Synthesis, Structure, and Reactivity of Chiral Rhenium Imine and Methyleneamido Complexes of the Formulas $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(R'')=C(R)R')]^+TfO^-$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}=C(R)R')$

D. Andrew Knight, Michael A. Dewey, Gene A. Stark, Brian K. Bennett, Atta M. Arif, and J. A. Gladysz*

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

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Three syntheses of σ-imine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(R'')=C(R)R')]^+TfO^-$ (**2**) have been developed. Reactions of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**1**) and R′(R)C=NR″ (R/R′/R″ = Ph/Ph/H (**a**), Me/Ph/H (**b**), H/Ph/Me (**c**); 25–110 °C) give **2a–c** (79–88%). Reactions of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_3)]^+TfO^-$ with *n*-BuLi and then R′(R)C=O give **2d–h** (R/R′/R″ = Me/Me/H (**d**), Me/Et/H (**e**), $(-CH_2-)_5$/H (**f**), H/Ph/H (**g**), H/CH=CHMe/H (**h**; after TfOH addition); 56–87%). Reactions of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N\equiv CR')]^+TfO^-$ with R^- and then TfOH give **2b,i,j** (R/R′/R″ = *p*-tol/*p*-tol/H (**i**), H/Me/H (**j**); 78–98%). Reaction of (+)-(*S*)-**1** (98% ee) and **c** gives (+)-(*S*)-**2c** (98% ee; retention). Complexes **2b,c,e,g,h,j** are obtained as (90–81):(10–19), 95:5, 68:32, >99:<1, >99:<1, and >99:<1 mixtures of *E*/*Z* N=C geometric isomers, which do not readily interconvert. Crystallization gives pure (*E*)-**2b,c**. Crystal structures of **2a** and (*E*)-**2c** show identical N=C bond lengths (1.272(5)–1.275(5) Å) but opposite Re—N= conformations. Methyleneamido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}=C(R)R')$ are isolated from reactions of **2a,b** and *t*-BuO^-K^+ (R/R′ = Ph/Ph, Me/Ph; 76–77%) or $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N\equiv CR')]^+TfO^-$ and R^- (R/R′ = Me/Ph, *p*-tol/*p*-tol (**8**); 55–61%). These undergo facile exchange of *E*/*Z* $\ddot{N}$=*C* substituents (**8**, $\Delta G^{\ddagger}$(181.4 K) = 8.9 kcal/mol) and N-methylation.

Transition-metal σ-imine complexes are one of the cornerstones of classical coordination chemistry.[1] However, multidentate imine ligands, in which additional nitrogen or oxygen atom donor groups are present, have traditionally received the greatest emphasis.[1,2] Recently, complexes of simple monodentate imines and low-oxidation-state organometallic fragments have attracted increasing attention.[3-6] These efforts have been prompted, in part, by the finding that coordinated imines are activated toward nucleophilic attack and the ensuing possibilities for diastereoselective or enantioselective additions in chiral coordination environments.[2,3] Furthermore, advances are rapidly being made in the development of asymmetric hydrogenation catalysts for imines.[7] Stable complexes can provide models for key intermediates and reaction steps.

We have conducted extensive studies of adducts of the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) and unsaturated organic molecules.[8-10] Such compounds are easily accessed in enantiomerically pure form, and numerous diastereoselective addition reactions have been discovered. For example, σ methyl ketone complexes of **I** undergo hydride addition to give alkoxide complexes of high diastereomeric purities, and these can in turn be converted to protected alcohols of high enantiomeric purities.[9a] Thus, we sought to synthesize and study the reactivity of analogous ketimine and aldimine complexes.

In this paper, we report three complementary syntheses of chiral rhenium σ-imine complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(R'')=C(R)R')]^+TfO^-$.[11a]

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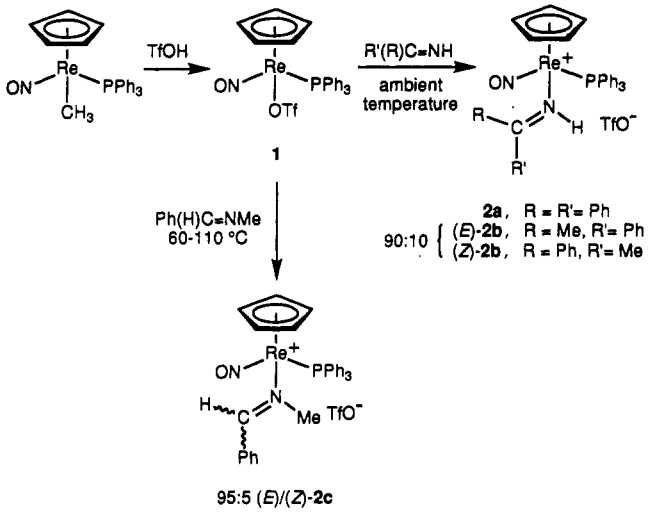
Scheme I. Synthesis of Ketimine and Aldimine Complexes from Free Imines



These feature displacements of triflate ligands by free ketimines and aldimines, condensations of amido ligands with ketones and aldehydes, and additions of nitrile ligands and nucleophiles. Crystal structures of two representative compounds, and the preparation of an optically active compound, are also described. Several methyleneamido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N{=}C(R)R')$, which are intermediates in two of the syntheses, are isolated and characterized. Preparations of aldimine complexes derived from cyclic amines, or nucleophilic or electrophilic additions to coordinated aromatic nitrogen heterocycles, are detailed in companion publications.[12-14]

Results

1. Syntheses from Free Imines. In earlier work, the triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**1**)[15] was shown to react with amines and aromatic nitrogen heterocycles (L) to give adducts of the type $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+TfO^-$.[16] Thus, **1** was generated from the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ and TfOH in toluene at −45 °C as previously described. Then, 3–5 equiv of the representative imines $Ph_2C{=}NH$ (**a**), Ph(Me)C=NH (**b**), and Ph(H)C=NMe (**c**) was added (Scheme I). The samples were kept at room temperature for 1–2 h. The reactions with *N*-protio imines **a,b** were complete, as assayed by ^{31}P NMR. However, that with the *N*-methyl imine **c** required heating at 60–110 °C. Workup gave the adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(R'')=C(R)Ph)]^+TfO^-$ (**2a–c**) in 79–88% yields as orange or yellow powders.

Complexes **2a–c**, and all new compounds isolated below, were characterized by NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy (Table I). They either gave correct microanalyses or could be crystallized to samples that did. The N=C moieties exhibited downfield ^{13}C NMR resonances (178–186 ppm) that were coupled to phosphorus ($^3J_{CP}$ = 2–3 Hz). For **2a**, the chemical shift was 6.3 ppm downfield from that of the free imine (177.0 ppm, $CDCl_3$). The aldimine complex **2c** gave a N=CH ^1H resonance at δ 8.41. The HN=C ^1H resonances of **2a,b** were further downfield (δ 10.98–11.63) and were broadened. The ^{31}P NMR chemical shift and IR ν_{NO} values (17.0–18.4 ppm; 1675–1679 cm^{-1}) were similar to those of the corresponding σ-ketone complexes.[9] Curiously, no IR $\nu_{N=C}$ bands were detected (CH_2Cl_2, KBr). A $\nu_{N=C}$ value of 1630 cm^{-1} (w, CH_2Cl_2) has been reported for a close relative of **2c**, the ruthenium complex $[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(\eta^1\text{-}N(Me){=}C(H)Ph)]^+SbF_6^-$.[4] Additional IR data are given below.

Two N=C geometric isomers are possible for the unsymmetrically substituted complexes **2b,c**. We had expected *E* isomers, in which the larger rhenium and phenyl substituents are *trans*, to dominate. Accordingly, **2b,c** formed as 90:10 and 95:5 *E*/*Z* mixtures, respectively.[17,18] Crystallization gave pure (*E*)-**2b,c**. Stereochemistry was confirmed as described below. Toluene-d_8 solutions of **2c** (95:5 and >99:<1 *E*/*Z*) were kept at 100 °C for 48 h. The *E*/*Z* ratios remained constant, showing that the isomers do not readily interconvert. Thus, (*E*)-**2c** must form from the *less* stable *Z* (*cis*) isomer of the free imine. However, *cis*/*trans* isomerizations of free imines are generally facile.[19]

The optically active triflate complex (+)-(*R*)-**1**[15] was analogously generated from TfOH and (+)-(*S*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ of 98% ee. Reaction with the *N*-methyl imine **c** (60 °C; Scheme II) gave (+)-(*S*)-**2c** in 56% yield as a 95:5 *E*/*Z* mixture. Crystallization gave (+)-(*S*)-(*E*)-**2c**, with $[\alpha]^{23}_{589}$ = 314 ± 5° (*c* 1.220, CH_2Cl_2).[20] The product configuration, which corresponds to retention, was assigned by analogy to other substitution reactions of **1**[15,16] and the commonly observed correlation with the sign of $[\alpha]_{589}$ in this series of compounds. We were unable to develop a direct assay for the enantiomeric purity of **2c**. However, complexes of **I** and other nitrogen-donor ligands react with cyanide ion to give the cyanide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**3**), the enantiomeric purity of which can be determined with the chiral NMR shift reagent (+)-Eu(hfc)$_3$.[11,16] Accordingly, reaction of (+)-(*S*)-**2c** and $Et_4N^+CN^-$ in CH_2Cl_2 at room temperature gave (+)-(*S*)-**3** in 87% yield and 98% ee.[21] Hence, the transformations in Scheme II, which originated with a sample of 98% ee, are highly enantioselective.

(11) Abbreviations: (a) TfO^- = $CF_3SO_3^-$; (b) hfc = 3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato.

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(17) (a) All isomer ratios are normalized to 100, and error limits on each integer are ±2; e.g., 95:5 ≡ (95 ● 2):(5 ± 2). (b) The presence of 1% of an *E*/*Z* N=C isomer would be easily detected under the NMR conditions utilized.

(18) (a) Partial NMR data for (*Z*)-**2b** ($CDCl_3$): ^1H (δ) 11.47 (br s, NH), 5.54 (s, C_5H_5), 2.52 (s, Me); $^{31}P\{^1H\}$ (ppm) 17.9 (s). (b) The NMR resonances of (*E*)-**2c** and (*Z*)-**2c** are better resolved in CD_3NO_2 than in $CDCl_3$. Partial data in CD_3NO_2 (*E*/*Z*): ^1H (δ) 8.30/8.35 (q/m, J_{HH} = 1.7 Hz, N=CH), 5.73/5.76 (s/s, C_5H_5), 3.93/3.52 (d/d, J_{HH} = 1.6/1.5 Hz, Me); $^{13}C\{^1H\}$ (ppm) 179.0/179.2 (d/d, J_{CP} = 3.5/3.5 Hz, N=C), 94.2/94.5 (d/d, J_{CP} = 1.5/1.5 Hz, C_5H_5); $^{31}P\{^1H\}$ (ppm) 18.1/17.1 (s/s). Partial data in CD_2Cl_2 (*E*/*Z*): ^1H (δ) 8.28/8.22 (m/m, N=CH), 5.62/5.48 (s/s, C_5H_5); $^{31}P\{^1H\}$ (ppm, −50 °C) 19.0/17.8 (s/s).

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(21) No evidence was observed for cyanide ion addition to the imine ligand of (+)-(*S*)-(*E*)-**2c**. However, aldehyde and ketone complexes of **I** react with cyanide to give cyanohydrin alkoxides.[5b] Experiments with other imine complexes show that the site of attack is influenced by the solvent and counterion.

Table I. Spectroscopic Characterization of New Rhenium Imine and Methyleneamido Complexes

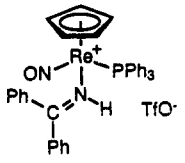
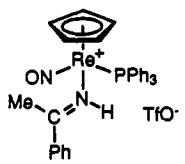
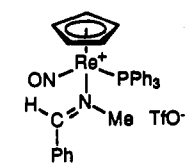
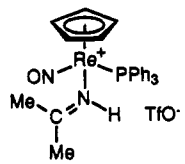
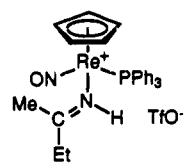
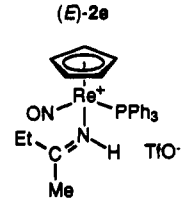
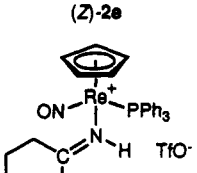
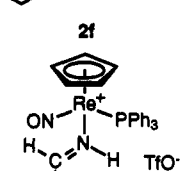
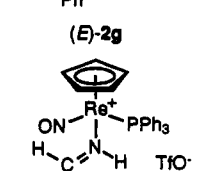
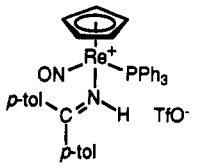
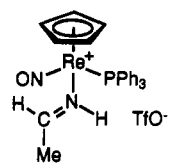
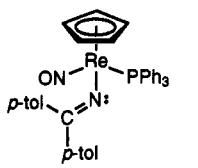
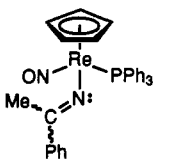
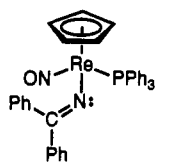
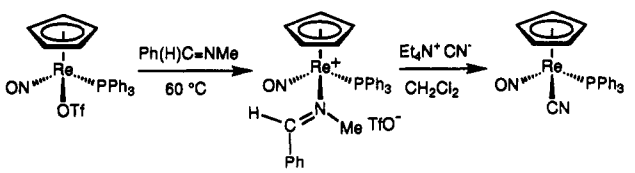
complex	^{1}H NMR (δ)[a]	^{13}C{^{1}H} NMR (ppm)[b,c]	^{31}P{^{1}H} NMR (ppm)[d]/IR ν_{NO} (cm^{-1}, KBr)
 **2a**	11.63 (br s, NH), 7.50–7.33 (m, 12H of 5Ph), 7.34–7.26 (m, 9H of 5Ph), 7.29–7.17 (m, 2H of 5Ph), 6.50 (m, 2H of 5Ph), 5.49 (s, C_5H_5)	183.3 (d, J = 3.0, C=N), PPh at 133.4 (d, J = 11.0, *o*), 131.4 (d, J = 55.6, *i*), 130.9 (d, J = 2.7, *p*), 129.0 (d, J = 10.5, *m*); 2CPh at 138.5 (s), 138.1 (s), 131.9 (s), 131.5 (s), 130.1 (s), 129.7 (s), 128.2 (s), 127.8 (s); 92.5 (s, C_5H_5)	18.1 (s)/1676 vs
 (*E*)-**2b**[e]	10.98 (br s, NH), 7.52–7.43 (m, 9H of 4Ph), 7.41–7.30 (m, 9H of 4Ph), 7.11–7.03 (m, 2H of 4Ph), 5.64 (s, C_5H_5), 2.65 (s, Me)[e]	186.0 (d, J = 2.3, C=N), PPh at 133.7 (d, J = 10.9, *o*), 131.3 (d, J = 2.5, *p*), 131.2 (d, J = 55.4, *i*), 129.3 (d, J = 10.5, *m*); CPh at 136.6 (s), 131.8 (s), 128.6 (s), 127.4 (s); 92.9 (s, C_5H_5), 25.5 (s, Me)	17.0 (s)/1675 vs
 (*E*)-**2c**[e]	8.41 (s, N=CH), 7.52–7.38 (m, 9H of 4Ph), 7.36–7.26 (m, 9H of 4Ph), 7.00–6.99 (m, 2H of 4Ph), 5.68 (s, C_5H_5), 3.80 (d, J_{HH} = 1.5 Me)[e]	178.2 (d, J = 2.7, C=N), PPh at 133.3 (d, J = 10.8, *o*), 131.4 (d, J = 2.2, *p*), 131.0 (d, J = 55.1, *i*), 129.3 (d, J = 10.6, *m*); CPh at 131.6 (s), 129.8 (s), 129.5 (s), 128.4 (s); 92.8 (s, C_5H_5), 55.3 (s, Me)[f]	18.4 (s)/1679 vs
 **2d**	10.87 (br s, NH), 7.50–7.43 (m, 9H of 3Ph), 7.37–7.29 (m, 6H of 3Ph), 5.50 (s, C_5H_5), 2.20 (s, Me), 2.06 (s, Me′)	189.4 (d, J = 2.2, C=N), PPh at 133.4 (d, J = 10.9, *o*), 131.7 (d, J = 55.4 *i*), 131.1 (d, J = 2.3, *p*), 128.9 (d, J = 10.7, *m*); 92.0 (s, C_5H_5), 28.7 (s, Me), 26.3 (s, Me′)	18.0 (s)/1674 vs
 (*E*)-**2e**	10.88 (br s, NH), 7.64–7.61 (m, 9H of 3Ph), 7.50–7.43 (m, 6H of 3Ph), 5.65 (s, C_5H_5), 2.66 (q, J_{HH} = 7.6, C*HH′*), 2.29 (s, N=CMe), 0.85 (t, J_{HH} = 7.6, CH_2*Me*)	195.0 (d, J = 2.2, C=N), PPh at 133.5 (d, J = 10.8, *o*), 132.2 (d, J = 55.5, *i*), 131.2 (d, J = 2.3, *p*), 129.0 (d, J = 10.9, *m*); 92.2 (s, C_5H_5), 36.1 (s, CH_2), 24.2 (s, N=C*Me*), 11.7 (s, CH_2*Me*)	17.8 (s)/1680 vs
 (*Z*)-**2e**	10.88 (br s, NH), 7.64–7.61 (m, 9H of 3Ph), 7.50–7.43 (m, 6H of 3Ph), 5.43 (s, C_5H_5), 2.57 (q, J_{HH} = 7.6, C*HH′*), 2.34 (s, N=CMe), 1.18 (t, J_{HH} = 7.6, CH_2*Me*)	194.6 (d, J = 2.2, C=N), PPh at 133.5 (d, J = 10.8, *o*), 132.2 (d, J = 55.5, *i*), 131.2 (d, J = 2.3, *p*), 129.0 (d, J = 10.9, *m*); 92.0 (s, C_5H_5), 32.7 (s, CH_2), 25.8 (s, N=C*Me*), 10.5 (s, CH_2*Me*)	17.8 (s)/1680 vs
 **2f**	10.62 (br s, NH), 7.53–7.45 (m, 9H of 3Ph), 7.39–7.29 (m, 6H of 3Ph), 5.51 (s, C_5H_5), 2.76 (m, 1H of C_6H_{10}), 2.57 (m, 1H of C_6H_{10}), 2.27 (m, 2H of C_6H_{10}), 1.60 (m, 4H of C_6H_{10}), 1.43 (m, 2H of C_6H_{10})	196.1 (d, J = 2.4, C=N), PPh at 133.7 (d, J = 10.8, *o*), 132.1 (d, J = 55.7, *i*), 131.2 (d, J = 2.4, *p*), 129.1 (d, J = 10.8, *m*); 92.1 (s, C_5H_5), 39.3 (s, N=C*C*), 36.6 (s, N=C*C′*), 27.0 (s, CH_2), 26.8 (s, CH_2), 24.6 (s, CH_2)	17.8 (s)/1671 vs
 (*E*)-**2g**	11.90 (br d, J_{HH} = 20.2, NH), 7.59 (d, J_{HH} = 20.2, N=CH), 7.50–7.41 (m, 9H of 4Ph), 7.41–7.29 (m, 9H of 4Ph), 7.27–7.25 (m, 2H of 4Ph), 5.70 (s, C_5H_5)	172.0 (d, J = 2.3, C=N), PPh at 137.2 (d, J = 10.8, *o*), 131.5 (d, J = 2.5, *p*), 129.4 (d, J = 10.8, *m*), 129.2 (d, J = 57.0, *i*); CPh at 134.1 (s), 132.7 (s), 128.6 (s), 128.4 (s); 93.1 (s, C_5H_5)	21.5 (s)/1678 vs
 (*E,E*)-**2h**	11.37 (br d, J_{HH} = 15.3, NH), 7.50–7.43 (m, 9H of 3Ph), 7.37–7.29 (m, 6H of 3Ph), 7.01 (ddd, J_{HH} = 19.2, 9.7, 1.2, N=CCH), 6.40 (ddd, J_{HH} = 15.3, 9.7, 1.8, N=CH), 5.53 (s, C_5H_5), 5.51 (m, C*H*Me), 2.65 (s, Me)	177.0 (d, J = 2.3, C=N), PPh at: 133.4 (d, J = 10.9, *o*), 131.1 (d, J = 55.4, *i*), 131.7 (d, J = 2.5, *p*), 128.9 (d, J = 10.5 *m*); 123.0 (s, *C*HC=N), 93.0 (s, C_5H_5), 90.0 (s, *C*HMe), 33.0 (s, Me)	20.1 (s)/1684 vs

Table I (Continued)

complex	^{1}H NMR (δ)[a]	^{13}C{^{1}H} NMR (ppm)[b,c]	^{31}P{^{1}H} NMR (ppm)[d]/IR ν_{NO} (cm^{-1}, KBr)
 **2l**	11.87 (s, NH), 7.52–7.28 (m, 19H of 3Ph, 2*p*-tol), 7.02–6.87 (m, 2H, of 3Ph, 2*p*-tol), 6.60–6.46 (m, 2H of 3Ph, 2*p*-tol), 5.62 (s, C_5H_5), 2.44 (s, Me), 2.30 (s, Me′)	182.7 (d, J = 2.3, C=N), PPh at 133.6 (d, J = 10.8, *o*), 131.6 (d, J = 55.0, *i*), 130.8 (s, *p*),128.9 (d, J = 10.6, *m*); 2*p*-tol at 142.4 (s), 140.2 (s), 135.9 (s), 133.9 (s), 129.9 (s), 129.8 (s), 129.1 (s), 128.7 (s); 93.0 (s, C_5H_5), 21.5 (s, Me), 21.4 (s, Me′)	18.5 (s)/1684 vs
 (*E*)-**2j**	11.73 (br d, J_{HH} = 22.8, NH), 7.52–7.41 (m, 9H of 3Ph), 7.38–7.20 (m, 6H of 3Ph), 6.02 (br s, N=CH), 5.30 (s, C_5H_5), 1.92 (br s, Me)	181.4 (d, J = 2.2, C=N), PPh at 134.2 (d, J = 10.8, *o*), 132.0 (d, J = 55.0, *i*), 131.8 (s, *p*), 129.4 (d, J = 10.6, *m*); 92.3 (s, C_5H_5), 24.7 (s, Me)	21.7 (s)/1678 vs
 **8**	7.36–7.21 (m, 15H of 3Ph, 2*p*-tol), 6.97 (s, 8H of 3Ph, 2*p*-tol), 5.51 (s, C_5H_5), 2.33 (s, 2Me)	159.1 (d, J = 3.3, C=N), PPh at: 136.0 (d, J = 52.6, *i*), 134.8 (d, J = 11.0, *o*), 130.7 (s, *p*), 128.9 (d, J = 10.2, *m*); 2*p*-tol at 140.5 (s), 135.5 (s), 129.1 (s), 128.4 (s); 96.2 (s, C_5H_5), 21.2 (s, 2Me)	21.0 (s)/1637 vs
 **9**	7.51–7.34 (m, 9H of 4Ph), 7.34–7.28 (m, 5H of 4Ph), 7.36–7.17 (m, 5H of 4Ph), 7.16–6.90 (m, 1H of 4Ph), 5.52 (s, C_5H_5), 1.70 (d, J_{HP} = 1.5, Me)	155.3 (d, J = 3.2, C=N), PPh at 135.5 (d, J = 52.8, *i*), 135.0 (d, J = 10.6, *o*), 130.8 (s, *p*), 128.8 (d, J = 10.1, *m*); CPh at 142.6 (s), 128.9 (s), 127.6 (s), 125.8 (s); 95.7 (s, C_5H_5), 63.3 (s, Me)	21.6 (s)/1629 vs
 **11**	7.36–7.17 (m, 16H of 5Ph), 7.16–6.90 (m, 9H of 5Ph), 5.51 (s, C_5H_5)	158.8 (d, J = 3.3, C=N), PPh at 135.6 (d, J = 52.5, *i*), 134.5 (d, J = 10.7, *o*), 130.4 (s, *p*), 126.7 (d, J = 10.3, *m*); 2CPh at 142.5 (s), 128.9 (s), 127.5 (s), 126.1 (s), 96.0 (s, C_5H_5)	20.8 (s)/1624 vs

[a] At 300 MHz in $CDCl_3$ (**2a–j**) or THF-d_8 (**8–11**) at ambient probe temperature and referenced to internal $SiMe_4$ unless otherwise noted. All couplings (J) are in Hz. [b] At 75 MHz in $CDCl_3$ (**2a–j**) or THF-d_8 (**8–11**) at ambient probe temperature and referenced to internal $SiMe_4$. All couplings (J) are to ^{31}P and are in Hz. Assignments of resonances to PPh carbons were made as described in: Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. [c] The triflate anion resonances of **2a–j** were observed at 120.2–122.4 ppm (q, J_{CF} = 319.1–320.8 Hz). [d] At 32 or 121 MHz in $CDCl_3$ (**2a–j**) or THF-d_8 (**8–11**) and referenced to external H_3PO_4. [e] Partial data for the Z isomer are given in ref 18. [f] In CD_3NO_2 and referenced to CD_3NO_2 at 62.8 ppm

Scheme II. Synthesis of Optically Active Complexes



(+)-(*R*)-**1** (+)-(*S*)-(*E*)-**2c** (+)-(*S*)-**3**

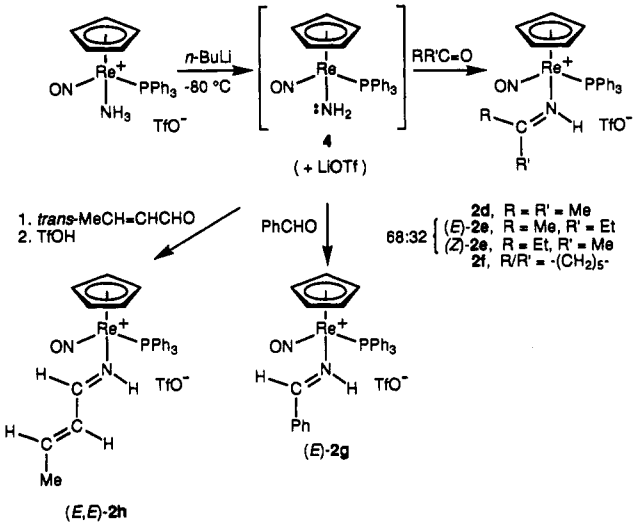
2. Syntheses from Free Ketones and Aldehydes. Faller has shown that cationic cyclopentadienylruthenium ammonia complexes can condense with aldehydes in the presence of base to give *N*-protio aldimine complexes.[4] This procedure allows imine ligands to be assembled within a metal coordination sphere. Thus, the rhenium ammonia complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_3)]^+TfO^-$ was treated with *n*-BuLi in THF at −80 °C to generate the neutral amido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\tilde{N}H_2)$ (**4**) as described earlier (Scheme III).[22] Then 5 equiv of acetone (**d**), 2-butanone (**e**), cyclohexanone (**f**), benzaldehyde (**g**) was added. Workups gave the corresponding *N*-protio imine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(H)=C(R)R')]TfO^-$ (R/R′ = Me/Me (**2d**), Me/Et (**2e**), $(-CH_2-)_5$ (**2f**), H/Ph (**2g**)) in 56–87% yields.

Complexes **2d–g** were characterized analogously to **2a–c**, as summarized in Table I and the Experimental Section. NMR and IR properties were similar to those noted above. In an attempt to locate an IR $\nu_{N=C}$ band, isotopically labeled **2d**-^{15}N was prepared from the corresponding ammonia-^{15}N complex.[16a] However, the IR spectra of **2d** and **2d**-^{15}N were identical between 2000 and 1400 cm^{-1} (CH_2Cl_2). Also, N=C geometric isomers are possible for **2e,g**. Only the *E* isomer of **2g** was detected.[17b] However, **2e** was isolated as a 68:32 *E*/*Z* mixture, consistent with the smaller difference in size of the N=C substituents (Et/Me vs Ph/H). Stereochemistry was assigned as described below. A benzene-d_6 solution of **2e** was kept at 65 °C for 12 h. The *E*/*Z* ratio remained unchanged.

The generation of **2e** was monitored by ^{31}P NMR. Upon

(22) (a) Dewey, M. A.; Knight, D. A.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1992**, *125*, 815. (b) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351.

Scheme III. Synthesis of Ketimine and Aldimine Complexes from an Amido Complex

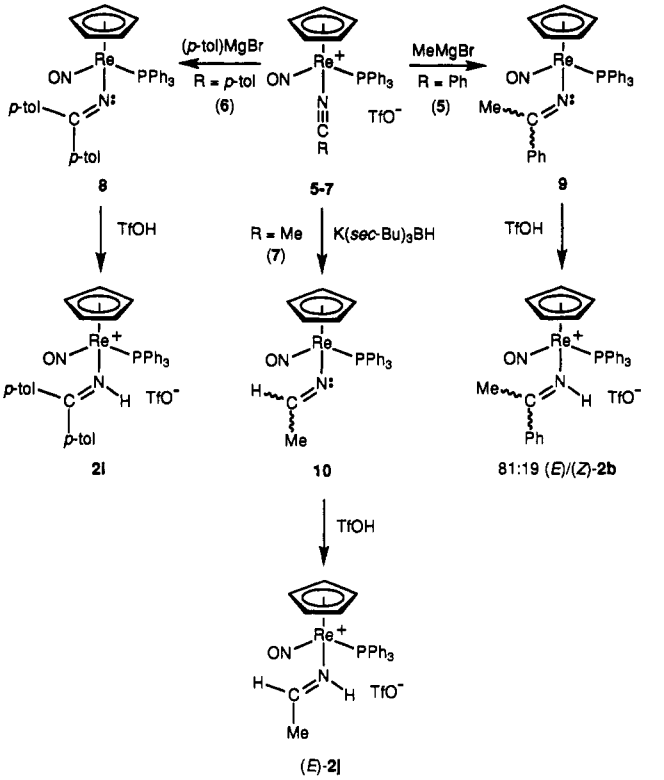


the addition of 2-butanone, amido complex **4** immediately converted to a new species with a resonance at 20.4 ppm. On the basis of data for related compounds isolated below, this was assigned to the methyleneamido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}{=}C(Me)Et)$. When the probe was warmed to 0 °C, the 20.4 ppm resonance slowly disappeared as a broad resonance due to **2e** grew in (17.8 ppm). We have previously shown that amido ligands in complexes such as **4** are much more basic and nucleophilic than organic amines.[22a] Therefore, the N-protonation of a Re-$\ddot{N}$=C(R)R′ linkage, presumably by the water liberated during $\ddot{N}$=C bond formation, or an adventitious source, is not surprising.

The amido complex **4** was also reacted with *trans*-crotonaldehyde (Scheme III). However, in this case the corresponding imine complex **2h** (R/R′ = H/CH=CHMe) formed only after the subsequent addition of TfOH, as assayed by ^{31}P NMR. Only *E* N=C and C=C isomers were detected, and no evidence was observed for any 1,4-addition product. Workup gave (*E,E*)-**2h** in 81% yield. IR spectra showed weak absorptions close to the strong ν_{NO} band, presumably associated with the unsaturated imine ligand (1653, 1640, 1607 cm^{-1}; CH_2Cl_2, KBr).

3. Syntheses from Nitrile Complexes. Coordinated nitriles are activated toward nucleophilic attack.[3,23] In elegant recent work, Templeton has effected the stepwise reduction of tungsten acetonitrile complexes to amine complexes via sequential additions of nucleophiles and electrophiles and isolated several intermediate imine complexes.[3] Thus, reactions of nucleophiles with nitrile complexes of **I** were examined. First, in procedures analogous to those used to prepare **2a,b** (Scheme I), the triflate complex **1** was treated with benzonitrile, *p*-tolunitrile, and acetonitrile. Workups gave the corresponding nitrile complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N{\equiv}CR)]^+TfO^-$ (R = Ph (**5**), *p*-tol (**6**), Me (**7**)) in 82–90% yields as analytically pure yellow powders. Data for these new compounds are summarized in the Experimental Section. Other salts of acetonitrile complex **7** have been characterized previously.[24]

Scheme IV. Synthesis of Ketimine and Aldimine Complexes from Nitrile Complexes



The *p*-tolunitrile complex **6** and *p*-tolMgBr were combined in THF at −80 °C (Scheme IV). As the solution was warmed to room temperature, the color turned to red. A ^{31}P NMR spectrum showed the clean formation of a new product, and workup gave the neutral methyleneamido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}{=}C(p\text{-}tol)_2)$ (**8**) in 55% yield. An analogous reaction of **5** and MeMgBr gave the unsymmetrically substituted compound $(\eta^5\text{-}C_5H_5)(Re(NO)(PPh_3)(\ddot{N}{=}C(Me)Ph)$ (**9**) in 61% yield. Complexes **8** and **9** were characterized analogously to **2**, as summarized in Table I and the Experimental Section. Additional properties are described below.

Reactions of **8** and **9** with TfOH gave the corresponding *N*-protio ketimine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(H){=}C(p\text{-}tol)_2)]^+TfO^-$ (**2i**) and **2b** (81:19 *E*/*Z*) in 93–98% yields after workup (Scheme IV). Similar syntheses of aldimine complexes were also sought. Hence, a suitable hydride nucleophile was required. Additions of $LiEt_3BH$ to THF solutions of acetonitrile complex **7** gave numerous products, as assayed by ^{31}P NMR. However, **7** and $K(sec\text{-}Bu)_3BH$ reacted cleanly at 0 °C to give the methyleneamido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}{=}C(H)Me)$ (**10**), which was isolated in crude form (^{31}P NMR: 25.8 ppm). Subsequent addition of TfOH gave the *N*-protio acetaldimine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(H){=}C(H)Me)]^+TfO^-$ (**2j**) in 78% yield after workup. Only the *E* N=C isomer was detected.[17b]

4. Structures of Imine Complexes. We sought to determine the structures of representative compounds in the solid state. Importantly, the rhenium fragment **I** is a strong π-base, with the high-lying d-orbital HOMO depicted in Chart I.[25] Unsaturated ligands usually adopt conformations that allow substantial overlap of their acceptor orbitals with this donor orbital. Although σ-imine ligands are not regarded as strong π-acceptors, there might

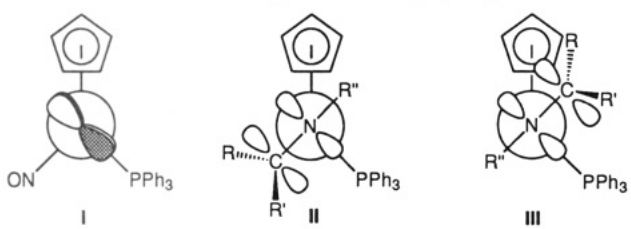
(23) (a) Kim, J. H.; Britten, J.; Chin, J. *J. Am. Chem. Soc.* **1993**, *115*, 3618. (b) Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.* **1990**, *29*, 140 and references therein.

(24) (a) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. (b) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

Table II. Summary of Crystallographic Data for 2a and (*E*)-2c

	2a	(*E*)-2c
Mol formula	$C_{37}H_{31}F_3N_2O_4PReS$	$C_{32}H_{29}F_3N_2O_4PReS$
Mol wt	873.908	811.832
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cell dimens (16 °C)		
a, Å	9.929(2)	12.322(2)
b, Å	13.657(3)	9.865(2)
c, Å	14.080(3)	13.723(1)
α, deg	88.00(2)	103.07(1)
β, deg	93.82(2)	103.51(1)
γ, deg	105.47(1)	82.65(1)
V, Å^3	1744.44	1575.09
Z	2	2
d_{calc}, g/cm^3	1.66	1.71
d_{obs}, g/cm^3	1.65	1.70
cryst dimens, mm	0.35 × 0.28 × 0.15	0.33 × 0.24 × 0.12
diffractometer	Syntex $P\bar{1}$	Enraf-Nonius CAD-4
radiation, Å	Mo Kα (0.710 73)	Cu Kα (1.540 56)
data collecn method	θ–2θ	θ–2θ
scan speed, deg/min	variable, 3.0–8.0	2.0
no. of reflns measd	4924	6309
range/indices (hkl)	0 to 12, –16 to +16, –16 to +16	0 to 14, –11 to +12, –16 to +15
scan range	Kα_1 – 1.0 to Kα_2 + 1.0	0.80 + 0.14 tan θ
2θ limit, deg	3.0–45.0	4.0–130.0
total bkgd time/scan time	0.5	0.0
no. of rflns between stds	98	1 X-ray h
total no. of unique data	4278	5938
no. of obs data, $I > 3\sigma(I)$	4205	5595
abs coeff, cm^{-1}	36.88	88.6
min transmissn, %	50.20	40.97
max transmissn, %	99.70	99.98
no. of variables	442	398
goodness of fit	2.61	1.70
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0342	0.0375
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.0389	0.0411
Δ/σ (max)	0.02	0.007
$\Delta\rho$(max), e/Å^3	0.870 (1.109 Å from Re)	1.165 (1.17 Å from Re)

Chart I. Pyramidal Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ with d-Orbital HOMO (I) and Newman Projections of Idealized Structures of σ-Imine Complexes of I (II, III)



I II III

nonetheless be some electronic preference for the Re–N conformations shown in idealized structures **II** and **III**—which maximize overlap of the N=C π*-orbital lobes on nitrogen. In **II**, the N—Re—N=C torsion angle is 0°, with the *Z* N=*C* substituent (R) directed at the small nitrosyl ligand. However, slight distortions should diminish any interaction. In **III**, the N—Re—N=C torsion angle is 180°, with the *Z* N=*C* substituent projected into the interstice between the large PPh_3 and medium-sized cyclopentadienyl ligands. Three crystal structures of σ-ketone and -aldehyde complexes of **I** have been determined. All exhibit N—Re—O=C torsion angles of 0–21°, similar to **II**.[8d,9a]

Thus, X-ray data were collected on **2a** and (*E*)-**2c** as outlined in Table II. Refinement, which included location of the N=C linkage hydrogens, yielded the structures in Figures 1 and 2. Atomic coordinates and selected bond lengths, bond angles, and torsion angles are summarized in Tables III and IV. Complex **2a** exhibited a N—Re—N=C torsion angle of 21.6(7)°, close to that of idealized conformer **II** (Figure 1, bottom). However, (*E*)-**2c** exhibited a N—Re—N=C torsion angle of 161.6(5)°, close to that of **III** (Figure 2, bottom). The distances between the triflate oxygens and HN=C proton in **2a** ranged from 5.98 Å (O4) to 7.50 Å (O2), far longer than those associated with N···H···O hydrogen bonds.[16a]

Next, the structures of unsymmetrically substituted imine complexes were probed in solution by ^{1}H difference NOE experiments.[26] For example, irradiation of the MeN= resonance of (*E*)-**2c** enhanced the =CPh resonances,[27] but not the =CH resonance—consistent with a *cis* MeN=CPh linkage as established by the crystal structure. Similarly, irradiation of the HN= resonance of **2b** enhanced two =CPh proton resonances (9.6%), but not the =CMe resonance—indicative of a *cis* HN=CPh linkage or *E* isomer. Irradiation of the HN= resonances of the *E* and *Z* isomers of **2e** enhanced the *cis* $=CCH_2$ (5.1%) and =CMe (5.7%) resonances, respectively.

The HN=CH linkages in *N*-protio aldimine complexes **2g,j** exhibited large vicinal couplings ($^3J_{HH}$ = 20.2–22.8 Hz; Table I). By analogy to values reported for other *trans* *N*-protio aldimine complexes ($^3J_{HH}$ > 20 Hz),[3,4] **2g,j** were assigned as *E* isomers. The HN=CH and HC=CH linkages in crotonaldimine complex **2h** also gave large $^3J_{HH}$ values (15.3, 19.2 Hz), consistent with an *E,E* isomer. The

(25) (a) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592. (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (c) Czech, P. T.; Gladysz, J. A.; Fenske, R. F. *Organometallics* **1989**, *8*, 1810.

(26) Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analyses*; VCH: New York, 1989; Chapter 7.

(27) The =CPh and PPh_3 ^{1}H NMR resonances were not resolved. The total integrated enhancement was 1.1%.

Table III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Located Atoms of 2a and (*E*)-2c[a]

atom	*x*	*y*	*z*	*B* (Å²)	atom	*x*	*y*	*z*	*B* (Å²)
				Complex **2a**					
Re	0.21796(3)	0.12069(2)	0.23746(2)	3.168(6)	C21	0.574(1)	0.5377(7)	0.2150(7)	6.6(3)
P	0.3167(2)	0.2673(1)	0.3476(1)	3.37(4)	C22	0.644(1)	0.5052(7)	0.3059(8)	6.8(3)
O1	0.1514(6)	−0.0084(4)	0.3984(4)	5.7(1)	C23	0.5665(9)	0.4243(7)	0.3483(7)	5.4(2)
N1	0.1686(6)	0.0443(4)	0.3325(5)	4.1(1)	C24	−0.1135(7)	0.1280(5)	0.1726(5)	3.3(2)
N2	0.0197(6)	0.1627(4)	0.1746(4)	3.3(1)	C25	−0.1623(7)	0.0369(6)	0.2256(5)	3.9(2)
C1	0.3734(8)	0.0410(6)	0.2057(6)	5.2(2)	C26	−0.1399(9)	−0.0557(6)	0.2046(6)	5.0(2)
C2	0.4292(7)	0.1474(6)	0.1992(6)	4.7(2)	C27	−0.193(1)	−0.1415(8)	0.2509(8)	7.1(3)
C3	0.3246(8)	0.1793(6)	0.1172(6)	4.8(2)	C28	−0.263(1)	−0.1359(9)	0.3182(8)	9.0(3)
C4	0.2071(9)	0.0911(7)	0.0747(6)	5.9(2)	C29	−0.283(1)	−0.047(1)	0.3418(7)	7.9(3)
C5	0.2363(9)	0.0069(7)	0.1277(6)	5.7(2)	C30	−0.2354(9)	0.0429(8)	0.2934(6)	5.9(2)
C6	0.4483(7)	0.2498(5)	0.4665(5)	3.7(2)	C31	−0.2264(7)	0.1781(6)	0.1134(6)	4.1(2)
C7	0.5166(8)	0.1718(6)	0.4738(6)	4.9(2)	C32	−0.3487(8)	0.1204(7)	0.0390(6)	5.0(2)
C8	0.6252(9)	0.1635(7)	0.5632(8)	6.3(3)	C33	−0.451(1)	0.1668(8)	−0.0212(7)	6.7(3)
C9	0.661(1)	0.2287(8)	0.6438(7)	6.8(3)	C34	−0.4337(9)	0.2678(8)	−0.0024(8)	8.0(3)
C10	0.592(1)	0.3046(7)	0.6367(7)	6.3(3)	C35	−0.318(1)	0.3250(8)	0.071(1)	8.2(3)
C11	0.4861(9)	0.3173(6)	0.5492(6)	4.8(2)	C36	−0.2107(9)	0.2795(7)	0.1303(8)	6.2(3)
C12	0.1833(7)	0.3087(5)	0.3888(5)	3.7(2)	C37	0.023(1)	−0.3988(8)	0.1315(9)	8.2(3)
C13	0.1016(8)	0.2389(6)	0.4371(6)	5.1(2)	F1	0.016(1)	−0.4013(7)	0.2269(6)	15.5(3)
C14	−0.0049(9)	0.2618(8)	0.4692(7)	6.4(2)	F2	−0.051(1)	−0.4874(5)	0.0931(9)	16.0(4)
C15	−0.036(1)	0.3533(9)	0.4497(8)	7.9(3)	F3	0.1566(7)	−0.3758(6)	0.1366(6)	11.2(2)
C16	0.045(1)	0.4242(7)	0.4013(8)	7.8(3)	O2	−0.0545(8)	−0.3084(6)	−0.0262(5)	9.1(2)
C17	0.1550(9)	0.4021(6)	0.3703(7)	5.8(2)	O3	−0.2153(7)	−0.3390(7)	0.0746(6)	9.0(2)
C18	0.4202(7)	0.3779(5)	0.2996(6)	3.8(2)	O4	0.0220(9)	−0.2138(5)	0.1300(8)	10.9(3)
C19	0.3494(9)	0.4126(6)	0.2088(6)	5.2(2)	S	−0.0674(3)	−0.3036(2)	0.0738(2)	5.87(6)
C20	0.429(1)	0.4935(7)	0.1680(7)	6.2(3)	H(N2)*	0.055	0.229	0.145	5.0
				Complex (*E*)-**2c**					
Re	0.17886(2)	0.24357(2)	0.41083(2)	2.853(4)	C23	−0.0526(4)	−0.0408(6)	0.1744(5)	3.9(1)
P	0.1091(1)	0.1563(1)	0.2325(1)	2.88(3)	C24	0.4041(4)	0.1640(6)	0.3556(4)	3.4(1)
O1	0.0789(4)	0.5294(5)	0.4048(5)	6.9(2)	C25	0.3721(5)	0.4106(6)	0.4143(5)	4.1(1)
N1	0.1226(4)	0.4129(5)	0.4041(4)	4.0(1)	C26	0.5243(4)	0.1651(6)	0.3552(4)	3.4(1)
N2	0.3360(4)	0.2656(4)	0.3843(3)	3.20(9)	C27	0.5987(5)	0.2424(6)	0.4331(5)	4.0(1)
C1	0.1045(5)	0.0769(7)	0.4588(5)	4.6(1)	C28	0.7116(5)	0.2343(7)	0.4279(6)	4.9(2)
C2	0.0875(6)	0.2029(8)	0.5266(5)	5.4(2)	C29	0.7473(5)	0.1491(7)	0.3459(5)	5.4(2)
C3	0.1972(8)	0.2465(9)	0.5812(5)	6.8(2)	C30	0.6731(5)	0.0697(9)	0.2688(5)	5.7(2)
C4	0.2766(6)	0.1445(8)	0.5454(5)	5.4(2)	C31	0.5617(5)	0.0772(7)	0.2735(5)	4.5(1)
C5	0.2208(5)	0.0412(6)	0.4694(5)	4.5(1)	C32	0.5033(6)	−0.3362(8)	0.1639(6)	5.7(2)
C6	0.2042(4)	0.1441(5)	0.1464(4)	3.1(1)	F1	0.6011(4)	−0.2809(5)	0.1847(4)	8.1(1)
C7	0.2520(5)	0.2653(6)	0.1477(5)	4.2(1)	F2	0.5224(5)	−0.4683(6)	0.1173(4)	9.6(2)
C8	0.3296(5)	0.2623(7)	0.0884(5)	5.2(1)	F3	0.4357(6)	−0.2712(7)	0.0964(4)	11.4(2)
C9	0.3601(5)	0.1384(8)	0.0271(5)	5.2(2)	O2	0.5371(5)	−0.3905(6)	0.3388(4)	7.9(2)
C10	0.3131(5)	0.0187(7)	0.0250(5)	4.8(1)	O3	0.4292(5)	−0.1795(6)	0.3103(5)	7.7(2)
C11	0.2353(5)	0.0200(6)	0.0841(4)	3.8(1)	O4	0.3493(4)	−0.3991(5)	0.2348(5)	7.2(1)
C12	−0.0139(4)	0.2619(6)	0.1786(4)	3.4(1)	S	0.4885(1)	−0.3246(2)	0.2731(1)	4.78(4)
C13	−0.0349(5)	0.2771(7)	0.0775(5)	4.5(1)	H21*	0.3886	0.0546	0.3320	5.0
C14	−0.1320(6)	0.3527(8)	0.0375(5)	5.6(2)	H22*	0.4433	0.4160	0.3945	5.0
C15	−0.2088(6)	0.4082(8)	0.0958(6)	5.4(2)	H23*	0.3886	0.4433	0.5000	5.0
C16	−0.1896(5)	0.3938(7)	0.1959(5)	4.8(2)	H24*	0.3046	0.4707	0.3750	5.0
C17	−0.0914(5)	0.3217(6)	0.2382(5)	4.1(1)	H25*	0.5820	0.3046	0.5000	5.0
C18	0.0606(4)	−0.0182(5)	0.2085(4)	3.0(1)	H26*	0.7773	0.2773	0.4785	5.0
C19	0.1365(5)	−0.1287(6)	0.2338(4)	3.8(1)	H27*	0.8320	0.1386	0.3320	5.0
C20	0.1003(5)	−0.2577(6)	0.2292(5)	4.4(1)	H28*	0.6953	0.0000	0.2089	5.0
C21	−0.0130(5)	−0.2783(6)	0.1969(5)	5.0(1)	H29*	0.5000	0.0000	0.2285	5.0
C22	−0.0881(5)	−0.1724(7)	0.1684(6)	4.9(2)					

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3$ [$a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\gamma)U(1,2) + ac(\cos\beta)U(1,3) + bc(\cos\alpha)U(2,3)$]. The starred atoms were not refined.

$^3J_{HH}$ value for the N=CH—CH= moiety (9.7 Hz) suggested, as analyzed earlier for 1,3-enal and enone complexes of **I**,[10g] a dominant *s-trans* conformation.

Only a few π-imine complexes have been reported in the literature.[6] However, appropriately substituted aldehyde and ketone complexes of **I** give mixtures of π- and σ-isomers.[8d,9c] The π-complexes exhibit IR ν_{NO} values ca. 40 cm^{-1} greater than the corresponding σ-complexes, and as little as 4% of one isomer can be detected in the presence of another.[8d] Of the preceding imine complexes, (*E*)-**2j** would have the greatest likelihood of giving an observable amount of a π-isomer, based upon substituent effects established earlier.[8d] However, (*E*)-**2j** showed only a single IR ν_{NO} band in KBr or CH_2Cl_2.

5. Methyleneamido Complexes. In the course of developing the chemistry in Scheme IV, some interesting properties of methyleneamido complexes **8**–**10** were noted. Although methyleneamido complexes are by no means rare,[28] they have not been as extensively studied as imine complexes. Thus, a few additional experiments were conducted. First, the *N*-protio ketimine complex **2a** was treated with 1.2 equiv of *t*-BuO$^-$K$^+$ in THF (Scheme V). Workup gave the methyleneamido complex (η^5-C_5H_5)Re(NO)(PPh_3)(N=CPh_2) (**11**) in 76% yield. An analogous reaction of **2b** and *t*-BuO$^-$K$^+$ gave **9** (77%), which was independently prepared in Scheme IV. The *N*-protio benzaldimine complex (*E*)-**2g** and *t*-BuO$^-$K$^+$ were combined in an NMR tube in CD_2Cl_2 at −80 °C. A ^{31}P NMR spectrum showed rapid conversion to the methyleneamido

(28) Some lead references: (a) Erker, G.; Frömberg, W.; Krüger, C.; Rabe, E. *J. Am. Chem. Soc.* **1988**, *110*, 2400. (b) Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1052. (c) Alelyunas, Y. W.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406.

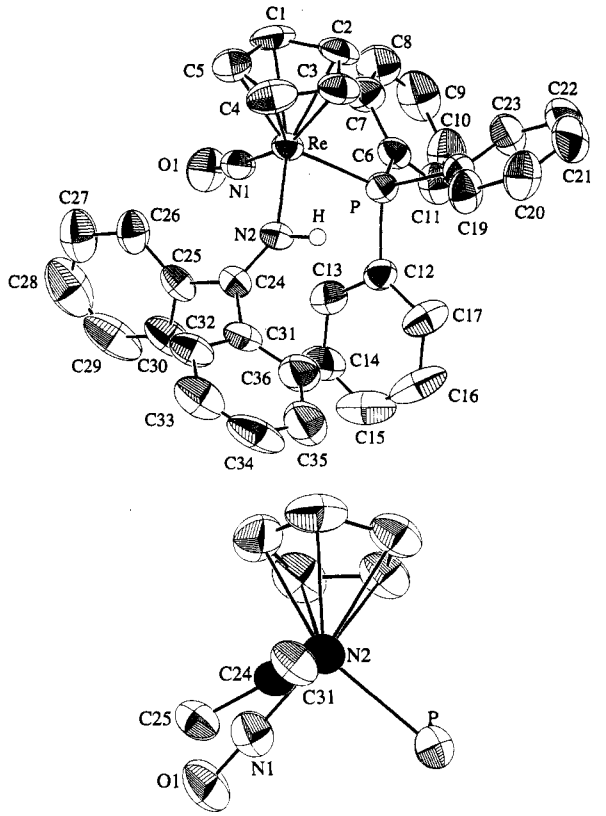


Figure 1. Structure of the cation of ketimine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}NH{=}CPh_2)]^+TfO^-$ (**2a**): (top) numbering diagram; (bottom) Newman-type projection with phenyl rings omitted.

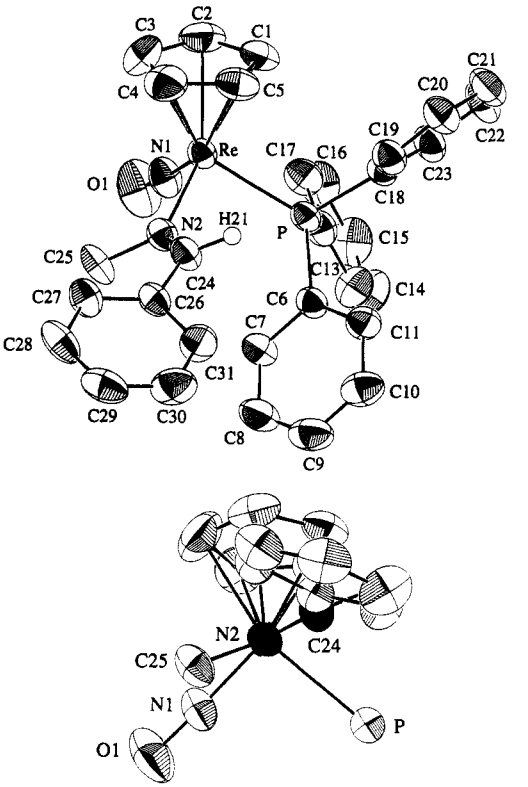


Figure 2. Structure of the cation of aldimine complex (E)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(Me){=}C(H)Ph)]^+TfO^-$ ((*E*)-**2c**): (top) numbering diagram; (bottom) Newman-type projection with phosphine phenyl rings omitted.

complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\bar{N}{=}C(H)Ph)$ (**12**), as evidenced by a resonance at 25.2 ppm. Then, TfOMe (2.0 equiv) was added. Over the course of 15 min at −50 °C, the *N*-methyl benzaldimine complex **2c** (Scheme I) formed in quantitative yield as a 94:6 mixture of *E*/*Z* isomers, as assayed by ^{31}P and ^1H NMR.[18b] These reactions show that the nitrogen lone pairs of **8**–**12** are less basic than *t*-BuO$^-$ but are readily alkylated.

Spectroscopic data for methyleneamido complexes **8**, **9**, and **11** are summarized in Table I. The N=C ^{13}C NMR chemical shifts (155.3–159.1 ppm) were upfield of those of **2a**–**j** (172.0–196.1 ppm), but similarly coupled to phosphorus ($^3J_{CP}$ = 3.2–3.3 Hz). The IR ν_{NO} values (1624–1637 cm^{-1}) were lower than those of **2a**–**j** (1671–1684 cm^{-1}), indicative of enhanced back-bonding into the nitrosyl ligands. These ranges parallel those of the corresponding neutral amido and cationic amine complexes of **I**.[16,22,29]

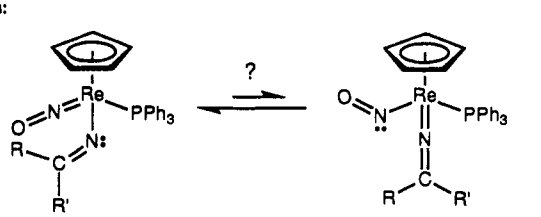
The *E*/*Z* N=*C* substituents of **8** and **11** gave only one set of ^{13}C and ^1H NMR resonances at ambient temperature (Table I). This suggested the operation of a dynamic process that rendered the substituents equivalent. Accordingly, the *E*/*Z* resonances decoalesced at lower temperatures, as illustrated for the *p*-tolyl methyl ^1H resonance of **8** in Figure 3 (δ 2.34/2.45, $\Delta\nu$ = 31.85 Hz, −117.4 °C; T_c = 181.4 ± 0.5 K). Application of the coalescence formula[30] gave a $\Delta G^{\ddagger}(T_c)$ value of 8.9 ± 0.1 kcal/mol for the process that exchanges the *p*-tolyl groups.

No decoalescence or line broadening was observed when ^1H NMR spectra of the unsymmetrically substituted complex **9** were recorded in CD_2Cl_2 at −95 °C. The *E* isomer, in which the larger rhenium and phenyl N=*C* substituents are *trans*, was presumed to dominate—consistent with data reported earlier for the sterically homologous acetophenone complex of **I**.[9a] Accordingly, the protonation of **9** gives mainly (*E*)-**2b** (Scheme IV), which can only be derived from an *E* isomer. Similarly, the methylation of **12** gives predominantly (*E*)-**2c** (Scheme V), which can only be derived from an *E* isomer.

Discussion

1. Scope of Syntheses. Schemes I–IV demonstrate that chiral rhenium imine complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(R'){=}C(R)R')]^+TfO^-$ (**2**) are readily accessed from a variety of precursors. No special attempts were made to optimize yields, and numerous variants of these routes can be envisioned. For example, other functional equivalents of the Lewis acid **I**, such as chlorohydrocarbon complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClR)]^+BF_4^-$,[24] can likely be used in place of the triflate complex **1** in Scheme I. However **1** is soluble in aromatic hydrocarbons, from which cationic products

(29) Note that the ground states of **8**–**12** are formulated with *bent* Re—N=CRR′ linkages and *linear* Re=N=O linkages. Alternatively, **8**–**12** could have linear Re=N=CRR′ linkages and bent Re—N=O linkages:



(i)

Since amido complexes of **I** give similar IR ν_{NO} values and exhibit linear nitrosyl and pyramidal amido ligands in the solid state,[16] the latter possibility is rejected. Furthermore, the sp^2-hybridized methyleneamido ligand lone pairs should be less basic than sp^3-hybridized amido ligand lone pairs. However, the two isomers may be in equilibrium. This, when coupled with rotation about a double bond of the Re=N=CRR′ linkage, provides a mechanism for the exchange of N=CRR′ substituents.

(30) Sandström, J. *Dynamic NMR Spectrometry*; Academic Press: New York, 1982; Chapter 7.

Table IV. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in 2a and (*E*)-2c[a]

2a		(*E*)-2c	
Re–N2	2.112(3)	Re–N2	2.097(3)
Re–P	2.364(1)	Re–P	2.393(1)
Re–N1	1.778(4)	Re–N1	1.739(4)
N1–O	1.182(5)	N1–O	1.204(5)
Re–C1	2.265(5)	Re–C1	2.266(5)
Re–C2	2.261(4)	Re–C2	2.279(5)
Re–C3	2.283(5)	Re–C3	2.289(5)
Re–C4	2.305(5)	Re–C4	2.301(5)
Re–C5	2.309(5)	Re–C5	2.273(5)
N2–C24	1.272(5)	N2–C24	1.275(5)
N2–H(N2)	1.004	N2–C25	1.492(5)
C24–C25	1.477(6)	C24–C26	1.484(5)
C24–C31	1.484(6)		
P–C6	1.825(5)	P–C6	1.824(4)
P–C12	1.821(5)	P–C12	1.829(4)
P–C18	1.825(5)	P–C18	1.829(4)
N2–Re–P	90.6(1)	N2–Re–P	91.3(1)
N2–Re–N1	98.3(2)	N2–Re–N1	96.7(2)
P–Re–N1	91.3(1)	P–Re–N1	93.2(1)
Re–N1–O1	172.4(4)	Re–N1–O1	175.0(4)
Re–N2–C24	136.2(3)	Re–N2–C24	124.4(3)
Re–N2–H(N2)	101.5	Re–N2–C25	115.4(3)
C24–N2–H(N2)	122.1	C24–N2–C25	119.8(4)
N2–C24–C25	122.3(4)	N2–C24–C26	128.7(4)
N2–C24–C31	119.9(4)	N2–C24–H21	127.2
C25–C24–C31	117.9(4)	C24–C26–C27	123.6(4)
C24–C25–C26	120.2(4)	C24–C26–C31	116.2(4)
C24–C25–C30	119.5(5)	C26–C27–C28	119.8(5)
C24–C31–C32	118.7(5)	C26–C31–C30	119.7(5)
C24–C31–C36	121.0(5)	C27–C26–C31	120.2(1)
		C27–C28–C29	119.5(5)
		C28–C29–C30	120.6(5)
		C29–C30–C31	120.1(5)
P–Re–N2–C24	−113.0(7)	P–Re–N2–C24	68.2(4)
P–Re–N2–H(N2)	63.2	P–Re–N2–C25	−119.4(4)
N1–Re–N2–C24	−21.6(7)	N1–Re–N2–C24	161.6(5)
N1–Re–N2–H(N2)	154.6	N1–Re–N2–C25	−26.1(4)
Re–N2–C24–C25	2(1)	Re–N2–C24–C26	166.1(4)
Re–N2–C24–C31	−176.5(5)	Re–N2–C24–H21	−7.9
H(N2)–N2–C24–C25	−173.6	C25–N2–C24–H21	−180.0
H(N2)–N2–C24–C31	8	C25–N2–C24–C26	−5.9(8)

[a] Since hydrogen atom positions were not refined, estimated standard deviations are not given for the corresponding metrical parameters.

such as **2a–c** are easily precipitated. Also, preliminary NMR experiments show that nitrile complexes of **I** can undergo cyanide ion addition to give functionalized methyleneamido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\dot{N}{=}C(R)CN)$.

In companion studies that will be reported separately, cyclic amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{NCH_2(CH_2)_{n-2}})$ have been found to react with $Ph_3C^+X^-$ to give the corresponding cyclic aldimine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{N{=}CH(CH_2)_{n-2}})]^+X^-$ (n = 4–7).[12] Related cyclic aldimine complexes have been isolated from the sequential addition of nucleophiles and electrophiles to an isoquinoline complex of **I**[13] and from reactions of *N*-pyrrole and indole derivatives with electrophiles.[14]

Scheme II establishes both the availability of imine complexes **2** in enantiomerically pure form and their configurational stability. Further, nitrile complexes of **I** are also easily prepared in enantiomerically pure form.[15,24] Thus, the reactions in Scheme IV can also likely be used to synthesize optically active imine complexes. Although amido complexes such as **4** (Scheme III) can be generated in enantiomerically pure form, they slowly lose configuration at room temperature.[13,22b] However, since **4** rapidly condenses with aldehydes and ketones, the potential for racemization appears minimal. Importantly, many of the

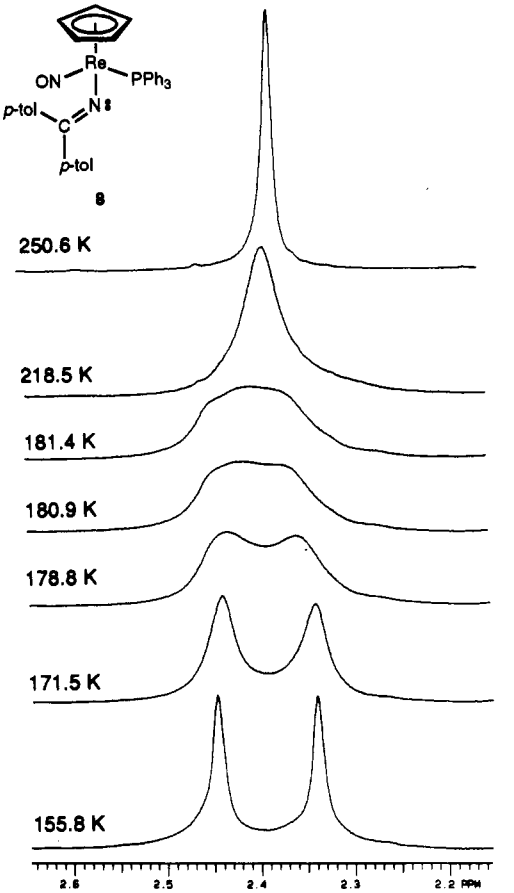
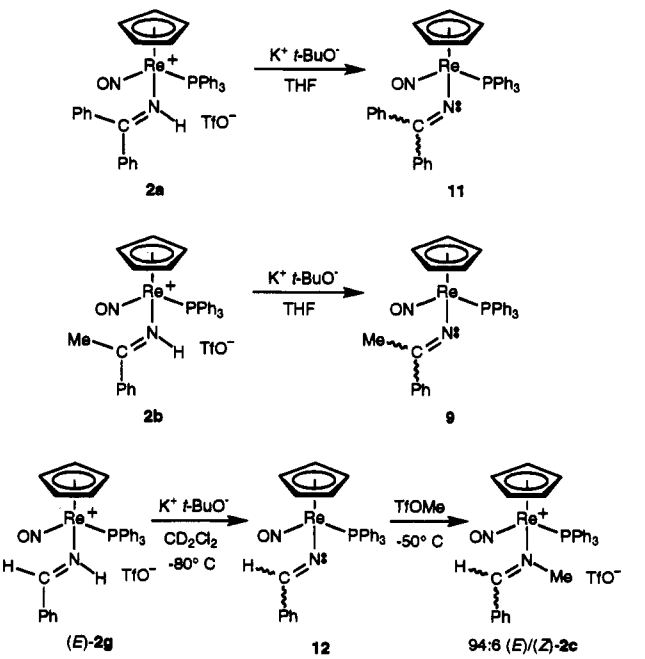


Figure 3. Variable-temperature ^1H NMR spectra of **8** (methyl resonance region).

Scheme V. N-Deprotonation and N-Methylation of Imine Complexes



preceding compounds undergo highly diastereoselective nucleophilic additions, as will be detailed in future reports.[31] Since most nitrogen-donor ligands are easily detached from **I**,[13,16] there is considerable potential for the enantioselective synthesis of organic amines.

2. Structural Properties. As illustrated in the bottom portions of Figures 1 and 2, crystalline **2a** and (*E*)-**2c** adopt

(31) Stark, G.; Knight, D. A.; Gladysz, J. A., manuscript in preparation.

opposite imine ligand conformations. These can be approximated by **II** and **III** (Chart I), although the N=C linkage is rotated ca. 20° in a clockwise direction in each case. The former has precedent in α-ketone and -aldehyde complexes of **I**.[8d,9a] The latter has precedent with the sterically related vinyl complex (*E*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH=$CHCH_2Ph$), which exhibits a ON—Re—C=C torsion angle of 175.5° in the solid state.[32] A cyclic aldimine complex of **I**, in which the N=C moiety is flanked by two bulky –CH(R)CH_2(TMS) substituents, also adopts a conformation of the type **III** in the solid state.[13]

Compounds need not crystallize in their lowest energy conformations. However, the limited data available do suggest a trend. Specifically, in *N*-protio imine complexes of **I**—such as **2a**—the bulkiest group on the ligating nitrogen is the =CHR or CRR′ moiety. The interstice between the small nitrosyl and medium-sized cyclopentadienyl ligands can best accommodate a large substituent. Hence, imine ligand conformations of the type found in Figure 1 should be more probable. However, in *cis* N-alkyl aldimine complexes of **I**—such as (*E*)-**2c**—only the small hydrogen of the =CHR group is directed toward the rhenium fragment. Thus, the N-alkyl substituent is likely to have a larger *effective* size, and imine ligand conformations of the type found in Figure 2 should be more probable.

The Re—N=C bond angles in **2a** and (*E*)-**2c** (136.2(3)–124.4(3)°) are similar to the Re—O=C bond angles in σ-ketone and -aldehyde complexes of **I** (138.3(4)–129.5(4)°).[8d,9a] The N=C bond lengths (1.272(5)–1.275(5) Å) are close to those of free benzaldimines Ph(H)C=NR (R = Ph, 1.286(8) Å; R = Me, 1.284(10) Å)[33a] and much shorter than the N—C bond length in methylamine (1.465(2) Å).[33b] In **2a**, the N=C bond makes 50.2 and 51.1° angles, respectively, with the least-squares planes of the *Z* and *E* phenyl rings. This indicates a significant loss of conjugation and can be attributed to steric interactions between the ortho hydrogens of the two phenyl rings and between the nitrosyl ligand and the *Z* phenyl ring. Analogous but less pronounced distortions occur in diaryl ketones, such as *p,p′*-dimethoxybenzophenone.[34] In (*E*)-**2c**, the angle of the N=C bond and the least-squares plane of the phenyl substituent is 40.2°. This can be ascribed to steric interactions between the ortho phenyl hydrogens and the *cis N*-methyl group.

Faller has prepared a ruthenium carbonyl analog of **2c**, [(η^5-C_5H_5)Ru(CO)(PPh_3)(η^1-N(Me)=C(H)Ph)]$^+SbF_6^-$.[4] Interestingly, ^{1}H NOE experiments suggest a *Z* N=C isomer, with the ruthenium and phenyl groups *cis*—opposite to the configuration indicated by X-ray and NOE data for the major isomer of **2c**. Faller has also crystallographically characterized several forms of the *N*-protio benzaldimine complex (*E*)-[(η^5-C_5H_5)Ru(PPh_3)$_2$(η^1-NH=C(H)Ph)]$^+PF_6^-$. However, these structures are complicated by ligand or solvate disorder.

3. Other Properties. No evidence is observed for any dynamic equilibria involving imine complexes **2a–j**. The *E* and *Z* N=C substituents in the symmetrically substituted complexes **2a,d,f,i** give distinct ^{1}H and ^{13}C NMR resonances (Table I). No coalescence has yet been found at elevated temperatures. The *E*/*Z* isomer ratios of unsymmetrically substituted complexes **2b,c,e,g,h,j** are unaffected by heating. Although a means of equilibrating *E*/*Z* isomers would provide valuable thermodynamic data,[35] their separability and independent stability is advantageous from the standpoint of controlling the stereochemistry of subsequent addition reactions.

In contrast, the methyleneamido complexes **8–12** undergo facile exchange of *E*/*Z* N=C substituents (8.9 kcal/mol, **8**). Other methyleneamido complexes, many of which have essentially linear M=N=C linkages, show analogous behavior.[28] The *E*/*Z* O=*C* substituents of related cationic ketone complexes, [(η^5-C_5H_5)Re(NO)(PPh_3)(η^1-O=CR_2)]$^+X^-$, are even more rapidly exchanged (6–7 kcal/mol, R = Me, Et).[9a,b] Due to the chirality of the rhenium fragment (and potential for π-binding), there is a particularly complex array of exchange mechanisms possible for **8–12**. Most are similar to those previously analyzed for the ketone complexes,[9a,b] but additional variants are possible.[29] Also, detailed mechanistic studies of other N=C bond isomerization processes have been reported.[19c,d,28a] Finally, since the rhenium methyleneamido complexes give higher *E*/*Z* substituent exchange barriers than rhenium ketone complexes, they may prove to be useful models for ketone complexes in cases where equilibrium data or activation parameters cannot be obtained.

In summary, we have developed three complementary syntheses of the chiral imine complexes **2**. Fundamental spectroscopic and structural properties, and the availability of enantiomerically pure complexes, have been established. Related methyleneamido complexes have also been isolated and selected acid/base and dynamic properties of both classes of compounds investigated. Additional reactions of **2**,[31] and syntheses of related cyclic aldimine complexes,[12–14] will be described in future reports.

Experimental Section

General Data. Reactions were carried out under dry N_2 atmospheres. IR and NMR spectra were recorded on standard FT instruments as outlined in Table I. Variable-temperature NMR (Figure 3) and difference ^{1}H NOE spectra were acquired as previously described.[36] The latter were recorded at ambient probe temperature in degassed $CDCl_3$ using septum-sealed tubes. Microanalyses were conducted by Atlantic Microlab. Melting points were determined in evacuated capillaries.[37]

Solvents were purified as follows: CH_2Cl_2, distilled from CaH_2; THF, benzene, and hexane, distilled from Na/O=CPh_2; toluene, distilled from Na; pentane, distilled from $LiAlH_4$; ether and $CDCl_3$, used as received; CD_2Cl_2 and THF-d_8, vacuum-transferred from CaH_2. Reagents were obtained as follows: Ph(H)C=NMe (Aldrich), vacuum distilled; Ph(Me)C=NH, prepared by a literature method;[38] *trans*-crotonaldehyde (Aldrich), distilled from $CaSO_4$ and stored over 4A sieves; acetonitrile and *p*-tolunitrile (Aldrich), distilled from CaH_2; Ph_2C=NH, K(*sec*-Bu)$_3$-

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(34) The angles of the O=C bond and the least-squares planes of the aryl rings are 35.3 and 20.0°: Norment, H. G.; Karle, I. L. *Acta Crystallogr.* **1962**, *15*, 873.

(35) for example, the N=*C* substituents of *N*-protio imine complexes might exchange in the presence of suitable bases via intermediate methyleneamido complexes. Exchange could also occur via the abstraction of protons α to the N=C carbon, which would give intermediate enamido complexes (η^5-C_5H_5)Re(NO)(PPh_3)(N(R″)—C(R)=CHR‴), or nucleophile addition/elimination sequences.

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BH, TfOH, TfOMe, benzonitrile (Aldrich), acetone, 2-butanone (EM Science), cyclohexanone, benzaldehyde (Baker), *t*-BuO$^-$K$^+$, Et$_4$N$^+$CN$^-$ (Fluka), used as received; *n*-BuLi, MeMgBr, and (*p*-tol)MgBr (Aldrich), standardized prior to use.[39]

[(η^5-C$_5$H$_5$)Re(NO)(η^1-NH=CPh$_2$)]$^+$TfO$^-$ (2a). A Schlenk flask was charged with (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_3$) (**13**; 0.920 g, 1.65 mmol),[40] toluene (40 mL), and a stirbar and was cooled to −45 °C (CH$_3$CN/CO$_2$). Then, TfOH (0.146 mL, 1.65 mmol) was added with stirring to generate (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(OTf) (**1**).[15] After 5 min, Ph$_2$C=NH (0.829 mL, 4.95 mmol) was added and the cold bath was removed. After 2 h, some precipitate had formed, and ether (40 mL) and hexane (150 mL) were sequentially added. The solid was collected by filtration, washed with hexane, and dried under oil-pump vacuum to give **2a** as an orange powder (1.265 g, 1.447 mmol, 88%), dec pt 205–208 °C. Anal. Calcd for C$_{37}$H$_{31}$F$_3$N$_2$O$_4$PReS: C, 50.85; H, 3.58. Found: C, 50.65; H, 3.53.

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(η^1-NH=C(Me)Ph)]$^+$TfO$^-$ (2b). A. Complex **13** (0.201 g, 0.360 mmol), toluene (10 mL), TfOH (0.0318 mL, 0.360 mmol) and Ph(Me)C=NH (0.429 g, 3.60 mmol) were combined in a procedure analogous to that given for **2a**. After 2 h, hexane (50 mL) was added. The orange solid was collected by filtration and dried under oil-pump vacuum to give **2b** as a spectroscopically pure 90:10 *E*/*Z* mixture (0.247 g, 0.304 mmol, 85%).[17,18] The powder was dissolved in CH$_2$Cl$_2$ (10 mL), and a layer of hexane (40 mL) was added. After 3 days, a mixture of orange plates and yellow needles formed. The former were manually separated to give (*E*)-**2b**·0.75CH$_2$Cl$_2$ (0.155 g, 0.191 mmol, 53%), dec pt 178–179 °C. Anal. Calcd for C$_{32}$H$_{29}$F$_3$N$_2$O$_4$PReS·0.75CH$_2$Cl$_2$: C, 44.93; H, 3.51. Found: C, 45.22; H, 3.48. The presence of the solvate was verified by ^{1}H NMR (δ 5.32, CDCl$_3$, 1.5H).

B. Complex **9** (0.122 g, 0.185 mmol; below), CH$_2$Cl$_2$ (5 mL), and TfOH (0.0160 mL, 0.185 mmol) were combined in a procedure analogous to that given for **2i**. A similar workup gave **2b** as a spectroscopically pure orange powder (0.147 g, 0.181 mmol, 98%; 81:19 *E*/*Z*).

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(η^1-N(Me)=C(H)Ph)]$^+$TfO$^-$ (2c). A. Complex **13** (5.00 g, 8.96 mmol), toluene (300 mL), TfOH (0.793 mL, 8.96 mmol), and Ph(H)C=NMe (5.523 mL, 44.81 mmol) were combined in a procedure analogous to that given for **2a**. The flask was placed in a 110 °C bath, and an orange precipitate began to form. After 6 h, the mixture was cooled to room temperature. The orange solid was collected by filtration and washed with hexane to give **2c** as a spectroscopically pure 95:5 *E*/*Z* mixture (5.70 g, 7.03 mmol, 79%).[18] A portion was crystallized (acetone/hexane, diffusion, −20 °C) to give (*E*)-**2c** as orange prisms, mp 214–216 °C dec. Anal. Calcd for C$_{32}$H$_{29}$F$_3$N$_2$O$_4$PReS: C, 47.34; H, 3.60. Found: C, 47.39; H, 3.69.

B. Complex (+)-(*S*)-**13** (1.72 g, 3.08 mmol; 98% ee),[40] toluene (100 mL), TfOH (0.272 mL, 3.077 mmol), and Ph(H)C=NMe (1.90 mL, 15.4 mmol) were combined in a procedure analogous to that given for **2c**. The flask was placed in a 60 °C bath. After 12 h, a similar workup gave an orange powder (1.41 g, 1.74 mmol, 56%; 95:5 *E*/*Z*), which was crystallized from CH$_2$Cl$_2$/hexane to give (+)-(*S*)-(*E*)-**2c** as orange prisms (0.900 g, 1.11 mmol, 36%), mp 214–217 °C dec, $[\alpha]^{23}_{589}$ = 314 ± 5° (*c* 1.220, CH$_2$Cl$_2$; 98% ee as assayed below).[20] Anal. Calcd for C$_{32}$H$_{29}$F$_3$N$_2$O$_4$PReS: C, 47.34; H, 3.60. Found: C, 47.30; H, 3.58.

C. A 5-mm NMR tube was charged with (*E*)-**2g** (0.028 g, 0.035 mmol) and capped with a septum. Then, CD$_2$Cl$_2$ (0.8 mL) was added, and the sample was cooled to −80 °C. *t*-BuO$^-$K$^+$ (0.040 mL, 0.040 mmol, 1.0 M in THF) was added, and the tube was transferred to a −80 °C NMR probe. Data were acquired, and TfOMe (0.008 mL, 0.07 mmol) was subsequently added, to give **2c** (94:6 *E*/*Z*) as described in the text.

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(η^1-NH=CMe$_2$)]$^+$TfO$^-$ (2d). A Schlenk flask was charged with [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(NH$_3$)]$^+$TfO$^-$ (**14**; 0.176 g, 0.248 mmol),[16a] THF (10 mL), and a stirbar and was cooled to −80 °C. Then, *n*-BuLi (0.157 mL, 0.248 mmol; 1.58 M in hexane) was added with stirring to generate (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(N̈H$_2$) (**4**).[22] After 10 min, acetone (0.091 mL, 1.24 mmol) was added and the cold bath was removed. After 1 h, the solvent was removed under oil-pump vacuum and the residue extracted with benzene (20 mL). The extract was filtered through a Celite plug and concentrated to ca. 5 mL. Hexane (50 mL) was added, and the resulting precipitate was collected by filtration, washed with hexane, and dried under oil-pump vacuum to give **2d** as a bright yellow powder (0.149 g, 0.199 mmol, 80%), mp 226–227 °C dec. Anal. Calcd for C$_{27}$H$_{27}$F$_3$N$_2$O$_4$PReS: C, 43.25; H, 3.63. Found: C, 43.13; H, 3.62.

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(η^1-NH=C(Me)Et)]$^+$TfO$^-$ (2e). Complex **14** (0.157 g, 0.221 mmol), THF (10 mL), *n*-BuLi (0.140 mL, 0.221 mmol), and 2-butanone (0.100 mL, 1.112 mmol) were combined in a procedure analogous to that given for **2d**. An identical workup gave **2e** as a yellow powder (0.095 g, 0.124 mmol, 56%; 68:32 *E*/*Z*), mp 193–197 °C. Anal. Calcd for C$_{28}$H$_{29}$F$_3$N$_2$O$_4$PReS: C, 44.26; H. 3.85. Found: C, 43.40; H, 3.75.

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(η^1-NH=C(CH$_2$)$_4$CH$_2$)]$^+$TfO$^-$ (2f). Complex **14** (0.070 g, 0.099 mmol), THF (10 mL), *n*-BuLi (0.038 mL, 0.099 mmol), and cyclohexanone (0.051 mL, 0.49 mmol) were combined in a procedure analogous to that given for **2d**. After 12 h, the solvent was removed under oil-pump vacuum and the residue extracted with CH$_2$Cl$_2$ (10 mL). The extract was filtered through a Celite plug and concentrated to ca. 2 mL. Ether (50 mL) was added, and the resulting precipitate was collected by filtration, washed with hexane, and dried under oil-pump vacuum to give **2f** as an orange powder (0.056 g, 0.71 mmol, 72%), mp 227–229 °C dec. Anal. Calcd for C$_{30}$H$_{31}$F$_3$N$_2$O$_4$PReS: C, 45.62; H, 3.96. Found: C, 45.71; H, 3.99.

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(η^1-NH=C(H)Ph)]$^+$TfO$^-$ (2g). Complex **14** (0.227 g, 0.320 mmol), THF (10 mL), *n*-BuLi (0.203 mL, 0.320 mmol), and benzaldehyde (0.163 mL, 1.604 mmol) were combined in a procedure analogous to that given for **2d**. An identical workup gave (*E*)-**2g** as an orange powder (0.341 g, 0.277 mmol, 87%), mp 188–191 °C dec.[17b] Anal. Calcd for C$_{31}$H$_{27}$F$_3$N$_2$O$_4$PReS: C, 46.67; H, 3.41. Found: C, 46.44; H, 3.36.

[(η^5-C$_5$H$_5$)Re(NO)PPh$_3$)(η^1-NH=C(H)CH=CHMe)]$^+$TfO$^-$ (2h). Complex **14** (0.206 g, 0.290 mmol), THF (20 mL), *n*-BuLi (0.18 mL, 0.28 mmol), and *trans*-crotonaldehyde (0.026 mL, 0.31 mmol) were combined in a procedure analogous to that given for **2d**. After 30 min, TfOH was added (0.039 mL, 0.305 mmol) with stirring and the cold bath was removed. After 1.5 h, hexanes (20 mL) was added, and the resulting orange precipitate was collected by filtration, washed with hexanes (20 mL), dried under oil-pump vacuum, and crystallized from CH$_2$Cl$_2$/hexanes to give (*E*,*E*)-**2h** as orange-red prisms (0.173 g, 0.234 mmol, 81%), mp 200–203 °C dec.[17b] Anal. Calcd for C$_{28}$H$_{24}$F$_3$N$_2$O$_4$PReS: C, 44.15; H, 3.57. Found: C, 44.10; H, 3.57.

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(N≡CPh)]$^+$TfO$^-$ (5). Complex **13** (0.244 g, 0.437 mmol), toluene (3 mL), and TfOH (0.0387 mL, 0.437 mmol) were combined in a procedure analogous to that given for **2a**. Then, benzonitrile (0.447 mL, 4.37 mmol) was added with stirring. After 12 h, the resulting precipitate was collected by filtration, washed with hexane, and dried under oil-pump vacuum to give **5** as a yellow powder (0.286 g, 0.359 mmol, 82%), mp 169–172 °C dec. Anal. Calcd for C$_{31}$H$_{25}$F$_3$N$_2$O$_4$PReS: C, 46.79; H, 3.17. Found: C, 46.66; H, 3.12. IR (cm^{-1}, KBr): ν_{NO} 1701 (vs). NMR (CDCl$_3$): ^{1}H (δ) 7.55–7.47 (m, 10H of 4Ph), 7.46–7.27 (m, 10H of 4Ph), 5.70 (s, C$_5$H$_5$); ^{13}C{^{1}H} (ppm) 141.4 (s, CN), 134.7, 133.8, 129.0, 109.2 (4 s, CPh), 133.4 (d, J_{CP} = 11.0 Hz, *o*-PPh), 131.6 (d, J_{CP} = 2.4 Hz, *p*-PPh), 131.5, (d, J_{CP} = 56.6 Hz, *i*-PPh), 129.4 (d, J_{CP} = 10.9 Hz, *m*-PPh), 122.2 (q, J_{CF} = 319.9 Hz, CF$_3$), 92.8 (s, C$_5$H$_5$); ^{31}P{^{1}H} (ppm) 15.8 (s).

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(N≡C(*p*-tol))]$^+$TfO$^-$ (6). Complex **13** (0.918 g, 1.64 mmol), toluene (15 mL), TfOH (0.145 mL, 1.64 mmol), and *p*-tolunitrile (1.96 mL, 16.4 mmol) were combined in a procedure analogous to that given for **5**. A similar workup gave **6** as a yellow powder (1.19 g, 1.47 mmol, 89%), mp 188–189 °C dec. Anal. Calcd for C$_{32}$H$_{27}$F$_3$N$_2$O$_4$PReS: C, 47.46; H, 3.36. Found: C, 47.29; H, 3.36. IR (cm^{-1}, KBr): ν_{NO} 1698 (vs). NMR

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($CDCl_3$): ^1H (δ) 7.55–7.40 (m, 9H of 3Ph/*p*-tol), 7.39–7.27 (m, 6H of 3Ph/*p*-tol), 7.25–7.11 (m, 4H of 3Ph/*p*-tol), 5.68 (s, C_5H_5), 2.42 (s, Me); $^{13}C\{^1H\}$ (ppm) 141.7 (s, CN), 146.3, 133.8, 129.8, 106.0 (4 s, CAr), 133.4 (d, J_{CP} = 10.9 Hz, *o*-PPh), 131.6 (d, J_{CP} = 2.3 Hz, *p*-PPh), 131.6 (d, J_{CP} = 56.3 Hz, *i*-PPh), 129.4 (d, J_{CP} = 11.0 Hz, *m*-PPh), 92.7 (s, C_5H_5), 22.0 (s, Me); $^{31}P\{^1H\}$ (ppm) 15.8 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(N≡CMe)]$^+$TfO$^-$ (7). Complex **13** (1.214 g, 2.176 mmol), toluene (30 mL), TfOH (0.193 mL, 2.18 mmol), and acetonitrile (0.568 mL, 10.9 mmol) were combined in a procedure analogous to that given for **5**. A similar workup gave **7** as a yellow powder (1.430 g, 1.950 mmol, 90%), mp 137–141 °C dec. Anal. Calcd for $C_{26}H_{23}F_3N_2O_4PReS$: C, 42.56; H, 3.16. Found: C, 42.47; H, 3.15. IR (cm^{-1}, KBr): ν_{NO} 1701 (vs). NMR ($CDCl_3$): ^1H (δ) 7.55–7.52 (m, 9H of 3Ph), 7.36–7.27 (m, 6H of 3Ph), 5.58 (s, C_5H_5), 2.56 (s, Me); $^{13}C\{^1H\}$ (ppm) 140.3 (s, CN), 133.5 (d, J_{CP} = 11.0 Hz, *o*-PPh), 131.5 (d, J_{CP} = 2.4 Hz, *p*-PPh), 131.4 (d, J_{CP} = 56.4 Hz, *i*-PPh), 129.3 (d, J_{CP} = 11.0 Hz, *m*-PPh), 120.7 (q, J_{CF} = 320.1 Hz, CF_3), 92.1 (s, C_5H_5), 4.5 (s, Me); $^{31}P\{^1H\}$ (ppm) 16.6 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(N̈=C(*p*-tol)$_2$) (8). A Schlenk flask was charged with **6** (0.227 g, 0.280 mmol), THF (10 mL), and a stirbar and was cooled to −80 °C. Then, (*p*-tol)MgBr (0.330 mL, 0.280 mmol; 0.85 M in ether) was added with stirring. The cold bath was removed, and the solution turned red as it warmed. The solvent was removed under oil-pump vacuum and the residue extracted with benzene (10 mL). The extract was filtered through a Celite plug and concentrated to 5 mL. Pentane was slowly added by vapor diffusion. The resulting spherical clusters of small red needles were collected by filtration and dried under oil-pump vacuum to give **8** (0.117 g, 0.155 mmol, 55%), dec pt 176–180 °C. Anal. Calcd for $C_{38}H_{34}N_2OPRe$: C, 60.70; H, 4.56. Found: C, 60.80; H, 4.59.

(η^5-C_5H_5)Re(NO)(PPh_3)(N̈=C(Me)Ph) (9). A. Complex **2b** (0.081 g, 0.099 mmol; 90:10 *E*/*Z*), *t*-BuO$^-$K$^+$ (0.13 g, 0.12 mmol), and THF (3 mL) were combined in a procedure analogous to that given for **11**. An identical workup gave **9** as red needles (0.050 g, 0.076 mmol, 77%), mp 184–186 °C. Anal. Calcd for $C_{38}H_{34}N_2OPRe$: C, 56.27; H, 4.26. Found: C, 56.13; H, 4.29.

B. Complex **5** (0.220 g, 0.276 mmol), THF (10 mL), and MeMgBr (0.092 mL, 0.25 mmol, 3.0 M in ether) were combined in a procedure analogous to that given for **8**. A similar workup gave **9** as red needles (0.112 g, 0.169 mmol, 61%).

(η^5-C_5H_5)Re(NO)(PPh_3)(N̈=CPh_2) (11). A Schlenk flask was charged with **2a** (0.141 g, 0.161 mmol), *t*-BuO$^-$K$^+$ (0.022 g, 0.19 mmol), and a stirbar and was cooled to 0 °C. Then, THF (10 mL) was slowly added with stirring, and a red solution formed. After 1 h, the solvent was removed under oil-pump vacuum and the residue extracted with benzene (6 mL). The extract was filtered through a Celite plug, and hexane was added. The solution was concentrated to a red oil, which was extracted with toluene (6 mL). Pentane was slowly added by vapor diffusion (−20 °C). After 48 h, the resulting clumps of red needles were collected by filtration and dried under oil-pump vacuum to give **11** (0.088 g, 0.12 mmol, 76%), mp 186–187 °C dec. Anal. Calcd for $C_{36}H_{30}N_2OPRe$: C, 59.74; H, 4.18. Found: C, 59.82; H, 4.18.

[(η^5-C_5H_5)Re(NO)(PPh_3)(η^1-NH=C(*p*-tol)$_2$)]$^+$TfO$^-$ (2i). A Schlenk flask was charged with **8** (0.113 g, 0.150 mmol), CH_2Cl_2 (5 mL), and a stirbar and was cooled to 0 °C. Then, TfOH (0.013 mL, 0.15 mmol) was added with stirring. After 10 min, the red solution was concentrated to ca. 2 mL, and hexane was added (20 mL). The resulting precipitate was collected by filtration and dried under oil-pump vacuum (ca. 60 °C, 48 h) to give **2i** as an orange powder (0.126 g, 0.140 mmol, 93%), mp 151–153 °C dec. Anal. Calcd for $C_{39}H_{35}F_3N_2O_4PReS$: C, 51.93; H, 3.91. Found: C, 51.41; H, 3.93.

[(η^5-C_5H_5)Re(NO)(PPh_3)(η^1-NH=C(H)Me)]$^+$TfO$^-$ (2j). A Schlenk flask was charged with **7** (0.283 g, 0.386 mmol), THF (7 mL), and a stirbar and was cooled to 0 °C. Then, K(*sec*-Bu)$_3$BH (0.424 mL, 0.424 mmol; 1.0 M in THF) was added with stirring, and the cold bath was removed. The solution turned orange as it warmed. After 2 h, the solvent was removed under oil-pump vacuum and the residue extracted with toluene (10 mL). The extract with filtered through a 2-cm Celite plug and cooled to 0 °C. Then, TfOH (0.034 mL, 0.386 mmol) was added with stirring, and the solution turned yellow. The cold bath was removed, and a yellow precipitate soon formed. Ether (10 mL) was added, and the solid was collected by filtration and dried under oil-pump vacuum to give (*E*)-**2j** as a yellow powder (0.221 g, 0.301 mmol, 78%), mp 149–151 °C dec.[17b] Anal. Calcd for $C_{26}H_{25}F_3N_2O_4PReS$: C, 42.45; H, 3.42. Found: C, 42.46; H, 3.40.

Reaction of (+)-(*S*)-2c and $Et_4N^+CN^-$. A Schlenk flask was charged with (+)-(*S*)-(*E*)-**2c** (0.108 g, 0.133 mmol; from **13** of 98% ee), CH_2Cl_2 (15 mL), and a stirbar. Then, solid $Et_4N^+CN^-$ (0.031 g, 0.20 mmol) was added with stirring. After 12 h, the solvent was removed under oil-pump vacuum and the residue extracted with THF. The extract was chromatographed on a 2-cm silica gel column (2.5 g, THF). Solvent was removed from a yellow band to give (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CN) ((+)-(*S*)-**3**)[16a] as a yellow powder (0.066 g, 0.116 mmol, 87%; 98% ee, (+)-Eu(hfc)$_3$). NMR and IR properties were identical with those previously reported.

Crystal Structures. A. Hexane was gently layered onto a CH_2Cl_2 solution of **2a**. Orange prisms formed, which were collected by filtration and dried under a N_2 stream. Data were collected as summarized in Table II. Cell constants were obtained from 15 reflections with 20° < 2θ < 27°. The space group was determined from least-squares refinement (no systematic absences). Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied. The structure was solved by standard heavy-atom techniques with the SDP/VAX package.[41] Non-hydrogen atoms were refined with anisotropic thermal parameters. The HN=C hydrogen was located, and the positions of the other hydrogens were calculated. These were added to the structure factor calculations but were not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[42]

B. Orange prisms of (*E*)-**2c** were obtained as described above. The cell constants and space group were analogously determined (25 reflections, 20° < 2θ < 30°). The structure was solved in a comparable manner and included the location of the imine ligand hydrogen atoms (H21–H29).

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Supplementary Material Available: A table of anisotropic thermal parameters for **2a** and (*E*)-**2c** (2 pages). Ordering information is given on any current masthead page.

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