtration, washed with hexane, and dried by oil pump vacuum to give **7** (3.92 g, 5.60 mmol, 47%), mp 226−228 °C dec. Anal. Calcd for $C_{27}H_{26}F_4NO_2PRe$: C, 46.30; H, 3.74. Found: C, 46.27; H, 3.77. IR (cm^{-1}, KBr): ν_{NO} 1752 vs, ν_{CO} 2017 vs.

NMR (CD_3CN):[39] ^{1}H 7.49−7.36 (m, 6H of $3C_6H_4$), 7.32−7.18 (m, 6H of $3C_6H_4$), 5.85 (s, C_5H_5), 2.43 (s, $3CH_3$); ^{13}C NMR 196.7 (d, J = 7.8, CO), 144.2 (s, *p*-PAr), 134.0 (d, J = 12.0, *o*-PAr), 131.1 (d, J = 12.0, *m*-PAr), 128.7 (d, J = 62.4, *i*-PAr), 95.9 (s, C_5H_5), 21.4 (s, $3CH_3$); ^{31}P{^{1}H} 7.7 (s).

(η^5-C_5H_5)Re(NO)(P(*p*-tol)$_3$)(CH_3) (8). A Schlenk flask was charged with **7** (1.368 g, 1.954 mmol) and THF (20 mL), and $NaBH_4$ (0.237 g, 6.26 mmol) was added with stirring. After 2 h, the mixture was filtered through Celite. The solvent was removed from the filtrate and the residue extracted with benzene. This extract was filtered through a short silica gel plug. The filtrate was concentrated to ca. 7 mL, and hexane (200 mL) was slowly added with stirring. The bright orange powder was collected by filtration, washed with hexane, and dried by oil pump vacuum to give **8** (0.951 g, 1.58 mmol, 76%), mp 205−206 °C dec. Anal. Calcd for $C_{27}H_{29}NOPRe$: C, 53.99; H, 4.87. Found: C, 54.18; H, 4.95. IR (cm^{-1}, KBr): ν_{NO} 1612 vs.

NMR (CD_2Cl_2):[39] ^{1}H 7.28−7.17 (m, $3C_6H_4$), 4.92 (s, C_5H_5), 2.36 (s, $3CCH_3$), 0.94 (d, J_{HP} = 6.2, $ReCH_3$); ^{13}C{^{1}H} 140.4 (s, *p*-PAr), 133.8 (d, J = 10.7, *o*-PAr), 133.6 (d, J = 52.8, *i*-PAr), 129.2 (d, J = 10.7, *m*-PAr), 89.9 (s, C_5H_5), 21.4 (s, $3CCH_3$), −37.4 (d, J = 7.3, $ReCH_3$); ^{31}P{^{1}H} 21.7 (s).

[(η^5-C_5H_5)Re(NO)(P(*p*-tol)$_3$)($NH_2CH(CH_3)Ph$)]$^+TfO^-$ (9). Complex **8** (0.154 g, 0.256 mmol), toluene (7 mL), HOTf (0.0227 mL, 0.256 mmol), and (±)-α-methylbenzylamine (0.165 mL, 1.28 mmol) were combined in a procedure analogous to method A of **2**. An identical workup gave **9** as a yellow powder (0.159 g, 0.186 mmol, 73%), mp 186−192 °C. Anal. Calcd for $C_{35}H_{37}F_3N_2O_4PReS$: C, 49.11; H, 4.36. Found: C, 48.95; H, 4.43. IR (cm^{-1}, KBr): ν_{NO} 1686 vs.

NMR:[39] ^{1}H ($CDCl_3$) 7.58−7.11 (m, C_6H_5 + $3C_6H_4$), 5.90/5.63 (dd/t, J = (11.5, 6.0)/11.4, NH), 5.36/4.87 (s/s, C_5H_5), 4.42/4.12 (d/d, J = 12.0/12.0, NH′), 3.92/3.72 (sept/dq, J = 6.3/(6.6, 11.7), C*H*CH_3), 2.42/2.36 (s/s, $3C_6H_4CH_3$), 1.45/1.27 (d/d, J = 6.6/6.6, CHCH_3); ^{31}P{^{1}H} ($CDCl_3$) 19.7/18.3 (s/s), (THF) 20.9/19.9 (s/s).

(η^5-C_5H_5)Re(NO)(P(*p*-tol)$_3$)(N̈HCH(CH_3)Ph) (6). Complex **9** (0.052 g, 0.074 mmol), THF (2 mL), and *n*-BuLi (0.043 mL, 0.074 mmol, 1.73 M in cyclohexane) were combined in a procedure analogous to that given for the generation of **5**. A similar workup gave spectroscopically pure **6**.

NMR:[39] ^{1}H (THF-d_8, −20 °C) 8.02−7.55 (m, C_6H_5 + $3C_6H_4$), 5.00/5.16 (s/s, C_5H_5), 4.11/3.89 (dq/dq, J = 6.5/6.6, 7.9/10.3, C*H*CH_3), 2.48/2.35 (s/s, $3C_6H_4CH_3$), 1.25/1.03 (d/d, J = 6.6/6.6, CHCH_3), 1.16/1.05 (d/d, J = 7.9/10.3, NH); ^{31}P{^{1}H} (THF) 25.0/24.4 (s/s).

(η^5-C_5H_5)Re(NO)(PPh_3)(N̈LiCH_3) (14). Method A. A 5 mm NMR tube was charged with [(η^5-C_5H_5)Re(NO)(PPh_3)(NH_2CH_3)]$^+TfO^-$ (**12**,[7a] 0.021 g, 0.029 mmol) and capped with a septum. Then THF (0.8 mL) was added. The tube was cooled to −100 °C (CH_3OH/N_2), and *n*-BuLi (0.012 mL, 0.029 mmol, 2.4 M in hexanes) was added dropwise. The tube was transferred to a −100 °C NMR probe and ^{31}P spectra were recorded. Additional *n*-BuLi (0.012 mL, 0.029 mmol) was added (−100 °C), and the probe was slowly warmed. Data: see text.

Method B. A Schlenk flask was charged with **12** (0.137 g, 0.189 mmol) and CH_2Cl_2 (20 mL) and cooled to −80 °C. Then *n*-BuLi (0.156 mL, 0.379 mmol, 2.4 M in hexanes) was added dropwise with stirring. After 0.25 h, CH_3OTf (0.110 mL, 0.416 mmol) was added and the cold bath removed. After 3 h, charcoal was added. The mixture was stirred (2 h), filtered through Celite, and concentrated to ca. 2 mL. Hexanes was added. The yellow-orange precipitate was collected by filtration, washed with pentane, and dried by oil pump vacuum to give [(η^5-C_5H_5)Re(NO)(PPh_3)($N(CH_3)_3$)]$^+TfO^-$ (**15**; 0.098 g, 0.13 mmol, 69%). The ^{1}H and ^{31}P NMR spectra ($CDCl_3$) were identical to those of an authentic sample.[7a]

Rate Experiments. General protocols have been detailed previously.[14c,17] The following runs are representative.

Method A. A THF-d_8 solution of (*SR*)-**5** in a 5 mm NMR tube was prepared from (+)-(*SR*)-**2** (0.050 ± 0.001 g, 0.061 mmol), THF (2 mL), and *n*-BuLi (0.035 mL, 0.061 mmol, 1.73 M in cyclohexane) as described above. The tube was transferred to a probe that had been preequilibrated to a temperature in Table 1. The magnet homogeneity was quickly adjusted, and after a 7−10 min period for thermal equilibration data acquisition was begun (e.g., 15 spectra every 450 s at 49.4 °C). The relative concentrations of (*SR*)-**5** and (*RR*)-**5** were assayed by integration of the cyclopentadienyl ^{1}H NMR signals. Standard analyses[24] gave the rate constants in Table 1.

Method B. Complex (+)-(*SR*)-**2** (0.049 g, 0.061 mmol), THF (2 mL), and *n*-BuLi (0.035 mL, 0.061 mmol, 1.73 M in cyclohexane) were combined in a procedure analogous to that given for (*SR*)-**5**. After the residue was dried by oil pump vacuum, P(*p*-tol)$_3$ (0.350 g, 1.15 mmol) was added. The mixture was cooled to −80 °C and extracted with THF-d_8 (1.2 mL) as in the procedure for (*SR*)-**5**. Data were acquired at 49.4 °C as in method A, with the disappearance of (*SR*)-**5** and appearance of (*SR*)-**6** and (*RR*)-**6** monitored by integration of the cyclopentadienyl ^{1}H NMR signals (δ 5.21, 5.17, 5.08; no (*RR*)-**5** at δ 5.11). Rate constants were obtained from ln([(*SR*)-**5**]$_t$/[(*SR*)-**5**]$_0$) vs time plots.[24a,c]

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