Synthesis, Structure, and Reactivity of *N*-Indolyl Complexes of the Chiral Rhenium Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$: Diastereoselective Electrophilic Additions

Todd J. Johnson, Atta M. Arif, and J. A. Gladysz*

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

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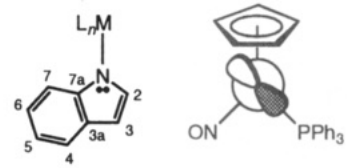
Reactions of the triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**3**) and indolide salts K(NCH=C(R)C=CCH=CHCH=CH) give the *N*-indolyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-(NCH=C(R)C=CCH=CHCH=CH) (**2**, R = H/CH_3/C_2H_5 (**a/b/c**); 71–59% after crystallization). Reactions of **2a,b** and HOTf give the indolenine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-(N=CHCH(R)C=CCH=CHCH=CH)]$^+$ TfO^- (**4**$^+TfO^-$; **a**, 93%; **b**, 77%, (86–92):(14–8) *SR,RS*/*SS,RR* Re,C diastereomers). Reaction of **2b** and CH_3OTf gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-(N=CHC$(CH_3)_2$C=CCH=CHCH=CH)]$^+TfO^-$ (**5**$^+TfO^-$, 96%). Reactions of **2b** and C_2H_5OTf, and **2c** and CH_3OTf, give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$(N=CHC$(CH_3)(C_2H_5)$C=CCH=CHCH=CH)]$^+$ TfO^- (**6**$^+TfO^-$, 92–96%; 65:35, 17:83 *SS,RR/SR,RS*, respectively). Reaction of **2b** and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IC_2H_5)]^+BF_4^-$ gives **6**$^+BF_4^-$ (93%, 91:9 *SS,RR/SR,RS*) and $(\eta^5\text{-}C_5H_5)$Re-(NO)(PPh_3)(I) (84%). Reactions of **5**$^+TfO^-$ and CH_3MgCl or $LiB(C_2H_5)_3H$ (THF, −80 °C) give addition products $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$(NCH(R)C$(CH_3)_2$C=CCH=CHCH=CH) (R = CH_3 (95:5 *SS,RR/SR,RS*), H). The latter and HOTf yield indoline complex $[(\eta^5\text{-}C_5H_5)Re(NO)$-$(PPh_3)$(HNC$H_2C(CH_3)_2$C=CCH=CHCH=CH)]$^+TfO^-$ (**9**$^+TfO^-$, 85%), which when treated with C≡NCH_2Ts (60 °C, $CHCl_3$) gives 3,3-dimethylindoline (81%) and $[(\eta^5\text{-}C_5H_5)Re(NO)$-$(PPh_3)$(C≡N$CH_2$Ts)]$^+TfO^-$ (**14**$^+TfO^-$, 77%). Reaction of **3** and C≡NCH_2Ts also gives **14**$^+TfO^-$ (94%), which is reduced by BH_3·THF (THF, reflux) to $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (60%). The crystal structure of **2c**, reactions of nonracemic compounds, and rationales for the preceding configurational assignments are also reported.

Indole alkaloids constitute a large and structurally diverse class of natural products[1] and have posed historically important strategic challenges in organic total synthesis.[2] Many transition metal mediated syntheses have been reported.[3-5] However, to our knowledge, none of these involve simple σ-bound, nitrogen-ligated indolyl complexes of the type L_nM-(NCH=CHC=CCH=CHCH=CH) (**1**; Chart 1). Although several such compounds have been isolated,[6] the reactivity of *N*-indolyl ligands appears to be unexplored.

Chart 1. Numbering System of Indolyl Complex (1) and the d-Orbital HOMO of the Chiral Rhenium Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I)



1 **I**

Electrophiles readily add to uncoordinated indoles at the 3 position, β to nitrogen.[7] We anticipated that

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1994.

(1) *Indoles*; Saxton, J. E., Ed.; Wiley: New York, 1983; Part 4.

(2) Martin, S. F.; Benage, B.; Geraci, L. S.; Hunter, J. E.; Mortimore, M. *J. Am. Chem. Soc.* **1991**, *113*, 6161 and references therein.

(3) Review: Hegedus, L. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1113.

(4) (a) Gill, U. S.; Moriarty, R. M.; Ku, Y. Y.; Butler, I. R. *J. Organomet. Chem.* **1991**, *417*, 313. (b) Blackman, A. *Adv. Heterocycl. Chem.* **1993**, *58*, 123.

(5) Other recent references: (a) Tidwell, J. H.; Senn, D. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 4685. (b) Semmelhack, M. F.; Knochel, P.; Singleton, T. *Tetrahedron Lett.* **1993**, *34*, 5051 and references therein. (c) Hsu, G. C.; Kosar, W. P.; Jones, W. D. *Organometallics* **1994**, *13*, 385. (d) Lomenzo, S. A.; Nolan, S. P.; Trudell, M. L. *Organometallics* **1994**, *13*, 676.

(6) (a) Pauson, P. L.; Qazi, A. R. *J. Organomet. Chem.* **1967**, *7*, 321. (b) Zakrzewski, J. *J. Organomet. Chem.* **1987**, *327*, C41. (c) Corbeil, M.-C.; Beauchamp, A. L. *Can. J. Chem.* **1988**, *66*, 2458. (d) Ladipo, F. T.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 4172.

(7) Gilchrist, T. L. *Heterocyclic Chemistry*, 2nd ed.; Wiley: New York, 1992; Chapter 6.5.

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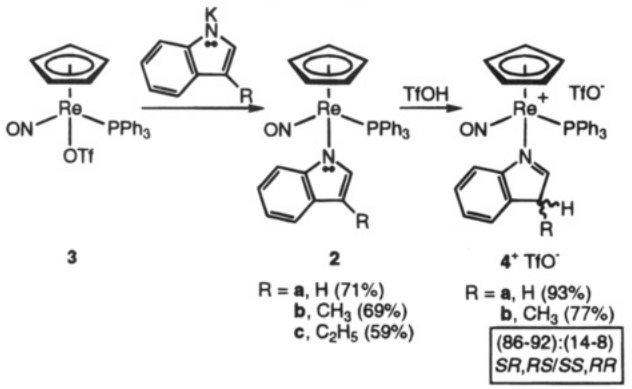
Scheme 1. Synthesis and Protonation of Rhenium Indolyl Complexes



transition metal indolyl complexes **1** would be even more reactive, due to the electropositive substituent on nitrogen. Thus, it seemed probable that *chiral* metal fragments could be employed to effect diastereoselective additions and, in favorable circumstances, enantioselective syntheses of free indolines or related species. In this context, we have had an ongoing interest in adducts of nitrogen donor ligands and the chiral rhenium Lewis acid [(η^5-C_5H_5)Re(NO)(PPh$_3$)]$^+$ (**I**). In particular, we have shown that neutral enamido (N̈(R)CH=CHR′) complexes of **I** can undergo highly diastereoselective electrophilic attack at C_β to give cationic imine complexes, which can in turn be elaborated to free amines of high enantiomeric purities.[8] We have also prepared *N*-pyrrolyl complexes of **I**[9] and adducts of other aromatic nitrogen donor ligands.[10]

In this paper, we report (1) syntheses of indolyl complexes of the formula (η^5-C_5H_5)Re(NO)(PPh$_3$)(NCH=C(R)C=CCH=CHCH=CH) (**2**), (2) a representative crystal structure, (3) protonations and alkylations that give cationic indolenine complexes with new C_β stereocenters in good to moderate diastereomeric excesses, (4) nucleophilic additions to the indolenine complexes, one of which generates an indolinyl complex with a new C_α stereocenter in high diastereomeric excess, (5) subsequent detachment of the nitrogen donor ligand, and recycling of the rhenium fragment, (6) selected reactions with nonracemic compounds, and (7) analyses of the stereochemistry of the preceding transformations.

Results

1. Synthesis and Structures of Indolyl Complexes. We sought to access indolyl complexes of **I** by routes analogous to that reported earlier for the corresponding pyrrolyl complex.[9] Thus, indole, 3-methylindole (skatole), and 3-ethylindole were treated with potassium to give the indolide salts K(NCH=C(R)C=CCH=CHCH=CH).[6a] Subsequent reactions with the triflate complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(OTf) (**3**)[11,12] gave deep red, air stable indolyl complexes (η^5-C_5H_5)Re(NO)(PPh$_3$)(NCH=C(R)C=CCH=CHCH=CH) (**2**; R = H (**a**); CH_3 (**b**); C_2H_5 (**c**)) in 71–59% yields after crystallization (Scheme 1). Similar reactions utilizing the chlorobenzene complex of **I**[13] were unsuccessful.

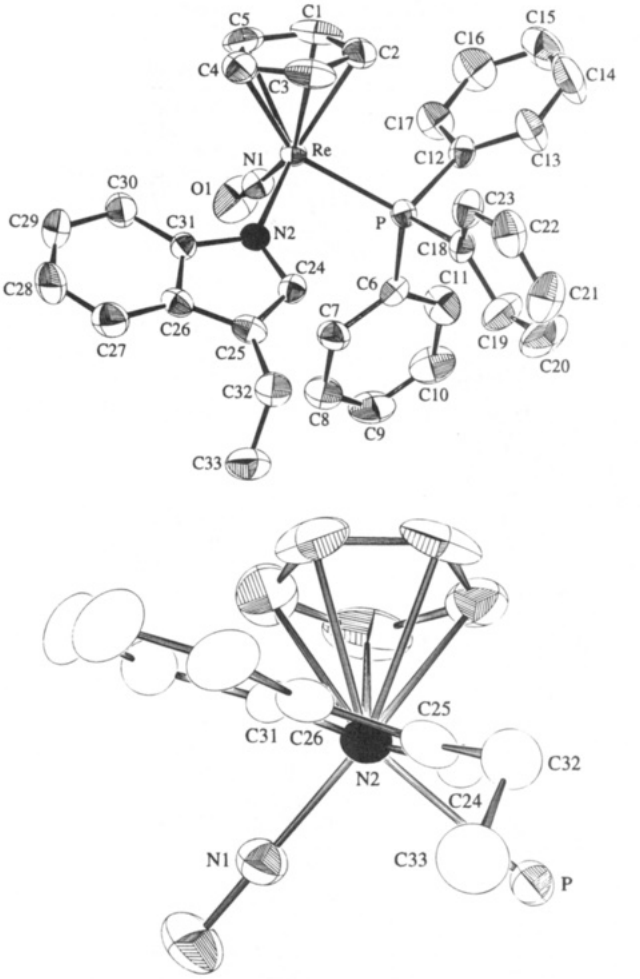


Figure 1. Structure of the 3-ethylindolyl complex **2c**: (top) numbering diagram; (bottom) Newman-type projection down the N2–Re bond with phenyl rings omitted.

Complexes **2a–c**, and all new compounds isolated below, were characterized by microanalysis (Experimental Section) and NMR (^{1}H, ^{13}C, ^{31}P) and IR spectroscopy (Table 1). Many NMR and IR features were similar to those of the pyrrolyl complex.[9] The ^{13}C NMR spectra showed N*C*H=*C*R resonances at 143–151 and 101–111 ppm, respectively. The ^{1}H NMR spectra showed cyclopentadienyl resonances at δ 5.21, NCH resonances at δ 6.50–6.19, and benzenoid =CH resonances at δ 6.98–7.68. Interestingly, related d^6 iridium(III) indolyl and 3-methylindolyl complexes give NCH ^{1}H resonances that are distinctly *downfield* (δ 7.81–8.04, acetone-d_6) of the benzenoid =CH resonances.[6d]

A crystal structure of a representative complex was sought. Thus, X-ray data were collected on the 3-ethylindolyl complex **2c** as outlined in Table 2. Refinement, described in the Experimental Section, yielded the structures in Figure 1. Atomic coordinates and selected bond lengths, bond angles, and torsion angles

(8) Richter-Addo, G. B.; Knight, A. D.; Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 11863.
(9) (a) Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4728. (b) Johnson, T. J.; Alvey, L. J.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. Manuscript in preparation.
(10) Dewey, M. A.; Knight, D. A.; Arif, A. M.; Gladysz, J. A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1992**, *47*, 1175.
(11) Abbreviations: (a) OTf = OSO_2CF_3; (b) Ts = SO_2-4-$C_6H_4CH_3$.
(12) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.
(13) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

Table 1. Spectroscopic Characterization of New Rhenium Indolyl, Indolenine, and Indoline Complexes

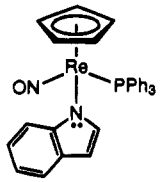
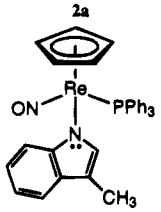
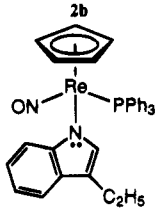
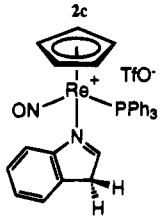
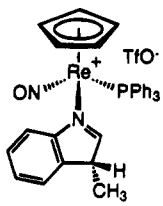
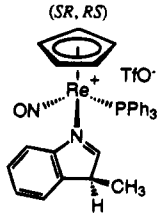
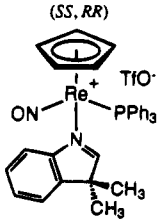
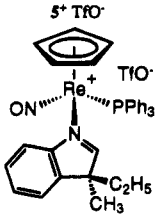
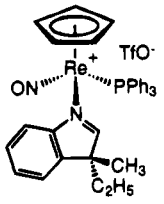
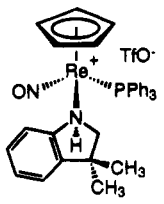
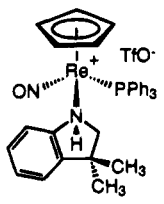
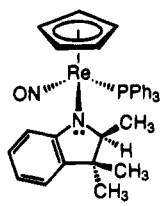
complex[a]	^{1}H NMR (δ)[b]	^{13}C{^{1}H} NMR (ppm)[c]	^{31}P{^{1}H} NMR (ppm)[d]/ IR ν_{NO} (cm^{-1}, KBr)
 **2a**	7.68 (d, J = 9.0, 1H of C_6H_4), 7.52 (d, J = 7.5, 1H of C_6H_4), 7.44−7.31 (m, 3Ph), 7.15 (dd, J = 8.0, 8.0, 1H of C_6H_4), 6.98 (dd, J = 8.0, 8.0, 1H of C_6H_4), 6.50 (d, J = 2.7, NC*H*), 6.12 (d, J = 2.7, NCHC*H*), 5.21 (s, C_5H_5)	PPh at 134.8 (d, J = 52.6, *i*), 133.8 (d, J = 10.7, *o*), 130.5 (d, J = 1.4, *p*), 128.6 (d, J = 10.4, *m*); NC_8H_6 at 150.5 (s, C7a), 145.5 (d, J = 3.5, C2), 130.8 (s, C3a), 119.1, 118.9, 117.9, 117.2 (4s, C4−C7), 101.9 (s, C3), 91.4 (s, C_5H_5)	16.8 (s)/1646 (vs)
 **2b**	7.60 (d, J = 8.4, 1H of C_6H_4), 7.45−7.36 (m, 3Ph, C_6H_4), 7.14 (dd, J = 8.1, 8.1, 1H of C_6H_4), 6.99 (dd, J = 8.1, 8.1, 1H of C_6H_4), 6.19 (br s, NC*H*), 5.21 (s, C_5H_5), 2.10 (s, CH_3)	PPh at 134.9 (d, J = 51.8, *i*), 133.8 (d, J = 10.0, *o*), 130.4 (s, *p*), 128.5 (d, J = 9.8, *m*); NC_8H_5 at 150.8 (s, C7a), 143.5 (s, C2), 131.0 (s, C3a), 118.6, 117.7, 117.0, 116.3 (4s, C4−C7), 110.7 (s, C3); 91.4 (s, C_5H_5), 9.7 (s, CH_3)	16.5 (s)/1646 (vs)
 **2c**	7.65−7.01 (m, 3Ph, C_6H_4), 6.27 (br s, NC*H*), 5.21 (s, C_5H_5), 2.57 (dq, J = 7.0, 7.0, C*HH'*), 0.96 (t, J = 7.0, CH_3)	PPh at 134.9 (d, J = 50.5, *i*), 133.8 (d, J = 9.9, *o*), 130.4 (s, *p*), 128.6 (d, J = 9.8, *m*); NC_8H_5 at 150.9 (s, C7a), 142.6 (s, C2), 130.0 (s, C3a), 118.7, 117.8, 117.2, 116.3 (4s, C4−C7), 111.2 (s, C3); 91.4 (s, C_5H_5), 18.3 (s, CH_2), 14.8 (s, CH_3)	17.0 (s)/1655 (vs)
 **4a$^+$ TfO$^-$**	8.33 (br s, N=CH), 7.92 (d, J = 8.1, 1H of C_6H_4), 7.54−7.16 (m, 3Ph, C_6H_4), 5.60 (s, C_5H_5), 4.35 (d, J = 26.1, C*HH'*), 3.27 (d, J = 26.1, CH*H'*)	PPh at 133.5 (d, J = 10.6, *m*), 131.4 (d, J = 2.3, *p*), 130.3 (d, J = 55.3, *i*), 129.3 (d, J = 10.7, *o*); NC_8H_7 at 186.5 (d, J = 3.3, N=C), 156.7 (s, C7a), 132.9 (s, C3a), 128.4, 128.0, 124.2, 121.0 (4s, C4−C7), 44.6 (s, C3); 92.1 (s, C_5H_5)	19.5 (s)/1690 (vs)
 **4b$^+$ TfO$^-$ (*SR, RS*)**	8.35 (br s, N=CH), 7.91 (d, J = 8.0, 1H of C_6H_4), 7.55−7.18 (m, 3Ph, C_6H_4), 5.58 (s, C_5H_5), 4.38 (q, J = 7.8, C*H*CH$_3$), 0.76 (d, J = 7.8, CHC*H*$_3$)	PPh at 133.5 (d, J = 10.7, *o*), 131.5 (d, J = 2.4, *p*), 130.9 (d, J = 55.2, *i*), 129.3 (d, J = 10.6, *m*); NC_8H_6 at 191.2 (d, J = 2.6, N=C), 156.1 (s, C7a), 138.7 (s, C3a), 128.4, 128.1, 123.2, 120.9 (4s, C4−C7), 50.4 (s, C3); 92.2 (s, C_5H_5), 11.6 (s, CH_3)	19.0 (s)/1686 (vs)
 **4b$^+$ TfO$^-$ (*SS, RR*)**	8.40 (br s, N=CH), 7.93 (d, J = 8.0, 1H of C_6H_4), 7.55−7.18 (m, 3Ph, C_6H_4), 5.64 (s, C_5H_5), 3.16 (q, J = 7.8, C*H*CH$_3$), 1.39 (d, J = 7.8, CHC*H*$_3$)	PPh at 133.5 (d, J = 10.7, *o*), 131.3 (d, J = 2.4, *p*), 129.9 (d, J = 55.2, *i*), 129.4 (d, J = 10.6, *m*); NC_8H_6 at 189.5 (d, J = 3.5, N=C), 155.5 (s, C7a), 138.4 (s, C3a), 128.5, 128.1, 122.9, 121.0 (4s, C4−C7), 50.6 (s, C3); 92.1 (s, C_5H_5), 13.6 (s, CH_3)	19.1 (s)/1686 (vs)
 **5$^+$ TfO$^-$**	8.42 (br s, N=CH), 7.94 (d, J = 7.8, 1H of C_6H_4), 7.55−7.15 (m, 3Ph, C_6H_4), 5.61 (s, C_5H_5), 1.40 (s, CH_3), 0.67 (s, CH_3')	PPh at 133.5 (d, J = 10.7, *o*), 131.5 (d, J = 2.4, *p*), 130.7 (d, J = 55.6, *i*), 129.3 (d, J = 10.7, *m*); NC_8H_5 at 193.2 (d, J = 2.9, N=C), 154.6 (s, C7a), 143.6 (s, C3a), 128.4, 128.3, 121.7, 121.2 (4s, C_6H_4), 53.3 (s, C3); 92.5 (s, C_5H_5), 22.6 (s, CH_3), 19.9 (s, CH_3')	17.9 (s)/1674 (vs)
 **6$^+$ TfO$^-$ (*SS, RR*)[e,g]**	8.44 (br s, N=CH), 7.97 (d, J = 7.8, 1H of C_6H_4), 7.58−7.10 (m, 3Ph, C_6H_4), 5.65 (s, C_5H_5), 2.24 (dq, J = 13.8, 7.5, C*HH'*), 1.85 (dq, J = 13.8, 7.5, CH*H'*), 0.63 (s, N=CHCC*H*$_3$), 0.37 (t, J = 7.5, CHH'C*H*$_3$)[e]	PPh at 133.5 (d, J = 10.8, *o*), 131.5 (s, *p*), 130.6 (d, J = 55.6, *i*), 129.3 (d, J = 10.7, *m*); NC_8H_5 at 193.0 (d, J = 1.9, N=C), 155.7 (s, C7a), 141.8 (s, C3a), 128.4, 128.2, 122.0, 121.0 (4s, C4−C7), 65.4 (s, C3); 92.7 (s, C_5H_5), 30.1 (s, *C*HH'), 19.1 (s, N=CHC*C*H$_3$), 9.1 (s, CHH'*C*H$_3$)	17.4 (s)[f]/1675 (vs)[g]

Table 1 (Continued)

complex[a]	^{1}H NMR (δ)[b]	^{13}C{^{1}H} NMR (ppm)[c]	^{31}P{^{1}H} NMR (ppm)[d]/ IR ν_{NO} (cm^{-1}, KBr)
 **6**$^+$ TfO$^-$ (*SR,RS*)[e,g]	8.47 (br s, N=CH), 7.93 (d, J = 7.8, 1H of C_6H_4), 7.58−7.10 (m, 3Ph, C_6H_4), 5.62 (s, C_5H_5), 1.38 (s, N=CHCC*H*$_3$), 1.21 (dq, J = 13.8, 7.5, C*H*H′), 1.07 (dq, J = 13.8, 7.5, CH*H*′), 0.37 (t, J = 7.5, CHH′C*H*$_3$)[e]	PPh at 133.5 (d, J = 10.8, *o*), 131.5 (s, *p*), 130.9 (d, J = 55.6, *i*), 129.4 (d, J = 10.7, *m*); NC_8H_5 at 192.5 (d, J = 1.8, N=C), 155.3 (s, C7a), 142.8 (s, C3a), 128.5, 128.4, 122.2, 121.3 (4s, C4−C7), 65.2 (s, C3); 92.7 (s, C_5H_5), 28.3 (s, CHH′), 20.1 (s, N=CHC*C*H$_3$), 9.4 (s, CHH′*C*H$_3$)	16.8 (s)[f]/1675 (vs)[g]
 **9**$^+$ TfO$^-$ (*SS,RR*)	7.48−7.28 (m, 3Ph, C_6H_4), 6.02 (br s, NH), 5.53 (s, C_5H_5), 3.09 (dd, J = 11, 11, C*H*H′), 2.94 (dd, J = 11, 5, CH*H*′), 1.39 (s, CH_3), 0.50 (s, CH_3′)	PPh at 133.6 (d, J = 53.4, *i*), 133.3 (d, J = 10.7, *o*), 131.1 (d, J = 2.2, *p*), 129.1 (d, J = 10.6, *m*); NC_8H_6 at 150.2 (s, C7a), 143.8 (s, C3a), 128.9, 127.9, 121.8, 121.7 (4s, C4−C7), 65.9 (s, C2), 43.7 (s, C3); 92.9 (s, C_5H_5), 26.7 (s, CH_3), 15.4 (s, CH_3′)	18.4 (s)/1678 (vs)
 **9**$^+$ TfO$^-$ (*SR,RS*)	7.48−7.28 (m, 3Ph, C_6H_4), 6.02 (br s, NH), 5.29 (s, C_5H_5), 3.22 (dd, J = 11, 11, C*H*H′), 2.96 (dd, J = 11, 5, CH*H*′), 1.56 (s, CH_3), 0.67 (s, CH_3′)	PPh at 133.1 (d, J = 54.1, *i*), 133.1 (d, J = 10.7, *o*), 131.8 (d, J = 2.4, *p*), 130.0 (d, J = 10.6, *m*); NC_8H_6 at 148.9 (s, C7a), 143.7 (s, C3a), 127.8, 127.5, 122.8, 122.3 (4s, C4−C7), 73.7 (s, C2), 44.5 (s, C3); 92.2 (s, C_5H_5), 28.6 (s, CH_3), 24.2 (s, CH_3′)	16.0 (s)/1678 (vs)
 **11** (*SS,RR*)	7.92−7.50 (m, 3Ph), 7.00−6.27 (m, 4H of C_6H_4), 5.38 (s, C_5H_5), 3.07 (s, C*H*CH$_3$), 1.12 (s, CHC*H*$_3$), 0.76 (s, CH_3), 0.15 (s, CH_3′)[h]	PPh at 134.8 (d, J = 49.8, *i*), 134.1 (d, J = 10.2, *o*), 130.1 (s, *p*), 129.7 (d, J = 10.0, *m*); NC_8H_5 at 162.4 (s, C7a), 138.1 (s, C3a), 126.7, 119.4, 111.0, 110.4 (4s, C4−C7), 77.4 (s, C2), 48.1 (s, C3); 91.5 (s, C_5H_5), 31.7 (s, CH*C*H$_3$), 21.3 (s, CH_3), 18.8 (s, CH_3′)[h]	15.7 (s)[h]

[a] Diastereomer assignments are provisional as described in the text, and all data are for racemates. [b] At 300 MHz in $CDCl_3$ at ambient probe temperature and referenced to internal $Si(CH_3)_4$ unless noted. All couplings (J) are to ^{1}H and are in hertz. [c] At 75 MHz in $CDCl_3$ at ambient probe temperature and referenced to internal $Si(CH_3)_4$. All couplings (J) are to ^{31}P and are in hertz. The PPh carbons are assigned as described in: Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. The indolyl derived carbons are numbered as shown in **1** (Chart 1) and assigned as described in: Morales-Ríos, M. S.; Espiñeira, J.; Joseph-Nathan, P. *Magn. Reson. Chem.* **1987**, *25*, 377. [d] At 121 MHz in $CDCl_3$ at ambient probe temperature and referenced to external 85% H_3PO_4. [e] Corresponding data for (*SS,RR*)-**6**$^+$ BF_4^-/SbF_6^-/I^-: 8.27/8.97/9.15 (br s), 7.94/7.96/8.99 (d, J = 7.8), 7.58−7.10/7.54−7.10/7.48−7.18 (m), 5.60/5.57/5.77 (s), 2.28/2.12/2.34 (dq, J = 13.8, 7.5), 1.85/1.86/1.95 (dq, J = 13.8, 7.5), 0.63/0.64/0.69 (s), 0.35/0.35/0.42 (t, J = 7.5). Corresponding data for (*SR,RS*)-**6**$^+$$BF_4^-$/$SbF_6^-$/$I^-$: 8.29/8.03/9.14 (br s), 7.93/7.96/8.99 (d, J = 7.8), 7.57−7.10/7.54−7.10/7.48−7.18 (m), 5.66/5.55/5.76 (s), 1.35/1.32/1.30 (s), 1.19/1.21/1.30 (dq, J = 13.8, 7.5), 1.10/1.06/1.18 (dq, J = 13.8, 7.5), 0.35/0.40/0.39 (t, J = 7.5). For **6**$^+$$SbF_6^-$·0.5 $O(C_2H_5)_2$ the $O(C_2H_5)_2$ solvate is also observed: 3.47 (q, J = 7.0, CH_2), 1.20 (t, J = 7.0, CH_3). [f] Corresponding data for (*SS,RR*)-**6**$^+$$BF_4^-$/$SbF_6^-$/$I^-$: 17.5/17.5/17.5 (s). Corresponding data for (*SR,RS*)-**6**$^+$$BF_4^-$/$SbF_6^-$/$I^-$: 16.9/16.8/16.7 (s). [g] Corresponding data for (*SR,RS*)- and (*SS,RR*)-**6**$^+$$BF_4^-$/$SbF_6^-$: 1681/1687 (vs). [h] CD_2Cl_2 (−80 °C).

are summarized in Tables 3 and 4. The indolyl nitrogen exhibits the expected planar geometry, as reflected by the sum the Re−N−C and C−N−C bond angles (360.0°). The indolyl bond lengths are within 0.03 Å of those of free indole, and most bond angles are also similar.[14] The rhenium−nitrogen conformation is analyzed below.

2. Protonation of Indolyl Complexes. We next sought to study reactions of **2** with electrophiles. In initial experiments, **2a,b** and triflic acid (HOTf) were combined in CH_2Cl_2 at room temperature. Workups gave the corresponding cationic indolenine complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(N=CHCH(R)C=CCH=CH-CH=CH)]$^+$TfO$^-$ (**4a,b**$^+$TfO$^-$) in 93−77% yields as air stable, yellow-gold powders (Scheme 1).

Complexes **4a,b**$^+$TfO$^-$ exhibited NMR and IR properties similar to those reported earlier for cyclic and acyclic imine complexes of **I** (Table 1).[15] These included characteristic downfield N=CH ^{1}H and ^{13}C resonances (δ 8.33−8.35; 187−191 ppm). As is commonly observed for related cationic and neutral complexes of **I**, the cyclopentadienyl ^{1}H resonances of **4a,b**$^+$TfO$^-$ were ca. 0.4 ppm downfield those of **2a−c**, and the IR ν_{NO} values were 20−45 cm^{-1} higher. Only a few other transition

(14) (a) Tai, J. C.; Yang, L.; Allinger, N. L. *J. Am. Chem. Soc.* **1993**, *115*, 11906. (b) The C−N−C and some N−C−C bond angles differ by up to 4.3°. Other bond angles are in closer agreement.

(15) (a) Knight, D. A.; Dewey, M. A.; Stark, G. A.; Bennett, B. K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4523. (b) Cantrell, W. R., Jr.; Richter-Addo, G. B.; Gladysz, J. A. *J. Organomet. Chem.* **1994**, *472*, 195.

Table 2. Summary of Crystallographic Data for 3-Ethylindolyl Complex (η^5-C_5H_5)Re(NO)(PPh_3)-(NCH=C(C_2H_5)C=CCH=CHCH=CH) (2c)

mol formula	$C_{33}H_{30}H_2OPRe$
mol wt	687.794
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
cell dimens (16 °C)	
a, Å	10.338(1)
b, Å	15.244(5)
c, Å	18.584(1)
β, deg	103.57(1)
V, Å^3	2846.81
Z	4
d_{calc}, g/cm^3 (16 °C)	1.60
d_{obs}, g/cm^3 (CCl_4/CH_2I_2, 22 °C)	1.62
cryst dimens, mm	0.36 × 0.31 × 0.25
diffractometer	Syntex P$\bar{1}$
radiation; λ, Å	λ(Mo Kα); 0.710 73
data collcn method	$\theta-2\theta$
scan speed, deg/min	variable
no. of reflns measd	5511
range/indices (h,k,l)	0−12; 0−18; −21 to +21
2θ limit, deg	4.0−50.0
std reflns check	1 X-ray h
total no. of unique data	4992
no. of obsd data, $I > 3\sigma(I)$	4260
abs coeff, cm^{-1}	44.08
min transm, %	67.27
max transm, %	99.88
no. of variables	344
goodness of fit	1.90
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.036
$R_w = \sum\|\|F_o\| - \|F_c\|\|w^{1/2}/\sum\|F_o\|w^{1/2}$	0.058
Δ/σ (max)	0.000
$\Delta\rho$ (max), e/Å^3	1.491 (ca. 1.060 Å from Re)

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Located Atoms of 2c[a]

atom	x	y	z	B (Å^2)
Re	0.22664(2)	0.11642(2)	0.48471(1)	1.791(5)
P	0.2873(2)	0.2668(1)	0.49057(9)	2.01(3)
O1	−0.0224(5)	0.1625(4)	0.5273(4)	5.2(1)
N1	0.0820(5)	0.1427(4)	0.5137(3)	2.5(1)
N2	0.3509(5)	0.0854(4)	0.5882(3)	2.2(1)
C1	0.1537(8)	0.0868(6)	0.3615(4)	4.4(2)
C2	0.2896(8)	0.1057(5)	0.3726(4)	3.5(2)
C3	0.3565(7)	0.0396(6)	0.4203(4)	4.0(2)
C4	0.2615(9)	−0.0162(5)	0.4389(4)	4.0(2)
C5	0.1372(8)	0.0117(6)	0.4017(4)	4.2(2)
C6	0.2210(6)	0.3301(4)	0.5563(4)	2.5(1)
C7	0.2100(7)	0.2910(5)	0.6224(4)	3.1(2)
C8	0.1529(8)	0.3359(6)	0.6714(4)	4.1(2)
C9	0.1045(8)	0.4190(6)	0.6564(4)	4.5(2)
C10	0.1139(8)	0.4590(5)	0.5915(5)	4.5(2)
C11	0.1705(8)	0.4130(5)	0.5411(4)	3.7(2)
C12	0.2127(6)	0.3183(4)	0.4020(4)	2.3(1)
C13	0.2887(8)	0.3598(6)	0.3580(4)	4.1(2)
C14	0.227(1)	0.3904(7)	0.2896(5)	6.0(2)
C15	0.094(1)	0.3838(6)	0.2629(5)	5.2(2)
C16	0.0169(8)	0.3431(6)	0.3057(5)	4.6(2)
C17	0.0774(7)	0.3111(5)	0.3741(4)	3.5(2)
C18	0.4628(6)	0.2985(4)	0.5093(4)	2.5(1)
C19	0.5105(9)	0.3740(5)	0.5523(6)	4.5(2)
C20	0.645(1)	0.3938(7)	0.5664(7)	6.4(3)
C21	0.7335(8)	0.3412(7)	0.5411(6)	5.2(2)
C22	0.6858(7)	0.2712(6)	0.4983(5)	4.2(2)
C23	0.5532(7)	0.2502(5)	0.4826(4)	3.3(2)
C24	0.4667(6)	0.1255(4)	0.6271(4)	2.2(1)
C25	0.5276(6)	0.0815(5)	0.6887(4)	2.6(1)
C26	0.4469(6)	0.0055(5)	0.6915(3)	2.5(1)
C27	0.4571(8)	−0.0656(5)	0.7394(4)	3.9(2)
C28	0.359(1)	−0.1275(5)	0.7264(5)	4.9(2)
C29	0.250(1)	−0.1212(5)	0.6654(5)	4.7(2)
C30	0.2366(7)	−0.0526(5)	0.6168(4)	3.3(2)
C31	0.3383(6)	0.0112(4)	0.6289(3)	2.1(1)
C32	0.6565(8)	0.1061(5)	0.7421(4)	3.3(2)
C33	0.643(1)	0.1307(6)	0.8175(5)	4.6(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3)[$a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$].

metal indolenine complexes appear to have been prepared previously.[16]

Importantly, the 3-methylindolenine complex **4b**$^+$TfO$^-$ was isolated as an 86:14 mixture of Re,C configurational diastereomers.[17] A separate NMR experiment showed that the diastereomer ratio was unaffected by workup. In an attempt to enhance diastereoselectivity, the reaction of **2b** and HOTf was repeated at −80 °C in CD_2Cl_2 in an NMR tube. A 92:8 mixture of diastereomers rapidly formed, as assayed by ^{31}P and ^{1}H NMR. No change occurred when the sample was warmed to room temperature. Thus, the chiral rhenium fragment **I** can exert a strong influence upon the stereochemistry of electrophilic addition to indolyl ligands. The methyl ^{1}H NMR resonance of the major diastereomer was upfield of that of the minor diastereomer (δ 0.76, 1.39; Table 1). Hence, the major and minor diastereomers were provisionally assigned *SR,RS* and *SS,RR* configurations, respectively, as illustrated in Table 1 and rationalized below.[18]

3. Alkylation of Indolyl Complexes. Encouraged by the preceding results, we turned to reactions of **2** with alkylating agents. Slower and potentially more diastereoselective reactions were anticipated. First, the 3-methylindolyl complex **2b** and methyl triflate (CH_3OTf; 3 equiv) were combined in CH_2Cl_2 at room temperature. After 3 h, workup gave the 3,3-dimethylindolenine complex [(η^5-C_5H_5)Re(NO)(PPh_3)(N=CHC(CH_3)$_2$C=CCH=CHCH=CH)]$^+$ TfO$^-$ (**5**$^+$TfO$^-$) in 96% yield (Scheme 2). Under similar conditions in CD_2Cl_2, 3-methylindole and CH_3OTf gave only 5% reaction after 24 h. Hence, the indolyl ligands are activated toward electrophilic attack. One methyl ^{1}H NMR resonance of **5**$^+$TfO$^-$ was distinctly upfield of the other (δ 0.67, 1.40; Table 1). These were assigned as illustrated in **II** (Scheme 2), consistent with the shielding trend in the diastereomers of **4b**$^+$TfO$^-$.

Alkylations that would generate new stereocenters were attempted. The reactions of 3-methylindolyl complex **2b** with C_2H_5OTf, and 3-ethylindolyl complex **2c** with CH_3OTf, gave the 3-methyl-3-ethylindolenine complex [(η^5-C_5H_5)Re(NO)(PPh_3)(N=CHC(CH_3)(C_2H_5)C=CCH=CHCH=CH)]$^+$TfO$^-$ (**6**$^+$TfO$^-$) in 92−96% yields as 65:35 and 17:83 mixtures of diastereomers (Scheme 2).[19] These were assigned *SS,RR* and *SR,RS* configurations, respectively, on the basis of the methyl ^{1}H NMR

(16) (a) Yamauchi, O.; Takani, M.; Toyoda, K.; Masuda, H. *Inorg. Chem.* **1990**, *29*, 1856. (b) For porphyrin-like complexes that bear this subunit, see: Arnold, D. P.; Gaete-Holmes, R.; Johnson, A. W.; Smith, A. R. P.; Williams, G. A. *J. Chem. Soc., Perkin. Trans. 1*, **1978**, 1660.

(17) Ratios of rhenium complexes are normalized to 100, and error limits are ±2 (86:14 ≡ (86 ± 2):(14 ± 2)).

(18) (a) From the distinctive chemical shifts of the methyl ^{1}H NMR resonances of **4b**$^+$TfO$^-$, **5**$^+$TfO$^-$, and **6**$^+$X$^-$ (either δ 0.63−0.76 *or* 1.38−1.40), the *relative* carbon configurations of the diastereomers of **4b**$^+$TfO$^-$ and **6**$^+$X$^-$ can be confidently assigned. However, the relative configurations at rhenium are tentative, as elaborated in the Discussion. Thus, there is a slight possibility that all diastereomer assignments must be reversed. (b) The rhenium configuration is specified prior to that of the carbon or nitrogen stereocenter, utilizing conventions described previously.[8]

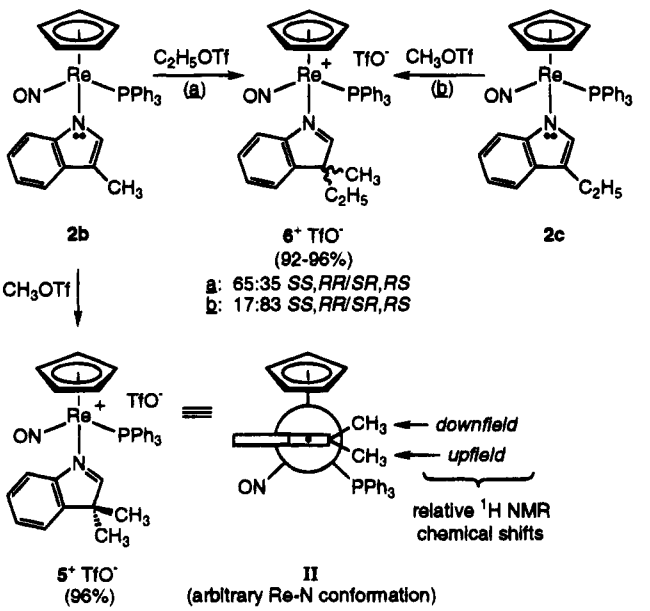
Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in 2c

Re—P	2.372(2)	C24—C25	1.35(1)
Re—N1	1.750(5)	C25—C26	1.44(1)
Re—N2	2.101(5)	C25—C32	1.51(1)
N1—O1	1.203(7)	C26—C27	1.39(1)
N2—C24	1.387(9)	C26—C31	1.42(1)
N2—C31	1.384(8)	C27—C28	1.36(1)
Re—C1	2.281(8)	C28—C29	1.40(2)
Re—C2	2.329(8)	C29—C30	1.37(1)
Re—C3	2.315(7)	C30—C31	1.41(1)
Re—C4	2.255(7)	C32—C33	1.49(1)
Re—C5	2.261(8)		

P—Re—N1	90.0(2)	C24—C25—C26	105.8(6)
P—Re—N2	94.4(2)	C25—C26—C31	106.0(6)
N1—Re—N2	98.8(2)	C26—C31—N2	109.9(6)
Re—N1—O1	174.3(6)	C25—C26—C27	134.0(7)
Re—N2—C24	130.2(5)	C26—C27—C28	119.0(8)
Re—N2—C31	124.7(4)	C27—C26—C31	120.0(7)
C1—C2—C3	107.7(3)	C27—C28—C29	121.2(8)
C2—C3—C4	108.5(3)	C28—C29—C30	121.8(8)
C3—C4—C5	108.0(3)	C29—C30—C31	117.5(8)
C4—C5—C1	108.2(3)	C30—C31—C26	120.4(8)
C5—C1—C2	107.5(3)	C30—C31—N2	129.7(6)
C24—N2—C31	104.8(5)	C24—C25—C32	126.8(7)
N2—C24—C25	105.1(3)	C25—C32—C33	114.6(7)

N1—Re—N2—C24	116.3(6)
P—Re—N2—C24	25.6(6)
N1—Re—N2—C31	−70.9(5)
P—Re—N2—C31	−161.6(5)

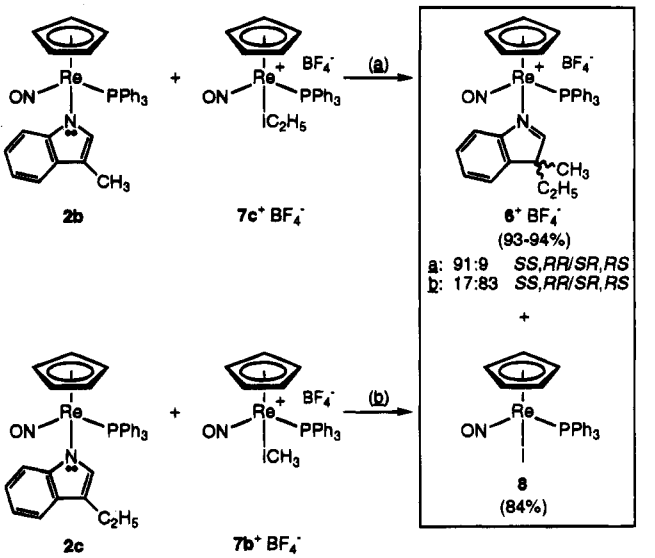
Scheme 2. Reactions of Indolyl Complexes and Alkyl Triflates



resonance shielding trends shown in **II** (δ 0.63 and 1.38; Table 1).[18,20] This gives the intuitively satisfying conclusion that electrophiles preferentially attack **2b** (HOTf, C_2H_5OTf) and **2c** (CH_3OTf) from the same direction with respect to the resident C3 substituent.

We were surprised that the alkylation of **2b** was less diastereoselective than protonation. We wondered whether better results might be achieved with other electrophiles, such as alkyl iodide complexes of **I**.[21] These are easily isolated and much more electrophilic than free alkyl iodides. Thus, the reaction of **2b** and ethyl iodide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IC_2H_5)]^+BF_4^-$ (**7c**$^+BF_4^-$) gave **6**$^+BF_4^-$ in 93% yield as 91:9 mixture of *SS,RR/SR,RS* diastereomers (Scheme 3)—*higher* than that obtained with C_2H_5OTf. The iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**8**)[12] was also isolated in 84% yield. However, the corresponding reaction of **2c** and methyl iodide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_3)]^+BF_4^-$ (**7b**$^+BF_4^-$) gave **6**$^+BF_4^-$ in 94% yield as 17:83 mixture of *SS,RR/SR,RS* diastereomers—*identical* with that obtained with CH_3OTf.[22,23]

Scheme 3. Reactions of Indolyl Complexes and Alkyl Iodide Complexes



In efforts to improve diastereoselectivities, alkylations were also conducted at low temperatures. The 3-methylindolyl complex **2b** and C_2H_5OTf and the 3-ethylindolyl complex **2c** and CH_3OTf were combined in separate NMR tubes in CH_2Cl_2 at −80 °C. The samples were gradually warmed as ^{31}P spectra were recorded. No detectable reaction occurred below −10 °C. After 1 h at 0 °C, alkylations were 20% and 60% complete, respectively. However, the *SS,RR/SR,RS* ratios were only slightly more biased (69:31 and 14:86) than those obtained at room temperature. The corresponding reactions with alkyl iodide complexes **7c,b**$^+BF_4^-$ were 10% complete after 1 h at −80 °C. In these cases, the diastereomer ratios *de*creased to 70:30 and 24:76.[22b]

All attempts to isolate **6**$^+X^-$ in diastereomerically pure form were unsuccessful. These included experiments with **6**$^+SbF_6^-$, which was prepared by metathesis.

(19) Reactions of **2a** and CH_3OTf were also conducted. However, in no case was the target complex **4b**$^+TfO^-$ the dominant product. Rather, comparable quantities of the dimethylation product **5**$^+TfO^-$ and the protonation product **4a**$^+TfO^-$ formed under all conditions investigated. This implies that proton transfer from **4b**$^+TfO^-$ to **2a** is rapid.

(20) The chemical shifts of certain ^1H NMR resonances of **6**$^+X^-$ show a distinct dependence upon the counteranion, as summarized in footnote *e* in Table 1. Although many explanations are possible, there may be varying degrees of association with the electrophilic N=CH carbon.

(21) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766.

(22) (a) Note that these experiments utilize *racemic* **2b,c** and **7b,c**$^+BF_4^-$. Reactions of *R* and *S* (or *S* and *R*) enantiomers can give product diastereomer ratios different from those of *R* and *R* (or *S* and *S*) diastereomers. The observed diastereomer ratios reflect the weighted contribution of each pathway. General references: Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. Rousch, W. R.; Palkowitz, A. D.; Ando, K. *J. Am. Chem. Soc.* **1990**, *112*, 6348. (b) The decreased diastereoselectivity at lower temperatures suggests that $\Delta\Delta G^{\ddagger}$ is less for the faster reacting pair of enantiomers. Thus, diastereoselectivity may increase with properly matched enantiomerically pure reactants.

(23) Complex **2c** and *free* methyl iodide were also reacted ($CDCl_3$). After 4 days, ^1H and ^{31}P NMR spectra showed only 27% conversion to **6**$^+I^-$ (20:80 *SS,RR/SR,RS*). Thus, the methyl iodide complex **7b**$^+BF_4^-$ is a much stronger electrophile.

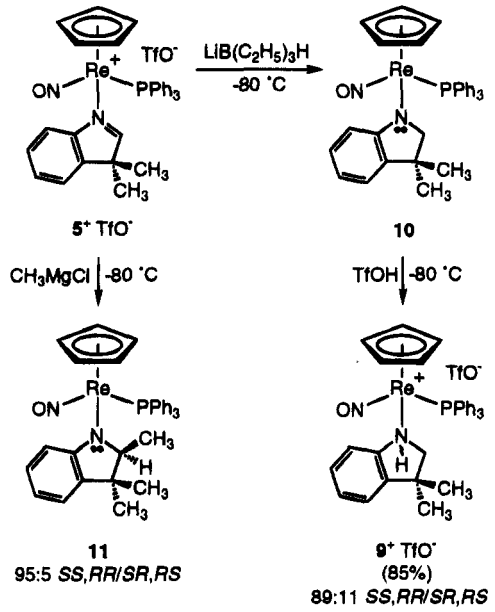
For example, $\mathbf{6}^+TfO^-$ could be crystallized to a 9:91 *SS,RR/SR,RS* mixture, but not further enriched. Hence, it was not possible to assign diastereomer configurations crystallographically.

4. Additions to Indolenine Complexes. Anticipating that higher diastereoselectivities might eventually be realized for the preceding transformations, we sought to develop the chemistry of the indolenine complexes. Thus, the 3,3-dimethylindolenine complex $\mathbf{5}^+TfO^-$ and borohydride $LiB(C_2H_5)_3H$ were combined in THF at −80 °C (Scheme 4). Workup with HOTf gave the 3,3-dimethylindoline complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HNCH_2C(CH_3)_2C{=}CCH{=}CHCH{=}CH)]^+\ TfO^-$ ($\mathbf{9}^+TfO^-$) in 85% yield as an 89:11 mixture of Re,N configurational diastereomers. This transformation was also monitored by ^{31}P NMR. An intermediate, 3,3-dimethylindolinyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCH_2C(CH_3)_2C{=}CCH{=}CHCH{=}CH)$ (**10**; 20.2 ppm), cleanly formed. In view of the chemical and configurational lability of *some* amido complexes of **I**,[24,25] no attempt was made to isolate **10**. However, **10** persisted at room temperature, was also observed in another reaction described below, and was further characterized by ^1H and ^{31}P NMR in CD_2Cl_2.[26,27]

The NMR and IR properties of $\mathbf{9}^+TfO^-$ resembled those of other secondary amine complexes of **I**.[28] Previous studies have established that when the atom ligating to **I** is a stereocenter, the diastereomer in which the largest group can reside in the spacious interstice between the nitrosyl and cyclopentadienyl ligands, while the smallest group resides between the nitrosyl and PPh_3 ligands, is the more stable.[29] Hence, the major and minor diastereomers of $\mathbf{9}^+\ TfO^-$ were assigned *SS,RR* and *SR,RS* configurations, assuming that (1) the major diastereomer is the more stable and (2) the benzenoid ring is the largest nitrogen substituent, and the hydrogen the smallest.

Complex $\mathbf{5}^+TfO^-$ and the carbon nucleophile CH_3MgCl were combined in THF at −80 °C in an NMR tube (Scheme 4). The 2,3,3-trimethylindolinyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCH(CH_3)C(CH_3)_2C{=}CCH{=}CHCH{=}CH)$ (**11**) cleanly formed over the course of 1 h as a 95:5 mixture of Re,C diastereomers,[27] as assayed by ^{31}P NMR. No change occurred when the sample was warmed to −20 °C. Hence, the chiral rhenium fragment can exert a strong influence upon the stereochemistry of nucleophilic addition to indolenine ligands. The major and minor diastereomers were provisionally assigned *SS,RR* and *SR,RS* configurations as described below. Complex **11** was further characterized by NMR in CD_2Cl_2 (Table 1). When THF or CD_2Cl_2 solutions of **11** were treated with HOTf, no evidence for the corresponding cationic amine complex was observed. One major cyclopentadienyl-containing product, and several unidentified organic products, formed. We assume that the amine complex is unstable, presumably due to steric congestion about the donor nitrogen.

Scheme 4. Additions to Indolenine Complexes



5. Displacements of Indoline Ligands. Attention was turned to detaching the 3,3-dimethylindoline ligand from $\mathbf{9}^+TfO^-$. Other secondary amine complexes of **I** rapidly react with the cyanide ion to give free amines and the cyanide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**12**).[8,28] The latter is easily recycled to triflate complex **3** or other functional equivalents of **I**.[8] Furthermore, optically active amine complexes give essentially complete overall retention of configuration at rhenium. Thus, $\mathbf{9}^+TfO^-$ and the cyanide salt $(C_2H_5)_4N^+CN^-$ were reacted in CD_2Cl_2 at room temperature. However, after 2 h ^1H and ^{31}P NMR spectra showed a 30:30:70 mixture of the cyanide complex **12**, 3,3-dimethylindoline (**13**),[30] and the unanticipated 3,3-dimethylindolinyl complex **10** (Scheme 5). Thus, the N-deprotonation of $\mathbf{9}^+TfO^-$ is faster than substitution—presumably due to the acidity enhancing benzenoid substituent. After 48 h, NMR spectra showed a 60:60:40 mixture of **12**, **13**, and **10**. This indicates that deprotonation is to some extent reversible.

Thus, alternative displacement reactions were investigated. First, $\mathbf{9}^+TfO^-$ was dissolved in trideuterioacetonitrile in an NMR tube. After 18 h at 65 °C, ^1H and ^{31}P spectra showed the spectroscopically quantitative formation of the known[15a] acetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N{\equiv}CCD_3)]^+TfO^-$ and indoline **13**. However, we were not able to devise a practical means of recycling the former compound. In contrast, the methyl isocyanide complex of **I** is easily converted to triflate complex **3** or other functional equivalents of **I**.[8] Thus, $\mathbf{9}^+TfO^-$ and the commercially available, relatively odorless isocyanide $C{\equiv}NCH_2Ts$[11b] were combined in $CDCl_3$ in a NMR tube (Scheme 5). After 6 h at 60 °C,

(24) Dewey, M. A.; Knight, D. A.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1992**, *125*, 815.

(25) (a) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351. (b) See also: Saura-Llamas, I.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 2136.

(26) NMR (CD_2Cl_2, 25 °C): ^1H 7.52–7.34 (m, $3C_6H_5$), 6.91 (t, J = 9 Hz, 1H of C_6H_4), 6.61 (d, J = 6, 1H of C_6H_4), 6.45 (d, J = 9, 1H of C_6H_4), 6.18 (t, J = 9, 1H of C_6H_4), 5.18 (s, C_5H_5), 3.02 (d, J = 10, CH*H*′), 2.74 (d, J = 10, CH*H*′), 1.04 (s, CH_3), 0.63 (s, CH_3′); $^{31}P\{^1H\}$ 17.8 (s).

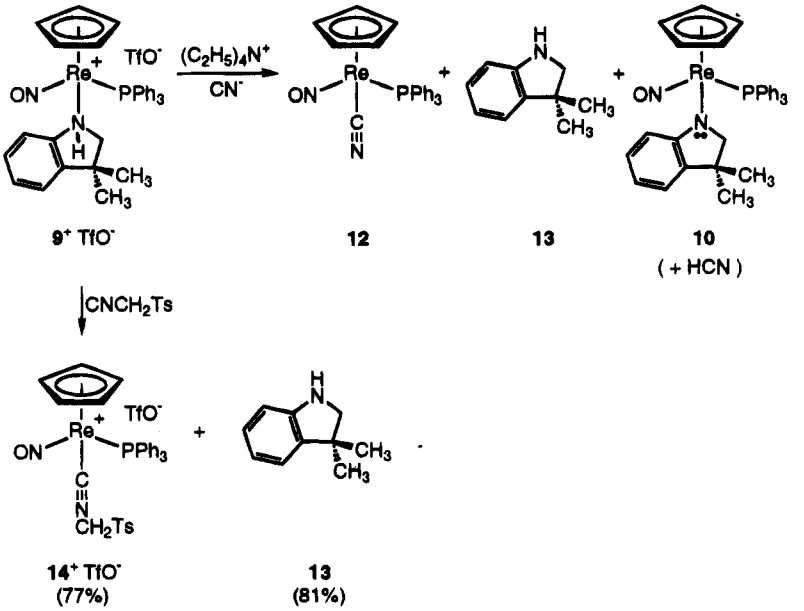
(27) Amido complexes of **I** undergo very rapid inversion at nitrogen.[24] Thus, only one diastereomer of **10** is observed by NMR, and the two resonances for **11** are assigned as Re,C (not Re,N) configurational diastereomers.

(28) Dewey, M. A.; Knight, D. A.; Klein, D. P.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1991**, *30*, 4995.

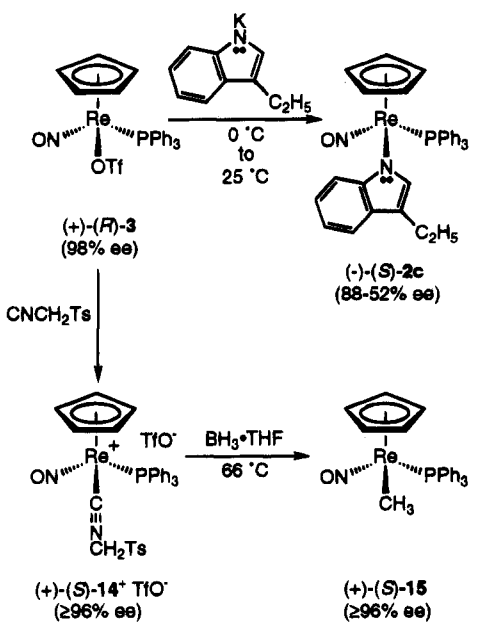
(29) (a) Crocco, G. L.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1990**, *9*, 2819. (b) Zwick, B. D.; Dewey, M. A.; Knight, D. A.; Buhro, W. E.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 2673.

(30) Jackson, A. H.; Smith, P. *J. Chem. Soc. C* **1968**, 1667.

Scheme 5. Displacement of 3,3-Dimethylindoline from 9⁺TfO⁻



Scheme 6. Synthesis of Nonracemic Compounds



^1H and ^{31}P NMR spectra showed the spectroscopically quantitative formation of the isocyanide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}NCH_2Ts)]^+TfO^-$ (**14**⁺TfO⁻) and indoline **13**.[31]

A similar preparative reaction gave **14**⁺TfO⁻ and **13** in 77% and 81% yields. Complex **14**⁺TfO⁻ was also isolated in 94% yield from the reaction of triflate complex **3** and $C{\equiv}NCH_2Ts$. Reduction of **14**⁺TfO⁻ with BH_3·THF in refluxing THF gave the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**15**)—the precursor to triflate complex **3**[12]—in 60% yield. The corresponding reactions involving enantiomerically enriched compounds are illustrated in Scheme 6. Curiously, $NaBH_4$, which readily reduces the methyl isocyanide complex of **I** to **15**,[8] gave much poorer yields with **14**⁺TfO⁻.

(31) (a) An analogous substitution was effected with benzyl isocyanide. However, this ligand is (like methyl isocyanide) extremely malodorous and more costly. (b) In a reaction sequence characterized by ^1H and ^{31}P NMR, the 3-methyl-3-ethylindolenine complex **6**⁺TfO⁻ was similarly converted ($LiB(C_2H_5)_3BH$, HOTf, and then $C{\equiv}NCH_2Ts$) to **14**⁺TfO⁻ and free 3-ethyl-3-methylindoline.

6. Nonracemic Complexes. Under optimized conditions, the enantiomerically pure iodide complex (+)-(*R*)-**8** and the cuprate reagent $LiCu(CH_3)_2$ react to give the methyl complex (+)-(*S*)-**15** in >98% ee.[32] The configuration of **15** corresponds to retention at rhenium. Thus, the triflate complex (+)-(*R*)-**3** was prepared[12] from (+)-(*S*)-**15** of 98% ee, and combined with potassium 3-ethylindolide, $K(\overline{NCH{=}C(C_2H_5)C{=}CCH{=}CHCH{=}CH})$, under various conditions (Scheme 6). One reaction sequence was conducted at room temperature, and the product was purified by a prolonged crystallization. This gave (−)-(*S*)-**2c** in 48% yield as a mixture of powder (52% ee) and prisms (16% ee), as assayed by chiral HPLC.[33,34] In another sequence, reaction and workup temperatures were kept below 0 °C. This gave (−)-(*S*)-**2c** in 88% ee—but as an oil containing 16 mol % of 3-ethylindole (56% corrected yield).

The configurational stability of (−)-(*S*)-**2c** was probed. A sample that was 52% ee was kept at 60 °C in $CDCl_3$. After 3 days, the sample was 20% ee (chiral HPLC). Amido complexes of **I** have been shown to racemize by a mechanism involving PPh_3 ligand dissociation.[25] Thus, racemic **2c** was similarly kept at 60 °C in $CDCl_3$ in the presence of P(*p*-tol)$_3$ (2.2 equiv). After 3 days, a 59:41 mixture of **2c** and the P(*p*-tol)$_3$ analog was present, as assayed by ^{31}P NMR and the upfield chemical shift diagnostic of this ligand transposition (15.1 ppm; ^1H NMR δ 5.20 (C_5H_5), 2.37 (CH_3)).[25]

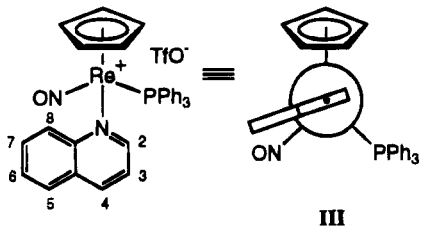
Finally, the recycling protocols developed above were applied to optically active complexes. First, the triflate complex (+)-(*R*)-**3** was generated *in situ* from (+)-(*S*)-

(32) Ramsden, J. A.; Peng, T.-S.; Gladysz, J. A. *Bull. Soc. Chim. Fr.* **1992**, *129*, 625.

(33) Ramsden, J. A.; Garner, C. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 1631.

(34) We presume, by analogy to many other substitution reactions in this series of compounds,[8,10,12,13] that (+)-(*R*)-**3** and potassium 3-ethylindolide react with retention of configuration at rhenium. However, the sign of the optical rotation of the product, (−)-(*S*)-**2c**, is reversed. This feature correlates with rhenium configuration in >90% of the many compound studied. The reaction of (+)-(*R*)-**3** and quinoline also gives a levorotatory substitution product, and in this case retention has been rigorously established.[10] Although it may be a coincidence, both **2c** and the quinoline complex possess a nitrogen donor atom with a benzenoid substituent.

Chart 2. Solid-State Rhenium–Nitrogen Conformation in the Quinoline Complex of I



III

15 of 98% ee, and C≡NCH$_2$Ts was added (Scheme 6). Workup gave the isocyanide complex (+)-(*S*)-**14**$^+$TfO$^-$ in 94% yield. Attempts to assay the enantiomeric purity with NMR shift reagents were unsuccessful. Thus, (+)-(*S*)-**14**$^+$TfO$^-$ and BH$_3$·THF were reacted in refluxing THF (Scheme 6). Workup gave (+)-(*S*)-**15** in 54% yield and 96% ee, as analyzed by chiral HPLC. Thus, the chiral Lewis acid **I** may be recycled via **14**$^+$TfO$^-$ with preservation of configuration at rhenium.

Discussion

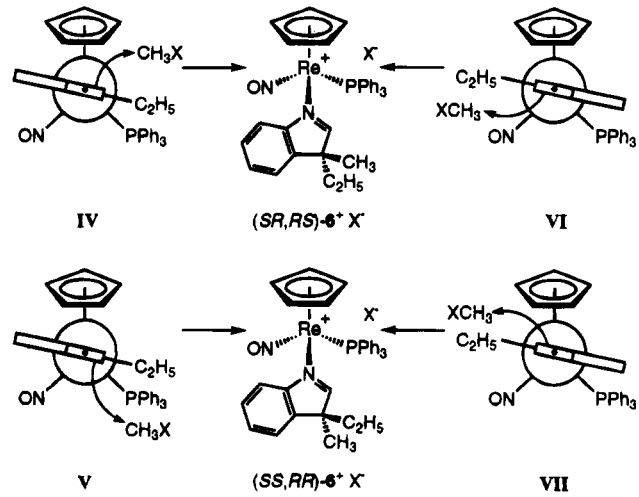
1. Mechanism of Diastereoselection in Electrophilic Additions. The preceding data establish that *N*-indolyl complexes **2** are activated toward electrophilic attack. The regiochemistry parallels that of free indoles, and the products, indolenine complexes **4**–**6**$^+$ X$^-$, are easily isolated. We anticipate that other *N*-indolyl complexes will react similarly. However, the chiral rhenium Lewis acid **I** does not give a uniformly high level of 1,3-asymmetric induction in these reactions. Indolenine complex diastereomer ratios range from a high of 92:8 to a low of 65:35. Designed (as opposed to empirical) improvements require an understanding of the mechanism of diastereoselection. We analyze the possibilities as follows.

First, consider the carbon substituents on the indolyl nitrogen, C7a and C2 (**1**, Chart 1). The steric bulk about the benzenoid carbon C7a will be a greater whenever C2 is unsubstituted. Thus, it is not surprising that **2c** crystallizes with the benzenoid ring in the spacious interstice between the small nitrosyl and medium-sized cyclopentadienyl ligand (Figure 1, bottom). However, the rhenium–nitrogen conformation is unusual in that the rhenium fragment HOMO (**I**, Chart I) is virtually orthogonal to any ligand π acceptor orbitals. Thus, the P–Re–N–C torsion angles are close to 0 and ±180° (25.6(6) and −161.6(5)°; Table 4).

The spatial relationship between the nitrogen donor atom and the benzenoid ring in indole is similar to that in quinoline. Interestingly, the crystal structure of the quinoline adduct of **I**—a cationic complex—exhibits a somewhat different rhenium–nitrogen conformation.[10] As shown in **III** in Chart 2, the benzenoid ring still occupies the same interstice. However, the P–Re–N–C torsion angles differ by 43–51° from those in **2c** (68.5(5) and −110.7(5)°).

We suggest that the rhenium–nitrogen conformations in **2c** and **III** bracket those that would be reasonable in transition states for electrophilic additions to **2**. Diastereoselection can then be reduced to the limiting possibilities in Scheme 7, which are arbitrarily illustrated (1) for the methylation of **2c** and (2) with rhenium–nitrogen conformations similar to that in **2c**. First, electrophiles can approach C3 from a direction

Scheme 7. Possible Transition State Models for Electrophilic Attack upon Indolyl Complexes 2a–c, Illustrated for the Methylation of 2c to 6$^+$X$^-$



anti to the bulky PPh$_3$ ligand, as shown in **IV**.[35] The PPh$_3$ ligand is the controlling steric feature in diastereoselective additions to many other Lewis base adducts of **I**.[8,36] Hence, configurations were assigned in accord with this model.[37] However, the faces of the indolyl ligand in crystalline **2c** do not have a strong *syn/anti* bias with respect to the PPh$_3$ ligand. Furthermore, attack *syn* to the PPh$_3$ ligand as in **V** would avoid interactions with the cyclopentadienyl ligand.[35] This would account for the modest diastereomer ratios obtained in some cases.

Transition states with reversed rhenium–nitrogen conformations, such as those arbitrarily depicted in **VI** and **VII**, also merit consideration. Alkylation *anti* or *syn* to the PPh$_3$ ligand would now give diastereomers opposite to those derived from **IV** and **V**. Related conformers have been shown to account for the minor diastereomers in electrophilic attack upon C$_\beta$ of vinyl complexes of **I**.[36b] However, we currently believe that transition states **VI** and **VII** are either minor contributors or energetically prohibitive, as the benzenoid substituent must reside in a more congested interstice of the rhenium fragment.

From the preceding analysis, strategies that would lead to higher diastereoselectivities are not obvious. Importantly, the chiral rhenium fragment is three atoms removed from the incipient carbon stereocenter. When the crystal structure of **2c** is viewed stereoscopically, with atoms set at van der Waals radii, it is apparent that the two faces of C3 (C24 in Figure 1) do not have greatly different steric environments. Thus, perhaps a bulkier phosphine would disfavor **V** relative to **IV**, enhancing diastereomer ratios. In other com-

(35) No directionality, other than the face of the indolyl ligand being attacked, is implied by the curvature of the arrows indicating the approach of CH$_3$X to **2c** in Scheme 7.

(36) (a) O'Connor, E. J.; Kobayashi, M.; Floss, H. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 4837 and references therein. (b) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688. (c) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096. (d) Dalton, D. M.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9198. (e) Klein, D. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 8710.

(37) This gives the ^{1}H NMR shielding trend for the methyl resonances shown in **II** (Scheme 2). As would be intuitively expected, the upfield resonance is associated with the position closest to the PPh$_3$ phenyl rings.

plexes of **I** that undergo electrophilic attack with efficient 1,3-asymmetric induction,[8,38] either the rhenium has been capable of hyperconjugation with the nucleophilic atom or an additional ligand stereocenter has been present.

2. Other Methodology Issues. To our knowledge, **I** constitutes the first chiral auxiliary capable of controlling carbon configurations in electrophilic additions to indoles. Although our original objective of developing methodology that might be applied to enantioselective syntheses of indolines and related targets has not yet been achieved, much insight relevant to this goal has been realized. Some of the key issues that need to be more completely addressed are as follows.

First, enantiomerically pure reactants must be readily available. Although we have not yet been able to prepare **2c** that is greater than 88% ee, we are confident that this can be improved with additional experimentation. Furthermore, based upon precedent with other cyclic amines, free indolines and the triflate complex (+)-(*R*)-**3** should react to give enantiomerically pure indoline complexes. These could likely be transformed to enantiomerically pure **2a**–**c** by sequential hydride abstraction ($Ph_3C^+X^-$) and deprotonation, as described for other cyclic amine complexes of **I**.[15b]

Second, it would be desirable to use the chiral metal auxiliary to introduce a *sequence* of new stereocenters. Here the initial results are promising, as the reaction of indolenine complex $\mathbf{5}^+TfO^-$ and CH_3MgCl gives predominantly one diastereomer of the addition product **11** (Scheme 4). Similar reactions of $\mathbf{6}^+X^-$ would give addition products with two carbon stereocenters. However, since we were unable to obtain $\mathbf{6}^+X^-$ in diastereomerically pure form, this chemistry was not pursued. Although we do not presently have a rigorous basis for assigning stereochemistry to the dominant diastereomer of **11**, we suggest that CH_3MgCl approaches the N=CH carbon from a direction opposite to the PPh_3 ligand in a transition state related to **II** (Scheme 2) and **IV** (Scheme 7).

Third, the protocols for detaching indoline ligands from **I** require further optimization. Although the cyanide ion displacement in Scheme 5 is complicated by competing *N*-deprotonation, the resulting cyanide complex **12** is easily recycled without loss of configuration at rhenium.[8] A possible improvement would be to follow additions of nucleophiles to indolenine complexes by methylation of the nitrogen. The resulting tertiary amine complexes should undergo ready substitution. Another approach would involve alternative displacing ligands. However, our initial choice, the isocyanide $C{\equiv}NCH_2Ts$, also has several limitations. For example, moderate heating is required, which can potentially compromise enantiomeric purities. Further, reduction of the resulting isocyanide complex $\mathbf{14}^+TfO^-$ to methyl complex **15** does not proceed in as high a yield as with the corresponding methyl isocyanide complex.[8] Although methyl isocyanide can likely be employed as a displacing ligand, it suffers from other well-known drawbacks.[31a]

In summary, this study has established the potential of chiral transition metal auxiliaries for the elaboration of indoles into optically active indolines with new C3 and C2 stereocenters. We expect that other metal fragments will eventually be identified that avoid some or all of the complications encountered with the rhenium Lewis acid **I**. Related studies of nucleophilic additions to cationic quinoline complexes of **I** will be described in the near future.[39]

Experimental Section

General procedures were given in an earlier paper.[15a] Solvents not specified previously[15a] were used without purification. Reagents were used as received from common commercial sources.

K(NCH=C(R)C=CCH=CHCH=CH).[6a] A. A Schlenk flask was charged with toluene (100 mL), freshly cut potassium (4.41 g, 113 mmol), indole (20.0 g, 171 mmol), and a stir bar. The mixture was refluxed with stirring (12 h). The resulting solid was isolated by filtration, washed with toluene (3 × 20 mL), and dried under oil pump vacuum to give K(NCH=CH-C=CCH=CHCH=CH) as a free flowing white powder (10.1 g, 65.0 mmol, 57%). B. THF (200 mL), potassium (0.911 g, 23.3 mmol), and 3-methylindole (6.02 g, 45.9 mmol) were similarly refluxed (4 h). The mixture was concentrated to 15 mL, and toluene (100 mL) was slowly added with stirring. The white solid, $K(NCH{=}C(CH_3)C{=}CCH{=}CHCH{=}CH)$, was isolated in an identical manner (3.56 g, 21.0 mmol, 90%). C. THF (100 mL), potassium (0.621 g, 15.9 mmol), and 3-ethylindole (2.91 g, 19.9 mmol)[40] were stirred for 12 h at room temperature. The mixture was concentrated to 15 mL, and hexane (100 mL) was slowly added with stirring. The white solid, $K(NCH{=}C(C_2H_5)C{=}CCH{=}CHCH{=}CH)$, was similarly isolated (hexane wash, 3 × 20 mL; 2.58 g, 14.0 mmol, 88%).

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$(NCH=CHC=CCH=CH-CH=CH) (2a). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)$-Re(NO)(PPh_3)(OTf) (**3**;[12] 1.85 g, 2.67 mmol), THF (50 mL), and a stir bar. Then K(NCH=CHC=CCH=CHCH=CH) (0.901 g, 5.81 mmol) was added with stirring. After 1 h, the mixture was filtered through a Celite plug. Solvent was removed from the filtrate by rotary evaporation (90–100 °C), and benzene (100 mL) was added. The mixture was filtered through a silica gel plug. Solvent was removed from the filtrate by rotary evaporation (90–100 °C). The oily residue was dissolved in CH_2Cl_2 (25 mL), and layers of ether and heptane were added (75, 10 mL). After 60 h, burnt umber prisms of **2a** were collected by filtration, washed with pentane (2 × 10 mL), and dried under oil pump vacuum (1.25 g, 1.89 mmol, 71%), mp 211–213 °C dec. Anal. Calcd for $C_{31}H_{26}N_2OPRe$: C, 56.44; H, 3.97. Found: C, 56.34, H, 3.99.

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$(NCH=C(CH$_3$)C=CCH=CH-CH=CH) (2b). Complex **3** (2.01 g, 2.90 mmol), K(NCH=C-(CH$_3$)C=CCH=CHCH=CH) (0.589 g, 3.48 mmol), and THF (50 mL) were combined in a procedure analogous to that for **2a**. An identical workup gave **2b** as a mixture of red needles and prisms (1.34 g, 1.99 mmol, 69%), mp 219–222 °C dec. Anal. Calcd for $C_{32}H_{28}N_2OPRe$: C, 57.05; H, 4.19. Found: C, 57.00; H, 4.19.

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3$(NCH=C(C$_2H_5$)C=CCH=CH-CH=CH) (2c). A. Complex **3** (1.50 g, 2.16 mmol), K(NCH=C-

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$(C_2H_5)C{=}CCH{=}CHCH{=}CH$) (0.475 g, 2.59 mmol), and THF (50 mL) were combined in a procedure analogous to that for **2a**. An identical workup gave **2c** as blood-red prisms (0.881 g, 1.27 mmol, 59%), mp 157–158 °C dec. Anal. Calcd for $C_{33}H_{30}N_2OPRe$: C, 57.63; H, 4.40. Found: C, 57.53; H, 4.47. B. Complex (+)-(*R*)-**3** (0.250 g, 0.361 mmol),[3] K(NCH=C-$(C_2H_5)C{=}CCH{=}CHCH{=}CH$) (0.100 g, 0.542 mmol), and THF (50 mL) were combined in an analogous procedure. After 15 min, the mixture was filtered through a Celite plug. Solvent was removed from the filtrate by rotary evaporation (25 °C). Benzene was added (100 mL), and the mixture was filtered through a silica gel plug. Solvent was removed from the filtrate by rotary evaporation (25 °C). The residue was dissolved in CH_2Cl_2 (25 mL), and layers of ether and heptane were added (75, 10 mL). After 7 days, a mixture of red powder and prisms was collected by filtration and dried under oil pump vacuum to give (−)-(*S*)-**2c** (0.120 g, 0.174 mmol, 48%). The powder and prisms were manually separated, and enantiomeric purities assayed by chiral HPLC (97.5:2.5 v/v hexane/2-propanol, 1 mL/min).[33] Powder: 52% ee, $[\alpha]_{589}^{25}$ −314 ± 2° (c = 0.580 mg/mL, $CHCl_3$).[41] Prisms: 16% ee; mp 143–144 °C dec. Found: C, 57.69; H, 4.39. C. A Schlenk flask was charged with (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) ((+)-(*S*)-**15**;[42] 0.084 g, 0.15 mmol, 98% ee), toluene (15 mL), and a stir bar, and cooled to −45 °C (CH_3CN/CO_2). Then HOTf (0.013 mL, 0.15 mmol) was added with stirring. After 0.5 h, the flask was transferred to a 0 °C bath, and K(NCH=C(C_2H_5)-C=CCH=CHCH=CH) (0.17 g, 0.90 mmol) and THF (1 mL) were added with stirring. After 3 h, solvent was removed under oil pump vacuum (0 °C). Benzene (100 mL) was added, and the mixture was filtered through a silica gel plug. Solvent was removed from the filtrate by rotary evaporation (25 °C) to give (−)-(*S*)-**2c** as a brown oil (0.060 g) that contained 16 mol % 3-ethylindole (0.084 mmol corrected, 56%; 88% ee).

[(η^5-C_5H_5)Re(NO)(PPh_3(N=CHCH$_2$C=CCH=CH-CH=CH)]$^+$TfO$^-$ (4a$^+$TfO$^-$). A Schlenk flask was charged with **2a** (0.101 g, 0.153 mmol), CH_2Cl_2 (25 mL), and a stir bar. Then HOTf (0.0150 mL, 0.169 mmol) was slowly added with stirring. After 15 min, the mixture was concentrated to 5 mL, and pentane (50 mL) was added. The solid was collected by filtration, washed with pentane (4 × 10 mL), and dried under oil pump vacuum to give **4a**$^+$TfO$^-$ as a gold powder (0.115 g, 0.142 mmol, 93%), mp 211–213 °C dec. A portion was dissolved in CH_2Cl_2 (4 mL) and layered with ether and heptane (4 and 2 mL). After 24 h, dark orange prisms of **4a**$^+$TfO$^-$ were collected by filtration, washed with pentane (2 × 10 mL), and dried under oil pump vacuum. Anal. Calcd for $C_{32}H_{27}F_3N_2O_4PReS$: C, 47.46; H, 3.36. Found: C, 47.20; H, 3.32.

[(η^5-C_5H_5)Re(NO)(PPh_3)(N=CHCH(CH$_3$)C=CCH=CH-CH=CH)]$^+$TfO$^-$ (4b$^+$TfO$^-$). Complex **2b** (0.037 g, 0.055 mmol), CH_2Cl_2 (5 mL), and HOTf (0.010 mL, 0.11 mmol) were combined in a procedure analogous to that given for **4a**$^+$TfO$^-$. After 5 min, ether (50 mL) was added. The solid was collected by filtration, washed with ether (4 × 10 mL), and dried under oil pump vacuum to give **4b**$^+$TfO$^-$ as a canary-yellow powder (0.035 g, 0.043 mmol, 77%; 14:86 *SS,RR/SR,RS*).[43] Anal. Calcd for $C_{33}H_{28}F_3N_2O_4PReS$: C, 48.17; H, 3.43. Found: C, 48.24; H, 3.49. B. A 5-mm NMR tube was charged with **2b** (0.084 g, 0.12 mmol) and CD_2Cl_2 (0.6 mL), capped with a septum, and cooled to −80 °C (C_2H_5OH/CO_2). Then HOTf (0.021 mL, 0.24 mmol) was added. The tube was immediately transferred to a −80 °C NMR probe. Both ^{1}H and ^{31}P NMR spectra showed complete conversion to **4b**$^+$TfO$^-$ (8:92 *SS,RR/SR,RS*; unchanged after 15 min at room temperature).

[(η^5-C_5H_5)Re(NO)(PPh_3)(N=CHC(CH$_3$)$_2$C=CCH=CH-CH=CH)]$^+$TfO$^-$ (5$^+$TfO$^-$). A Schlenk flask was charged with **2b** (0.176 g, 0.261 mmol), CH_2Cl_2 (3 mL), and a stir bar. Then CH_3OTf (0.0950 mL, 0.839 mmol) was quickly added with stirring. After 3 h, ether (50 mL) was added. The solid was collected by filtration, washed with ether (4 × 10 mL), and dried under oil pump vacuum to give **5**$^+$TfO$^-$ as a yellow powder (0.210 g, 0.251 mmol, 96%), mp 227–232 °C dec. Anal. Calcd for $C_{34}H_{31}F_3N_2O_4PReS$: C, 48.74; H, 3.73. Found: C, 48.96; H, 3.96.

[(η^5-C_5H_5)Re(NO)(PPh_3)(N=CHC(CH$_3$)(C$_2$H$_5$)C=C-CH=CHCH=CH)]$^+$X$^-$ (6$^+$X$^-$). A. A Schlenk flask was charged with **2b** (0.027 g, 0.040 mmol), CH_2Cl_2 (5 mL), and a stir bar. Then C_2H_5OTf (0.011 mL, 0.085 mmol) was quickly added with stirring. After 12 h, ether (50 mL) was added. The solid was collected by filtration, washed with ether (4 × 10 mL), and dried under oil pump vacuum to give **6**$^+$TfO$^-$ as an orange powder (0.032 g, 0.037 mmol, 92%; 65:35 *SS,RR/SR,RS*).[43] B. Complex **2c** (0.041 g, 0.058 mmol), CH_2Cl_2 (5 mL), and CH_3OTf (0.015 mL, 0.13 mmol) were similarly combined. After 4 h, ether (50 mL) was added. An identical workup gave **6**$^+$TfO$^-$ as an orange powder (0.047 g, 0.056 mmol, 96%; 17:83 *SS,RR/SR,RS*). A portion was dissolved in CH_2Cl_2 (4 mL) and layered with ether and heptane (4 and 2 mL). After 24 h, dark orange prisms of **6**$^+$TfO$^-$ were collected by filtration, washed with pentane (2 × 10 mL), and dried under oil pump vacuum (17:83 *SS,RR/SR,RS*). Anal. Calcd for $C_{35}H_{33}F_3N_2O_4PReS$: C, 49.35; H, 3.90. Found: C, 49.33; H, 3.99. C. A Schlenk flask was charged with **2b** (0.113 g, 0.168 mmol), [(η^5-C_5H_5)Re(NO)(PPh_3)(IC_2H_5)]$^+$$BF_4^-$ (**7c**$^+$$BF_4^-$;[21] 0.198 g, 0.252 mmol), CH_2Cl_2 (5 mL), and a stir bar. The mixture was stirred for 30 min and then flash chromatographed on a 20-cm silica gel column with benzene/pentane/CH_2Cl_2 (2:2:1 v/v/v, 250 mL). First (η^5-C_5H_5)Re(NO)(PPh_3)(I) (**8**;[12] 0.0945 g, 0.141 mmol, 84%) eluted as a purple band. A yellow band was eluted with THF (50 mL) and concentrated to 5 mL. Then ether (50 mL) was added. The solid was collected by filtration, washed with ether (4 × 10 mL), and dried under oil pump vacuum to give **6**$^+$$BF_4^-$ as a yellow powder (0.123 g, 0.156 mmol, 93%; 91:9 *SS,RR/SR,RS*). D. Complex **2c** (0.156 g, 0.227 mmol), [(η^5-C_5H_5)Re(NO)(PPh_3)(ICH_3)]$^+$$BF_4^-$ (**7b**$^+$$BF_4^-$;[21] 0.280 g, 0.363 mmol), and CH_2Cl_2 (5 mL) were similarly combined. An identical workup gave **6**$^+$$BF_4^-$ as a yellow powder (0.168 g, 0.213 mmol, 94%; 17:83 *SS,RR/SR,RS*). A portion was dissolved in CH_2Cl_2 (4 mL) and layered with ether and heptane (4 and 2 mL). After 24 h, dark orange prisms of **6**$^+$ BF_4^-·0.5CH_2Cl_2 were collected by filtration, washed with pentane (2 × 10 mL), and dried under oil pump vacuum (17:83 *SS,RR/SR,RS*). Anal. Calcd for $C_{34.5}H_{34}ClBF_4N_2OPReS$: C, 49.80; H, 4.12. Found: C, 49.32; H, 4.04. E. A 5-mm NMR tube was charged with **2c** (0.051 g, 0.074 mL), $CDCl_3$ (0.6 mL), and CH_3I (0.010 mL, 0.16 mmol) and capped with a septum. After 4 days, ^{1}H and ^{31}P NMR spectra showed 27% conversion to **6**$^+$I$^-$ (20:80 *SS,RR/SR,RS*). F. A Schlenk flask was charged with **6**$^+$TfO$^-$ (0.222 g, 0.261 mmol, 17:83 *SS,RR/SR,RS*), $Na^+SbF_6^-$ (0.701 g, 2.71 mmol), acetone (5 mL), and a stir bar. The mixture was stirred for 10 min. Solvent was removed under oil pump vacuum, and the residue was extracted with CH_2Cl_2 (100 mL). The extract was filtered through a Celite plug. The filtrate was concentrated to 25 mL and layered with ether and heptane (75 and 10 mL). After 2 h, yellow needles of **6**$^+$$SbF_6^-$·0.5$O(C_2H_5)_2$ were collected by filtration, washed with ether (2 × 10 mL) and dried under oil pump vacuum (0.191 g, 0.196 mmol, 75%; 17:83

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SS,RR/SR,RS). Anal. Calcd for $C_{36}H_{38}F_6N_2O_{1.5}PReSb$: C, 44.32; H, 3.93. Found: C, 44.04; H, 3.85.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HNCH_2C(CH_3)_2C{=}CCH{=}CH\text{-}CH{=}CH)]^+TfO^-$ (9^+TfO^-). A Schlenk flask was charged with 5^+TfO^- (0.390 g, 0.465 mmol), THF (10 mL), and a stir bar and cooled to −80 °C. Then $LiB(C_2H_5)_3H$ (1.0 M in THF, 0.650 mL, 0.650 mmol) was added with stirring. After 3 h, HOTf (0.0600 mL, 0.678 mmol) was added. After 2 h, a precipitate had formed, and the cold bath was removed. Pentane (40 mL) was added. The solid was collected by filtration, washed with pentane (4 × 50 mL), and dried under oil pump vacuum to give 9^+TfO^- as a yellow powder (0.330 g, 0.393 mmol, 85%; 89:11 *SS,RR/SR,RS* Re,N diastereomers). A portion was dissolved in CH_2Cl_2 (4 mL) and layered with ether and heptane (4 and 2 mL). After 24 h, dark orange prisms of 9^+TfO^- were collected by filtration, washed with pentane (2 × 10 mL), and dried under oil pump vacuum. Anal. Calcd for $C_{34}H_{33}F_3N_2O_4PReS$: C, 48.62; H, 3.96. Found: C, 48.66; H, 3.83.

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCH(CH_3)C(CH_3)_2C{=}C\text{-}CH{=}CHCH{=}CH)$ (11). A 5-mm NMR tube was charged with 5^+TfO^- (0.079 g, 0.094 mmol) and THF-d_8 (0.6 mL), capped with a septum, and cooled to −80 °C. Then CH_3MgCl (3.0 M in THF, 0.15 mL, 0.45 mmol) was added. The tube was immediately transferred to a −80 °C NMR probe. Over the course of 1 h, ^{31}P NMR spectra showed the complete conversion of 5^+TfO^- (19.8 ppm) to **11** (16.4, 14.2 ppm; 95:5 *SS,RR/SR,RS* Re,C diastereomers). Solvent was removed under oil pump vacuum at 0 °C. The residue was cooled to −80 °C, and CD_2Cl_2 was added (NMR data: Table 1).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}NCH_2Ts)]^+TfO^-$ (14^+TfO^-). A. A Schlenk flask was charged with **3** (1.25 g, 1.80 mmol), $C{\equiv}NCH_2Ts$ (0.423 g, 2.17 mmol),[11b] CH_2Cl_2 (15 mL), and a stir bar. The mixture was stirred for 2 h, and pentane (100 mL) was added. The solid was collected by filtration, washed with pentane (4 × 10 mL), and dried under oil pump vacuum to give 14^+TfO^- as a yellow powder (1.50 g, 1.69 mmol, 94%), mp 105−108 °C dec. A portion was dissolved in CH_2Cl_2 (4 mL) and layered with ether and heptane (4 and 2 mL). After 24 h, yellow prisms of $14^+BF_4^-{\cdot}0.5CH_2Cl_2$ were collected by filtration, washed with pentane (2 × 10 mL), and dried under oil pump vacuum. Anal. Calcd for $C_{33.5}H_{30}ClF_3N_2O_6PReS_2$: C, 43.25; H, 3.25. Found: C, 43.38; H, 3.26. IR (cm^{-1}, KBr): ν_{CN} 2150 (m), ν_{NO} 1726 (vs). NMR (CD_2Cl_2): ^1H 7.76 (d, J = 7 Hz, 2H of C_6H_4), 7.55 (m, 9H of 3 C_6H_5), 7.42 (d, J = 7, 2H, of C_6H_4), 7.32 (m, 6H of $3C_6H_5$), 5.63 (s, C_5H_5), 5.59 (d, J = 15, CHH'), 5.14 (d, J = 15, CH*H'*), 2.48 (s, CH_3); $^{13}C\{^1H\}$ 151.2 (d, J = 10.5, *C*=N), PPh_3 at 133.4 (d, J = 11.1, *m*), 132.2 (d, J = 2.7, *p*), 131.8 (d, J = 58.9, *i*), and 129.7 (d, J = 11.4, *o*), C_6H_4 at 147.2 (s), 133.1 (s), 131.4 (s), and 129.4 (s); 121.3 (q, J = 324.1, CF_3), 93.4 (d, J = 1, C_5H_5), 64.8 (s, CH_2), 21.8 (s, CH_3); $^{31}P\{^1H\}$ 13.8 (s). B. A Schlenk flask was charged with (+)-(*S*)-**15** (0.301 g, 0.540 mmol, 98% ee), toluene (5 mL), and a stir bar, and cooled to −45 °C. Then HOTf (0.0480 mL, 0.542 mmol) was added with stirring. After 15 min, $C{\equiv}NCH_2Ts$ (0.129 g, 0.661 mmol) was added. After 2 h, the cold bath was removed. After 1 h, pentane (50 mL) was added with stirring. The solid was collected by filtration, washed with pentane (4 × 10 mL), and dried under oil pump vacuum to give (+)-(*S*)-14^+TfO^- as a yellow powder (0.453 g, 0.510 mmol, 94%; ≥96% ee as assayed by BH_3·THF reduction below), $[\alpha]_{589}^{25}$ 91 ± 2° (*c* = 0.856 mg/mL, $CHCl_3$), mp 118−120 °C dec. Anal. Calcd for $C_{33}H_{29}F_3N_2O_6PReS_2$: C, 44.64; H, 3.29. Found: C, 44.88; H, 3.36.

3,3-Dimethylindoline (13).[30] A Schlenk flask was charged with 9^+TfO^- (0.298 g, 0.355 mmol), $C{\equiv}NCH_2Ts$ (0.139 g, 0.710 mmol), $CHCl_3$ (10 mL), and a stir bar. The solution was stirred at 60 °C for 6 h. Then the mixture was concentrated to 5 mL, and flash chromatographed on a 20-cm silica gel column with benzene/pentane/CH_2Cl_2 (2:2:1 v/v/v, 100 mL; 20-mL fractions). Solvent was removed from fractions 3−5 by rotary evaporation to give **13** as a yellow oil (0.0421 g, 0.286 mmol, 81%). ^1H NMR ($CDCl_3$): 7.04 (d, J = 9, CH), 7.03 (t, J = 9, CH), 6.74 (t, J = 9, CH), 6.64 (d, J = 9, CH), 3.31 (s, CH_2), 1.31 (s, $2CH_3$). HRMS (*m/e*): calcd for $C_{10}H_{13}N$, 147.1049; found, 147.1047. A red band was eluted from the column with THF (30 mL), concentrated to 2 mL, and slowly added to pentane (100 mL) with stirring. The solid was collected by filtration, washed with pentane (4 × 10 mL), and dried under oil pump vacuum to give 14^+TfO^- as a beige powder (0.242 g, 0.273 mmol, 77%).

Reduction of 14^+TfO^-. A. A Schlenk flask was charged with 14^+TfO^- (0.11 g, 0.12 mmol), THF (20 mL), BH_3·THF (1.0 M in THF, 2.0 mL, 2.0 mmol), and a stir bar. The solution was refluxed for 24 h and cooled to room temperature. Then CH_3OH (10 mL) was added with stirring. Solvent was removed by rotary evaporation (90−100 °C), and benzene (25 mL) was added. The mixture was filtered through a silica gel plug. The filtrate was concentrated to 5 mL by rotary evaporation, and hexane (50 mL) was added with stirring. The orange powder was collected by filtration, washed with pentane (4 × 10 mL), and dried under oil pump vacuum to give **15** (0.041 g, 0.074 mmol, 60%). B. Complex (+)-(*S*)-14^+TfO^- (0.12 g, 0.13 mmol; from procedure B) and BH_3·THF (1.0 M in THF, 1.0 mL, 1.0 mmol) were similarly reacted. Then CH_3OH (5 mL) was added with stirring. Solvent was removed by rotary evaporation (25 °C), and benzene (25 mL) was added. The mixture was filtered through a silica gel plug. The filtrate was concentrated by rotary evaporation to give (+)-(*S*)-**15** as a red oil (0.039 g, 0.070 mmol, 54%; 96% ee, HPLC 95:5 v/v hexane/2-propanol, 0.25 mL/min).

Crystallography. Data were collected on a prism of **2c** as outlined in Table 2. Cell constants were obtained from 30 reflections with 10° < 2θ < 20°. The space group was determined from systematic absences ($h0l$ $h + l = 2n + 1$, $0k0$ $k = 2n + 1$) and subsequent least squares refinement. Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied. The structure was solved by standard heavy-atom techniques with the SDP-VAX package.[44] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and included in the final refinement. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[45]

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Supplementary Material Available: Tables of thermal parameters for **2c** (1 page). Ordering information is given on any current masthead page.

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