Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters for **1–4** (Tables S1–S4), positional parameters for all atoms (Tables S5–S8), anisotropic thermal parameters (Tables S9–S12), and complete bond distances (Tables S13–S16) and bond angles (Tables S17–S20) and figures showing the structure and atomic numbering scheme for the cation of **3** (Figure S1) and the ^{1}H NMR spectra of the trans and cis isomers of $[ReH_2(mhp)_2(PPh_3)_2]PF_6$ (Figure S2) (78 pages); tables of observed and calculated structure factors (136 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of Chiral Rhenium Amine Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NRR'R'')]^+TfO^-$

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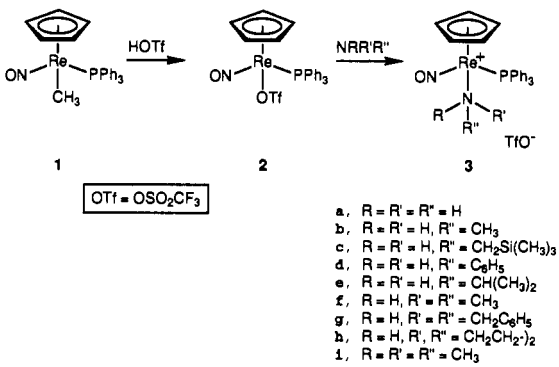
Reactions of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**2**) and (**a**) ammonia, (**b**) methylamine, (**c**) [(trimethylsilyl)methyl]amine, (**d**) aniline, (**e**) isopropylamine, (**f**) dimethylamine, (**g**) dibenzylamine, (**h**) pyrrolidine, and (**i**) trimethylamine give amine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NRR'R'')]^+TfO^-$ (**3**, 55–99%). An analogous reaction of optically active (+)-(*R*)-**2** and methylamine gives (+)-(*S*)-**3b** (79%, >98% ee, retention of configuration). The spectroscopic properties of **3a–i** and isotopomer **3a**-$^{15}NH_3$ are studied in detail. The crystal structure of **3f** (monoclinic, $P2_1/n$, a = 13.925 (2) Å, b = 24.467 (3) Å, c = 8.148 (1) Å, β = 93.398 (4)°, Z = 4) shows P–Re–N–H and ON–Re–N–H torsion angles of −52 and 40°, and a N···H···OTf hydrogen bond (H···O 2.37 (5) Å). Reactions of **3a,b,f** with $(CH_3CH_2)_4N^+CN^-$ and $PPN^+N_3^-$ (PPN = $Ph_3P{=}N{=}PPh_3$) give the substitution products $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**4**, 86–94%) and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N_3)$ (**5**, 61–98%). Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ with $HBF_4{\cdot}OEt_2$ and then $PPN^+N_3^-$ in chlorobenzene also gives **5** (67%). Reaction of (+)-(*S*)-**3b** and $(CH_3CH_2)_4N^+CN^-$ gives (+)-(*S*)-**4** (>98% ee, retention of configuration).

Amines are probably the most widespread σ donor ligands in inorganic coordination compounds, and also occur frequently in organometallic complexes.[1] Further, many biological molecules contain amine functional groups. These can bind to metals in both enzymes and purely synthetic molecules.[2] Metal amine complexes have also received attention as reactivity models for catalytic hydrodenitrogenation (HDN),[3] and their physical properties have been the subject of detailed studies.[4]

The readily available chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) forms adducts with a variety of σ- and π-donor ligands.[5,6] We have studied the chemical and physical properties of the resulting complexes in detail. Many highly diastereoselective reactions have been found which entail formal transfer of the rhenium-centered chirality to a new ligand-based chiral center.[7] As a preface to investigations involving unsaturated nitrogen-containing ligands, we sought to define preparative routes to amine complexes, as well as basic spectroscopic, structural, and chemical properties.

Scheme I. Synthesis of Amine Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NRR'R'')]^+TfO^-$ (**3**)



In this paper, we report (1) high-yield syntheses of racemic and optically active chiral amine complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NRR'R'')]^+ TfO^-$, (2) a thorough characterization of their spectroscopic properties, (3) a crystal structure of a representative complex, and (4) substitution reactions of selected compounds. A portion of this work has been communicated.[8]

Results

1. Synthesis and Spectroscopic Characterization of Amine Complexes. The methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**)[9] and triflic acid (HOTf) were reacted at −45 °C in toluene to generate the triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**2**).[10] Then excesses of (**a**) ammonia, (**b**) methylamine, (**c**) [(trimethylsilyl)methyl]amine, (**d**) aniline, (**e**) isopropylamine, (**f**) dimethylamine, (**g**) dibenzylamine, (**h**) pyrrolidine, and (**i**) trimethylamine were added, as shown in Scheme I. The resulting

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(2) See, for example, the following references. (a) Amino sugars: Yano, S. *Coord. Chem. Rev.* **1988**, *92*, 113. (b) Amino acids: Zahn, I.; Wagner, K. P.; Beck, W. *J. Organomet. Chem.* **1990**, *394*, 601 and references therein. (c) Adenine–uracil base pairs: Ghose, R. *Inorg. Chim. Acta* **1989**, *156*, 303. (d) Roundhill, D. M. Submitted for publication in *Chem. Rev.*
(3) (a) Laine, R. M. *New J. Chem.* **1987**, *11*, 543 and references therein. (b) Fish, R. H.; Baralt, E.; Kim, H.-S. *Organometallics* **1991**, *10*, 1965 and references therein.
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(6) Some recent references: (a) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427. (b) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *Ibid.* **1989**, *111*, 4766. (c) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191. (d) Agbossou, S. K.; Smith, W. W.; Gladysz, J. A. *Chem. Ber.* **1990**, *123*, 1293. (e) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 1079. (f) Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *Ibid.* **1991**, *10*, 2199.
(7) Representative examples: (a) Garner, C. M.; Quirós Méndez, N.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146. (b) Peng, T.-S.; Gladysz, J. A. *Tetrahedron Lett.* **1990**, *31*, 4417. (c) Crocco, G. L.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1990**, *9*, 2819. (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) Dalton, D. M.; Garner, C. M.; Fernández, J. M.; Gladysz, J. A. *J. Org. Chem.* **1991**, *56*, 6823.
(8) Dewey, M. A.; Bakke, J. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1349.
(9) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.
(10) (a) Merrifield, J. H.; Fernández, J. M.; Buhro, W E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022. (b) OTf = OSO_2CF_3.

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mixtures were kept at room temperature for 1–2 h, except for that with dibenzylamine, which was refluxed. Workup gave the amine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NRR'R'')]^+TfO^-$ (**3a–i**) in 55–99% yields as analytically pure yellow or orange powders. Complexes **3a–i** were indefinitely stable in dichloromethane at room temperature.

Amine complexes **3a–i** were characterized by microanalysis (Experimental Section) and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy (Table I). They exhibited IR ν_{NO} values close to those previously reported for related alcohol and ether complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROR')]^+X^-$.[6d] The PPh_3 ^{31}P NMR chemical shifts strongly depended upon the type of amine ligand. Primary amine complexes **3a–e** were the furthest downfield (21.5–20.0 ppm), tertiary amine complex **3i** was the furthest upfield (11.6 ppm), and secondary amine complexes **3f–h** were intermediate (19.1–15.2 ppm).

The hydrogen atoms of primary amines (RNH_2) and the alkyl groups of secondary amines (R_2NH) become diastereotopic upon complexation to a chiral metal fragment. Accordingly, distinct NMR resonances were observed for diastereotopic nitrogen substituents in **3** (Table I). For example, the ^1H NMR chemical shifts of the nitrogen protons of primary amine complexes **3b,c,e** differed by more than 2 ppm, although those of aniline complex **3d** were closely spaced ($\Delta\delta$ 0.04 ppm). Also, dimethylamine complex **3f**, dibenzylamine complex **3g**, and pyrrolidine complex **3h** exhibited separate ^1H and ^{13}C NMR resonances for the methyl and methylene groups.

The phosphorus protons in primary and secondary phosphine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PHRR')]^+X^-$ commonly give $^3J_{HP}$ of 4–5 Hz.[6a,11] However, the nitrogen protons of primary and secondary amine complexes **3a–h** did not exhibit analogous $^3J_{HP}$ coupling. Also, the geminal couplings between diastereotopic nitrogen protons in **3b–e** ($^2J_{HH}$) were not resolved. These features were attributed to ^{14}N quadrupolar broadening, as verified by the ^{15}N labeling experiments described below.

When IR spectra of **3** were recorded in KBr, traces of moisture were often evident (ca. 3448 cm^{-1}, br). This interferred with the assignment of ν_{NH} absorptions. Thus, IR spectra of **3a,c** were recorded in dichloromethane. Two medium-intensity ν_{NH} bands were observed, as summarized in Table I (3343–3279 and 3207 cm^{-1}). These assignments were confirmed as described below. The lower frequency bands were much sharper, in contrast to the pattern commonly found for uncoordinated primary amines.[12a] No δ_{NH} absorptions were observed,[12a] possibly due to overlap with the broad and intense ν_{NO} bands.

Hydrogen bonding can greatly affect IR ν_{NH} absorptions.[13] Furthermore, primary and secondary amine complexes have been previously shown to serve as hydrogen-bond donors.[14,15] Such equilibria are commonly concentration dependent. Thus, IR spectra of 0.14 and 0.014 M dichloromethane solutions of **3a** were recorded. The ν_{NH} absorptions differed by less than 1 cm^{-1}. Identical values were obtained in THF (0.05 M).

2. Crystal Structure of Dimethylamine Complex 3f. In order to aid the interpretation of the preceding spectroscopic properties, a crystal structure of a representative complex was sought. Thus, X-ray data were collected on **3f** under the conditions summarized in Table II and the supplementary material. Refinement (Experimental Section) gave the structures shown in Figure 1. The nitrogen-bound hydrogen (H21) was located, and other hydrogen atom positions were calculated.

The atomic coordinates of **3f** and key bond lengths, bond angles, and torsion angles are summarized in Tables III and IV. In addition, distances between the triflate oxygens and the nitrogen and hydrogen atoms of the dimethylamine ligand were calculated. The closest contacts (O3–N2 and O3–H21) were 3.06 (5) and 2.37 (6) Å, respectively. The latter distance is within the range commonly associated with N··H··O hydrogen bonds[13,14,16] and is shorter than those found in crystalline ammonium triflate (2.49–2.78 Å).[16a]

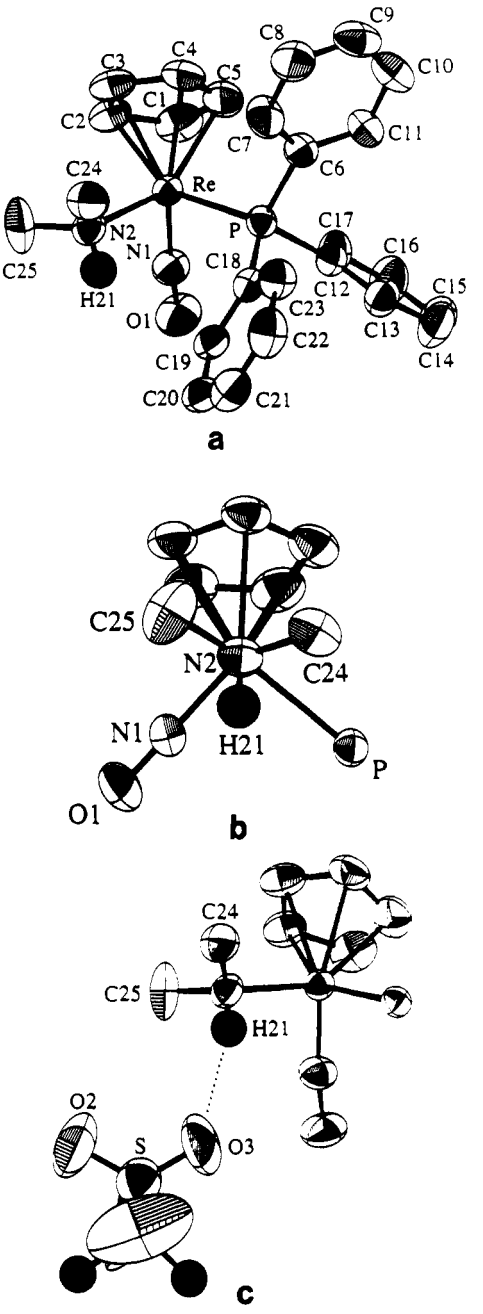

Figure 1. Structure of the cation of the dimethylamine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)_2)]^+TfO^-$ (**3f**): (a) numbering diagram; (b) Newman-type projection with phenyl rings omitted; (c) interaction of the triflate anion with the dimethylamine ligand.

3. Isotopically Labeled and Optically Active Complexes. The isotopically labeled complex **3a**-^{15}N was prepared from $^{15}NH_3$ by a procedure analogous to that shown in Scheme I. The heavier ^{15}N isotope has a nuclear spin (I) of $^1/_2$ and lacks the electrical

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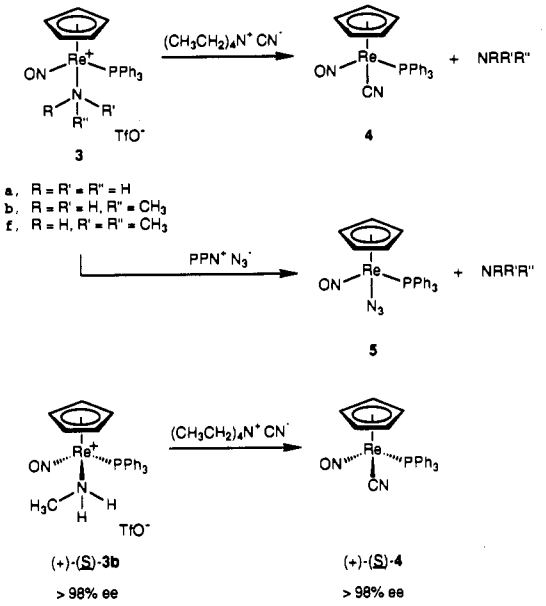
(13) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974.
(14) Osterberg, C. E.; Arif, A. M.; Richmond, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 6903.
(15) Conroy-Lewis, F. M.; Simpson, S. J. *J. Organomet. Chem.* **1990**, *396*, 83.
(16) (a) Gänswein, B.; Brauer, G. *Z. Anorg. Allg. Chem.* **1975**, *425*, 125. (b) For representative N··H··O hydrogen bond lengths in coordination compounds, see: Whuler, A.; Brouty, C.; Spinat, P. *Acta Crystallogr.* **1980**, *B36*, 1267. (c) For N··H··O hydrogen bond lengths in organic crystals, see: Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320. Depending upon the nature of the donor and acceptor, mean H··O distances range from 1.84 to 1.96 Å.

Scheme II. Representative Substitution Reactions of Amine Complexes **3**



quadrupole moment of ^{14}N ($I = 1$). Accordingly, the ^1H NMR spectrum of **3a**-^{15}N exhibited a doublet of doublets for the three nitrogen protons, with clearly resolved coupling to phosphorus ($^3J_{HP}$ = 2.6 Hz, $^1J_{NH}$ = 70.9 Hz). The large $^1J_{NH}$ value enabled the detection of a small amount of **3a**-^{14}N. Integration of this residual bounded the isotopic enrichment as >98%.

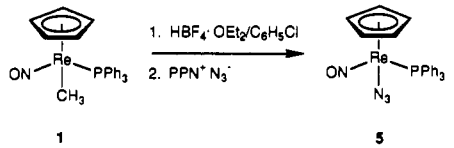
The IR ν_{NH} pattern of **3a**-^{15}N was identical to that of **3a**. However, both absorptions shifted by 7–8 cm^{-1} to lower frequency (3335, 3300 cm^{-1}; CH_2Cl_2). In theory, corresponding $\nu_{^{14}NH}$ and $\nu_{^{15}NH}$ bands should differ by 7 cm^{-1}.[12b] When IR spectra of **3a** and **3a**-^{15}N were overlayed, no other absorptions were shifted more than 1 cm^{-1}.

The ^{15}N NMR spectrum of **3a**-^{15}N was recorded in CD_3NO_2 (−464.4 ppm, q, $^1J_{NH}$ = 70.9 Hz).[17] The low relative sensitivity of ^{15}N necessitated higher than usual sample concentrations (ca. 100 mg/mL) and long acquisition times. A $^{15}N\{^1H\}$ NMR spectrum (−464.4 ppm, s) required considerably less acquisition time. No phosphorus–nitrogen coupling ($^2J_{^{15}NP}$) was detected in either $^{15}N\{^1H\}$ or $^{31}P\{^1H\}$ NMR spectra. For comparison, a $^{15}N\{^1H\}$ NMR spectrum of neat ammonia was also recorded (−383.6 ppm, s; sealed tube, external CD_3NO_2).

We next sought to establish the availability of optically active amine complexes. Thus, the optically active methyl complex (+)-(*S*)-**1**[18] was treated with HOTf and methylamine in a procedure analogous to that in Scheme I. Workup gave the optically active methylamine complex (+)-(*S*)-**3b** in 79% yield, $[\alpha]^{25}_{589}$ 422 ± 10°.[19] The configuration at rhenium, which corresponds to retention, was assigned by analogy to closely related substitution reactions, and the commonly observed correlation with the sign of $[\alpha]_{589}$ for this series of compounds.[5,6a,c,7a,b,d,e,10,11,18] A CH_2Cl_2 solution of (+)-(*S*)-**3b** was kept at room temperature for 6 days. No change in $[\alpha]$ was observed, within experimental error. This establishes a high degree of configurational stability.

4. Reactions of Amine Complexes with Nucleophiles. Complexes **3a,b,f** readily reacted with the cyanide salt $(CH_3CH_2)_4N^+CN^-$ in CH_2Cl_2 at room temperature (Scheme II). Workup gave the previously characterized cyanide complex (η^5-C_5H_5)Re(NO)(PPh_3)(CN) (**4**) in 86–94% yields.[5b] The displaced amines can also be readily recovered from these reaction mixtures, as described elsewhere.[20,21]

Next, analogous reactions were conducted with **3a,b,f** and the azide salt $PPN^+N_3^-$.[22] Workup gave the new azide complex (η^5-C_5H_5)Re(NO)(PPh_3)(N_3) (**5**) in 61–98% yields (Scheme II). A sample of **5** was independently prepared by the sequential reaction of methyl complex **1** with HBF_4·OEt_2 (C_6H_5Cl solvent) and $PPN^+N_3^-$ (67%; eq i). Complex **5** exhibited spectroscopic



(i)

properties (Experimental Section) that were similar to those of cyanide complex **4** and an intense ν_{NNN} band characteristic of azide ligands at 2038 cm^{-1}.[23]

Complex **3f** was similarly treated with the iodide salt $Ph_3PMe^+I^-$. No reaction was observed at room temperature. However, slow substitution occurred in refluxing chlorobenzene (ca. 130 °C) to give the iodide complex (η^5-C_5H_5)Re(NO)-(PPh_3)(I).[10] This nucleophilicity order ($I^- < CN^-, N_3^-$) is opposite to that commonly observed for organic electrophiles.[24]

The displacement of amine ligands by neutral nucleophiles was attempted next. Samples of the [(trimethylsilyl)methyl]amine complex **3c** were dissolved in neat dimethylsulfide and benzyl cyanide. The corresponding substitution products [(η^5-C_5H_5)-Re(NO)(PPh_3)(L)]$^+X^-$ have been previously characterized.[5a,6f] No reactions occurred over the course of 12 h at 80 °C, as assayed by ^{31}P NMR spectroscopy. Over longer time periods, the samples decomposed without substitution.

The racemic cyanide complex **4** and the chiral NMR shift reagent (+)-Eu(hfc)$_3$ (0.5 equiv) were combined in $CDCl_3$, and a ^1H NMR spectrum was recorded. As shown in Figure 2 (supplementary material), the cyclopentadienyl resonances of the two enantiomers exhibited baseline resolution ($\Delta\delta \simeq 0.28$ ppm). Enantiomers of the iron cyanide complex (η^5-C_5H_5)Fe(CO)-(PPh_3)(CN) can be similarly differentiated.[25] However, enantiomers of the azide complex **5** gave only partially resolved cyclopentadienyl resonances.

Next, the optically active amine complex (+)-(*S*)-**3b** and $(CH_3CH_2)_4N^+CN^-$ were reacted in CH_2Cl_2 (Scheme II). Workup gave (+)-(*S*)-**4** in 51% yield, $[\alpha]^{25}_{589}$ 179 ± 4°.[19] The absolute configuration, corresponding to retention at rhenium, was assigned as described above. NMR analysis with (+)-Eu(hfc)$_3$ established an enantiomeric purity of >98% ee (Figure 2). This in turn bounded the enantiomeric purity of (+)-(*S*)-**3b** as >98% ee. The enantiomeric purity of **4** can also be assayed by chiral HPLC, as described elsewhere.[26]

Discussion

The preceding data show that racemic and optically active complexes **3** can be prepared from a variety of amines in high chemical and optical yields. Analogous reactions involving aromatic nitrogen heterocycles have been reported elsewhere.[27]

(17) All ^{15}N NMR chemical shifts are referenced to internal CD_3NO_2 (δ 0.0) unless noted and employ the sign convention described by: von Philipsborn, W.; Müller, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 383.

(18) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(19) (a) Absolute configurations are assigned according to the Baird–Sloan modification of the Cahn–Ingold–Prelog priority rules. The cyclopentadienyl ligand is considered to be pseudoatom of atomic number 30, which gives the priority sequence η^5-C_5H_5 > PPh_3 > OTf > NO > NRR'R'' > CN. Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1. See also: Lecomte, C.; Dusausy, Y.; Protas, J.; Tirouflet, J.; Dormond, A. *J. Organomet. Chem.* **1974**, *73*, 67. (b) All $[\alpha]$ are recorded in CH_2Cl_2 in thermostated cells with *c* (Experimental Section) optimized for each compound on the basis of solubility and light absorption.

(20) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351.

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(22) (a) Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *31*, 645. (b) PPN^+ = $[Ph_3P{=}N{=}PPh_3]^+$.

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(24) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; Table 4.11.

(25) Reger, D. L. *Inorg. Chem.* **1975**, *14*, 660.

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

(27) Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *384*, C29.

Table I. Spectroscopic Characterization of New Rhenium Amine Complexes

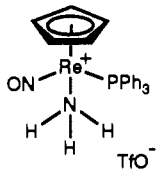
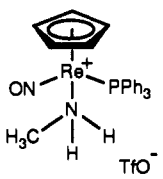
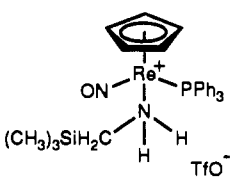
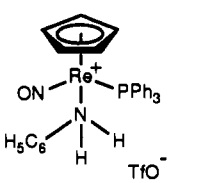
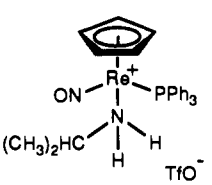
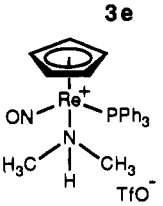
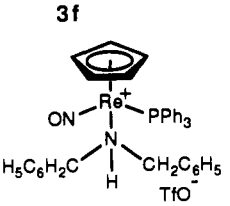
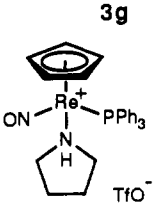
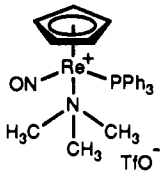
complex	IR (KBr), cm^{-1}	^1H NMR,[a] δ	$^{13}C\{^1H\}$ NMR,[b] ppm	$^{31}P\{^1H\}$ NMR,[c] ppm
 **3a**	ν_{NO} 1698 vs ν_{NH} 3343, 3307 m[d]	7.52–7.49 (m, 9 H of 3 C_6H_5), 7.34–7.26 (m, 6 H of 3 C_6H_5), 5.46 (s, C_5H_5), 4.05 (s, br, NH_3)	PPh_3 at 133.16 (d, J = 11.0, *o*), 131.56 (d, J = 54.4, *i*), 131.27 (d, J = 2.3, *p*), 129.24 (d, J = 10.8, *m*); 120.24 (q, J_{CF} = 319.7, CF_3), 91.07 (d, J = 1.6, C_5H_5)	20.2 (s)
 **3b**	ν_{NO} 1676 vs	7.55–7.45 (m, 9 H of 3 C_6H_5), 7.36–7.27 (m, 6 H of 3 C_6H_5), 5.65 (s, br, NH), 5.50 (s, C_5H_5), 3.57 (s, br, NH′), 2.91 (t, J = 6.0, CH_3)	PPh_3 at 133.07 (d, J = 11.0, *o*), 131.46 (d, J = 2.4, *p*), 131.33 (d, J = 55.0, *i*), 129.33 (d, J = 10.5, *m*); 120.18 (q, J_{CF} = 318.8, CF_3), 91.18 (d, J = 1.5, C_5H_5), 45.60 (d, J = 2.5, CH_3)	20.1 (s)
 **3c**	ν_{NO} 1686 vs ν_{NH} 3279, 3207 m[d]	7.55–7.47 (m, 9 H of 3 C_6H_5), 7.38–7.27 (m, 6 H of 3 C_6H_5), 5.49 (s, 6 H of C_5H_5, NH), 3.28 (m, br, NH′), 2.65 (ddd, J = 5.0, 10.2, 15.0, CH), 2.40 (ddd, J = 3.2, 9.6, 15.0, CH′), −0.10 (s, $(CH_3)_3Si$)	PPh_3 at 133.46 (d, J = 11.0, *o*), 131.74 (d, J = 55.2, *i*), 131.52 (d, J = 2.7, *p*), 129.49 (d, J = 10.8, *m*); 120.41 (q, J_{CF} = 319.9, CF_3), 91.62 (s, C_5H_5), 52.19 (d, J = 2.7, CH_2), −3.12 (s, $(CH_3)_3Si$)	20.3 (s)
 **3d**	ν_{NO} 1681 vs	7.81–7.69 (m, 1 H of 4 C_6H_5), 7.64–7.53 (m, 8 H of 4 C_6H_5), 7.49–7.39 (m, 6 H of 4 C_6H_5), 7.35–7.28 (m, 2 H of 4 C_6H_5), 7.13–7.02 (m, 3 H of 4 C_6H_5), 5.43 (s, C_5H_5), 5.39 (s, br, NH), 5.35 (s, br, NH′)	C_6H_5 at 149.03 (d, J = 2.7, *i*), 129.36 (s, *m*), 125.93 (s, *p*), 119.79 (s, *o*) PPh_3 at 133.42 (d, J = 10.9, *o*), 131.63 (d, J = 2.4, *p*), 131.41 (d, J = 55.1, *i*), 129.49 (d, J = 10.7, *m*); 120.24 (q, J_{CF} = 319.4, CF_3), 91.75 (s, C_5H_5)	20.0 (s)
 **3e**	ν_{NO} 1688 vs	7.56–7.52 (m, 9 H of 3 C_6H_5), 7.37–7.30 (m, 6 H of 3 C_6H_5), 5.49 (s, 6 H of C_5H_5, NH),[e] 3.63 (s, br, NH′), 2.85 (m, CH), 1.15 (d, J = 6.4, CH_3), 0.98 (d, J = 6.4, CH_3')	PPh_3 at 133.44 (d, J = 10.9, *o*), 131.51 (d, J = 2.1, *p*), 131.13 (d, J = 54.4, *i*), 129.34 (d, J = 10.7, *m*); 120.30 (q, J_{CF} = 319.5, CF_3), 91.22 (s, C_5H_5), 57.67 (s, CH), 23.89 (s, CH_3), 22.87 (s, CH_3')	21.5 (s)
 **3f**	ν_{NO} 1696 vs	7.53–7.52 (m, 9 H of 3 C_6H_5), 7.35–7.27 (m, 6 H of 3 C_6H_5), 5.71 (s, br, NH), 5.46 (s, C_5H_5), 2.87 (d, J = 5.5, CH_3), 2.75 (d, J = 5.5, CH_3')	PPh_3 at 133.91 (d, J = 55.0, *i*), 133.37 (d, J = 10.5, *o*), 131.52 (s, *p*), 129.45 (d, J = 10.6, *m*); 120.60 (q, J_{CF} = 320.0, CF_3), 92.44 (s, C_5H_5), 54.44 (d, J = 2.6, CH_3), 54.33 (s, CH_3')	15.2 (s)
 **3g**	ν_{NO} 1690 vs	7.61–7.49 (m, 9 H of 5 C_6H_5), 7.33–7.14 (m, 12 H of 5 C_6H_5), 6.94 (dd, J = 3.5, 5.9, 2 H of 5 C_6H_5), 6.44 (dd, J = 7.9, 2 H of 5 C_6H_5), 5.67 (s, C_5H_5), 4.66 (t, br, NH), 4.55 (d, J = 12.8, 1 H of 2 CH_2),[f] 4.15–3.90 (m, 3 H of 2 CH_2)[f]	C_6H_5 at 135.74 (s, *i*), 135.31 (s, *i*′), 133.68 (s, *m*), 133.54 (s, *m*′), 129.21 (s, *p*), 129.11 (s, *p*′), 128.21 (s, *o*), 125.28 (s, *o*′) PPh_3 at 133.32 (d, J = 10.8, *o*), 131.03 (d, J = 2.5, *p*), 129.95 (d, J = 55.8, *i*), 129.94 (d, J = 11.4, *m*); 92.46 (s, C_5H_5), 69.38 (s, CH_2), 66.38 (s, $C'H_2$)	19.1 (s)
 **3h**	ν_{NO} 1703 vs	7.52–7.49 (m, 9 H of 3 C_6H_5), 7.37–7.30 (m, 6 H of 3 C_6H_5), 5.45 (s, C_5H_5), 5.33 (s, br, NH), 3.44 (m, 1 H of C_4H_9N), 2.88 (m, 1 H of C_4H_9N), 2.75 (m, 1 H of C_4H_9N), 2.49 (m, 1 H of C_4H_9N), 1.64 (m, 4 H of C_4H_9N)	PPh_3 at 134.12 (d, J = 53.7, *i*), 133.27 (d, J = 10.4, *o*), 131.08 (s, *p*), 129.01 (d, J = 10.7, *m*); 120.34 (q, J_{CF} = 319.3, CF_3), 92.04 (s, C_5H_5) C_4H_9N at 65.19 (s, NCH_2), 61.40 (d, J = 2.0, $NC'H_2$), 25.42 (s), 25.17 (s)	16.6 (s)

Table I (Continued)

complex	IR (KBr), cm^{-1}	^1H NMR,[a] δ	$^{13}C\{^1H\}$ NMR,[b] ppm	$^{31}P\{^1H\}$ NMR,[c] ppm
 **3i**	ν_{NO} 1698 vs	7.58–7.49 (m, 9 H of 3 C_6H_5), 7.39–7.30 (m, 6 H of 3 C_6H_5), 5.54 (s, C_5H_5), 3.02 (s, 3 CH_3)	PPh_3 at 134.53 (d, J = 53.7, *i*), 133.58 (d, J = 10.0, *o*), 131.40 (s, *p*), 129.71 (d, J = 11.4, *m*); 120.60 (q, J_{CF} = 320.7, CF_3), 93.78 (s, C_5H_5), 64.97 (s, 3 CH_3)	11.6 (s)

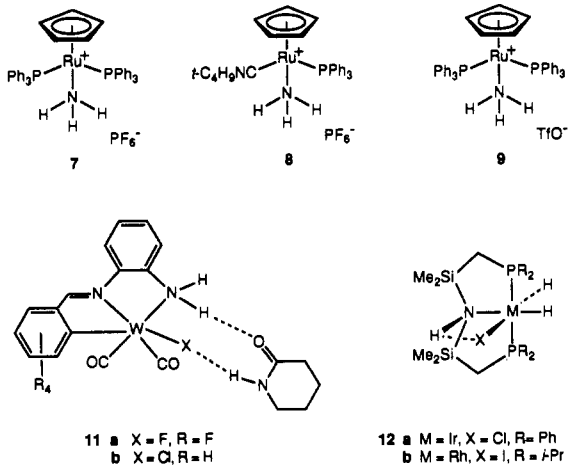
[a] At 300 MHz at ambient probe temperature in $CDCl_3$ and referenced to internal $SiMe_4$; all couplings are to ^1H and are in Hz. [b] At 75 MHz at ambient probe temperature in $CDCl_3$ and referenced to internal $SiMe_4$; all couplings are to ^{31}P unless noted and are in Hz; assignments of resonances to phenyl carbons are 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 (Table I). [c] At 32 MHz at ambient probe temperature in $CDCl_3$ and referenced to external H_3PO_4. [d] In CH_2Cl_2 (0.14 M). [e] This degeneracy is removed in C_6D_6. Partial data: δ 6.09 (s, NH), 5.03 (s, C_5H_5), 3.50 (s, NH′). [f] Selected data, 400 MHz (CD_2Cl_2): δ 5.63 (s, C_5H_5), 4.75 (t, br, NH), 4.53 (dd, J = 1.5, 12.5, C*H*H′), 3.97 (dd, J = 1.5, 12.1, C′*H*H′), 3.88 (dd, J = 7.5, 12.5, CH*H*′), 3.80 (dd, J = 12.1, 12.5, C′H*H*′). The methylene proton assignments were confirmed by decoupling experiments.

Table II. Summary of Crystallographic Data for $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)_2)]^+TfO^-$ (**3f**)

molecular formula	$C_{26}H_{27}F_3N_2O_4PReS$
mol wt	737.749
space group	$P2_1/n$
a, Å	13.925 (2)
b, Å	24.467 (3)
c, Å	8.148 (1)
β, deg	93.398 (4)
V, Å^3	2771.20
Z	4
d_{calc}, g/cm^3	1.768
d_{obs}, g/cm^3	1.748
radiation (λ, Å)	Mo Kα (0.71073)
abs coeff, cm^{-1}	46.3
R^a	0.0388
R_w[a]	0.0436

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$.

Chart I. Structurally Characterized Organometallic Amine Complexes That Exhibit Hydrogen Bonding



Preliminary ^{31}P NMR experiments show that amine complexes can also be accessed from the substitution-labile chlorocarbon complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$.[5]

Complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+X^-$ are formally octahedral, and thus commonly exhibit bond angles of ca. 90° between the non-cyclopentadienyl ligands.[6] Accordingly, the crystal structure of **3f** shows ON–Re–P, P–Re–NH, and ON–Re–NH bond angles of 92.4–95.5° (Table IV). The C–N–C bond angle of the dimethylamine ligand (110.3 (4)°) is slightly smaller than that of free dimethylamine (112.2 (2)°), where the nitrogen is tricoordinate. However, the C–N bond lengths are identical within experimental error (1.464 (6) and 1.478 (6) Å vs 1.462 (5) Å).[28]

The Re–NH bond in **3f** (2.193 (4) Å) is slightly longer than the Re–NC bond in the analogous isoquinoline complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}NC_9H_7)]^+TfO^-$ (2.147 (3) Å).[27] This

Table III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Refined Atoms in **3f**

atom	x	y	z	B,[a] Å^2
Re	0.34047 (2)	0.19922 (1)	0.20293 (4)	2.990 (6)
P	0.2691 (2)	0.12402 (9)	0.0580 (3)	3.07 (4)
O1	0.4443 (5)	0.2335 (3)	−0.0841 (8)	5.9 (2)
N1	0.3976 (6)	0.2225 (3)	0.0269 (9)	4.2 (2)
N2	0.2175 (5)	0.2543 (3)	0.1581 (9)	3.8 (2)
C1	0.4753 (7)	0.1911 (5)	0.364 (1)	5.2 (2)
C2	0.4242 (7)	0.2370 (5)	0.425 (1)	4.7 (2)
C3	0.3392 (7)	0.2169 (5)	0.485 (1)	4.6 (2)
C4	0.3331 (8)	0.1583 (5)	0.459 (1)	4.9 (2)
C5	0.4173 (8)	0.1435 (5)	0.384 (1)	5.4 (2)
C6	0.2274 (6)	0.0710 (4)	0.194 (1)	3.6 (2)
C7	0.1499 (8)	0.0183 (4)	0.289 (1)	5.4 (2)
C8	0.1185 (9)	0.0418 (5)	0.398 (1)	6.4 (3)
C9	0.1666 (8)	−0.0078 (5)	0.411 (1)	5.7 (2)
C10	0.2405 (8)	−0.0184 (4)	0.314 (1)	5.7 (3)
C11	0.2708 (7)	0.0205 (4)	0.204 (1)	4.5 (2)
C12	0.3521 (6)	0.0891 (3)	−0.070 (1)	3.3 (2)
C13	0.3188 (7)	0.0545 (4)	−0.196 (1)	4.6 (2)
C14	0.3816 (8)	0.0263 (5)	−0.291 (1)	6.0 (3)
C15	0.4799 (8)	0.0360 (5)	−0.270 (1)	6.0 (3)
C16	0.5140 (8)	0.0698 (5)	−0.145 (2)	4.5 (2)
C17	0.4516 (7)	0.0972 (4)	−0.047 (1)	3.3 (2)
C18	0.1668 (6)	0.1365 (4)	−0.089 (1)	3.9 (2)
C19	0.1731 (6)	0.1802 (4)	−0.195 (1)	4.7 (2)
C20	0.1021 (7)	0.1914 (4)	−0.315 (1)	4.7 (2)
C21	0.0232 (7)	0.1578 (5)	−0.331 (1)	5.3 (2)
C22	0.0152 (7)	0.1141 (5)	−0.226 (1)	5.6 (3)
C23	0.0875 (7)	0.1029 (4)	−0.103 (1)	4.6 (2)
C24	0.1241 (7)	0.2371 (5)	0.213 (5)	5.0 (2)
C25	0.2396 (8)	0.3107 (4)	0.214 (2)	6.4 (3)
C26	0.331 (1)	0.3771 (8)	−0.301 (2)	13.7 (4)
F1	0.3772 (7)	0.3534 (4)	−0.411 (1)	13.2 (3)
F2	0.3889 (8)	0.3890 (4)	−0.180 (2)	16.6 (4)
F3	0.316 (1)	0.4327 (5)	−0.372 (2)	18.8 (4)
O2	0.1839 (8)	0.3937 (4)	−0.150 (1)	11.5 (3)
O3	0.2548 (8)	0.3026 (4)	−0.179 (1)	11.2 (3)
O4	0.1746 (9)	0.3492 (9)	−0.406 (2)	18.9 (6)
S	0.34047 (2)	0.19922 (1)	0.20293 (4)	7.06 (8)
H21	0.202 (7)	0.255 (4)	0.05 (1)	5.0

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

(28) Wollrab, J. E.; Laurie, V. W. *J. Chem. Phys.* **1968**, *11*, 5058.

Table IV. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in **3f**

Re–N2	2.193 (4)	Re–C5	2.233 (5)
Re–P	2.372 (1)	N2–C24	1.464 (6)
Re–N1	1.775 (4)	N2–C25	1.478 (6)
O1–N1	1.176 (4)	P–C6	1.823 (4)
Re–C1	2.233 (4)	P–C12	1.818 (4)
Re–C2	2.288 (5)	P–C18	1.830 (4)
Re–C3	2.344 (4)	O3–H21	2.37 (6)
Re–C4	2.321 (5)	N2–H21	0.88 (6)
N2–Re–P	95.4 (1)	C1–C2–C3	107.2 (5)
N2–Re–N1	92.9 (2)	C2–C3–C4	109.7 (5)
P–Re–N1	92.4 (1)	C3–C4–C5	106.1 (5)
Re–N2–C24	118.1 (3)	C4–C5–C1	109.4 (5)
Re–N2–C25	112.1 (3)	C5–C1–C2	107.6 (5)
C24–N2–C25	110.3 (4)	O3–H21–N2	136 (5)
P–Re–N2–H21	−52 (7)	N1–Re–N2–H21	40 (7)
P–Re–N2–C24	57.8 (6)	N1–Re–N2–C24	150.5 (7)
P–Re–N2–C25	−172.4 (7)	N1–Re–N2–C25	−79.7 (7)

might be a result of greater π back-bonding to unsaturated nitrogen donor ligands. However, the Re–NH bond is also longer than that in the neutral phenylamido complex $(\eta^5\text{-}C_5H_5)$Re(NO)(PPh$_3$)(ṄHPh) (2.076 (6) Å).[29] Interestingly, an opposite Re–P bond length trend is found for the cationic bis(phosphine) complex[30] $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PH_2(t\text{-}C_4H_9))]^+Cl^-$ and the neutral phosphido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{P}R_2)$.[6a]

The Re–NH bond conformation in **3f** (see Figure 1b) is analogous to the Re–S bond conformation found in the crystalline dimethyl sulfide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(CH_3)_2)]^+TfO^-$ (**6**).[6f] In each case, the smallest donor atom substituent (hydrogen atom or lone pair) resides between the nitrosyl and large PPh$_3$ ligand. Several studies have identified this as the sterically most congested interstice.[31,32] The P–Re–S–C and N–Re–S–C torsion angles in **6** (66.2 (5) and −174.7 (5)°; 156.5 (6) and −95.1 (6)°) are within 2–15° of the corresponding torsion angles in **3f** (Table IV). The secondary alkyl complex (*SS*,*RR*)-$(\eta^5\text{-}C_5H_5)$Re(NO)(PPh$_3$)(CH(CH$_2$C$_6$H$_5$)C$_6$H$_5$) exhibits a similar Re–C bond conformation.[33]

A key structural issue in amine complexes **3** is the question of hydrogen bonding between nitrogen protons and the triflate counteranion. The crystal structure of **3f** establishes that hydrogen bonding can occur in the solid state (H··O = 2.37 (5) Å). However, the primary phosphine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PH_2(t\text{-}C_4H_9))]^+Cl^-$ crystallizes with the chloride counteranion 8.36 Å away from the nearest phosphorus proton.[30] Thus, generalizations should not be made without additional structural data.

The crystal structures of several cationic ruthenium(II) amine complexes have recently been reported by Simpson and Roundhill (Chart I).[15,34] On the basis of calculated hydrogen atom positions, the hexafluorophosphate salts $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(NH_3)]^+PF_6^-$ (**7**) and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(NC\text{-}t\text{-}C_4H_9)(NH_3)]^+PF_6^-$ (**8**) exhibit close contacts between nitrogen protons and the phosphorus fluorines (**7**, 2.56–2.87 Å; **8**, 2.42–2.94 Å).[15] Hydrogen atoms can be located in the triflate salt $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(NH_3)]^+TfO^-$ (**9**). The closest ammonia proton/triflate oxygen contact is 2.20 Å. However, distances between nitrogen protons and triflate oxygens in the related *tert*-butyl amine complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(P(OMe)_3)(NH_2\text{-}t\text{-}C_4H_9)]^+TfO^-$ (**10**) are all greater than 3.59 Å.[34]

Structural data exist for other interesting hydrogen-bonding phenomena involving amine ligands. For example, Richmond has reported that neutral tungsten(II) amine halide complexes can form intermolecular hydrogen bonds with lactams and nucleosides, as shown in **11** (Chart I).[14] Fryzuk has found intramolecular N··H··X hydrogen bonds in iridium(III) and rhodium(III) amine halide complexes of the formula $(H)_2(X)M[NH(SiMe_2CH_2PR_2)_2]$ (**12**).[35] Also, Bergman has observed a 2.35-Å contact between a nitrogen proton and the chloride in the cationic iridium(III) azametallacyclobutane $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(NH_2C(CH_3)_2CH_2)]^+Cl^-$.[36]

Since our main interest has been in the reactivity of amine complexes **3**, we have not attempted to address the issue of hydrogen bonding in solution. However, we have established that the nitrogen lone pairs in amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$ are considerably more basic than those in organic amines.[20,21] Thus, primary and secondary amine complexes **3a–g** should be somewhat poorer hydrogen-bond donors than ammonium salts.

The PPh$_3$ ligand ^{31}P NMR chemical shifts trends shown by **3** (primary amine > secondary > tertiary) might seemingly be attributed to solution-phase hydrogen bonding. Interestingly, a parallel trend is found for primary phosphine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PH_2R)]^+X^-$ (17.2–14.7 ppm, X$^-$ = TfO$^-$, TsO$^-$),[11] secondary phosphine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PHR_2)]^+X^-$ (14.7–6.9 ppm, X$^-$ = TfO$^-$, TsO$^-$),[6a,11,37] and the tertiary phosphine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2CH_2Cl)]^+Cl^-$ (6.6 ppm).[6a] However, amido and phosphido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{P}RR')$, which lack analogous hydrogen-bonding capability, show similar chemical shift behavior.[6a,11,20,21] Thus, these trends may be a simple consequence of the number of alkyl substituents on the donor atom.

Other spectroscopic properties of **3** are of interest. For example, the ^{15}N NMR chemical shift of the ammonia ligand in **3a**-^{15}N (−464.4 ppm) is close to that of the ruthenium complex **7**-^{15}N (−446.1 ppm)[15] and is in a range typical of transition-metal ammonia complexes.[38] However, in contrast to **3a**-^{15}N, **7**-^{15}N exhibits a detectable $^2J_{PN}$ (2.9 Hz). Also, the $^1J_{NH}$ values in these compounds (70.9, 69.3 Hz) are much closer to that of the ammonium salt $NH_4^+Cl^-$ (73.3 Hz) than ammonia (61.2 Hz).[39]

The facile displacement of amine ligands by cyanide and azide ions with retention of configuration at rhenium (Scheme II) will be of future practical value. In work in progress, we have elaborated analogous complexes of unsaturated nitrogen-containing ligands to amine complexes containing new stereocenters.[21] These reactions allow the isolation of free amines in high enantiomeric purities.[20,21] Also, the primary and secondary amine complexes can be deprotonated to amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$, which themselves have a variety of interesting physical and chemical properties.[8,21,29] Full details of these studies will be described in the near future.

Experimental Section

General Data. All reactions were conducted under dry N_2 atmospheres. IR spectra were recorded on a Mattson Polaris (FT) spectrometer. All ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian spectrometers as outlined in Table I. All ^{15}N NMR spectra were similarly acquired at 30.4 MHz.[17] Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter.[19b] Microanalyses were performed

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by Atlantic Microlab. Melting points were determined in evacuated capillaries.[40]

Solvents were purified as follows: CH_2Cl_2, distilled from CaH_2; C_6H_5Cl, distilled from P_2O_5; THF and benzene, distilled from sodium/benzophenone; toluene, distilled from sodium; hexane (EM Science), ether (Mallinckrodt), $CDCl_3$ and CD_3NO_2 (Cambridge Isotope Laboratories), used as received. Silica gel (Baker, 60–200 mesh unless noted) was used as received. Florisil was treated with concentrated NH_4OH (30% v/w).

Reagents were obtained as follows: NH_3 (Matheson), $(CH_3)_3SiCH_2NH_2$ and pyrrolidine (Fluka), $^{15}NH_3$ (98 atom%), CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $(CH_3)_2CHNH_2$, $(C_6H_5CH_2)_2NH$, HOTf, and (+)-Eu(hfc)$_3$ (Aldrich), used as received; $(CH_3CH_2)_4N^+$ CN^- (Fluka), dried under vacuum over P_2O_5; $HBF_4{\cdot}OEt_2$ (Aldrich), standardized as previously described.[5a]

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(NH$_3$)]$^+$TfO$^-$ (3a). A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH_3) (**1**, 0.210 g, 0.376 mmol),[9,41] toluene (5 mL), and a stir bar and cooled to −45 °C (CH_3CN/liquid N_2 bath). Then HOTf (0.0333 mL, 0.376 mmol) was added with stirring to generate (η^5-C_5H_5)Re(NO)(PPh$_3$)(OTf) (**2**).[10] After 5 min, a stream of NH_3 gas was passed over the red solution for 1 min. Over the course of 15 min, the solution turned orange and a precipitate formed. The bath was removed, and the mixture was allowed to warm to room temperature. After 1 h, hexane (50 mL) was added with stirring to complete precipitation. The resulting orange powder was collected by filtration, washed with hexane, and dried under oil pump vacuum to give **3a** (0.138 g, 0.323 mmol, 86%), mp 222–223 °C. Anal. Calcd for $C_{24}H_{23}F_3N_2O_4PReS$: C, 40.62; H, 3.27. Found: C, 40.50; H, 3.26.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(^{15}NH$_3$)]$^+$TfO$^-$ (3a-^{15}N). Complex **1** (0.443 g, 0.794 mmol), toluene (25 mL), and HOTf (0.0703 mL, 0.794 mmol) were combied in a procedure analogous to that given for **3a**. The red solution was frozen (liquid N_2 bath) and a break/seal flask containing $^{15}NH_3$ (100 mL, 4.09 mmol) was attached via a glass transfer tube. A static vacuum was applied to the system, and the seal was broken. The bath was removed, and the mixture was allowed to thaw. The transfer tube was replaced by a septum, and the mixture was allowed to warm to room temperature. Some product precipitated. After 2 h, hexane (100 mL) was added to complete precipitation. The resulting orange powder was collected as above to give **3a**-^{15}N (0.537 g, 0.754 mmol, 95%). Anal. Calcd for $C_{24}H_{23}F_3N^{15}NO_4PReS$: C, 40.56; H, 3.26. Found: C, 40.29; H, 3.17.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(NH$_2$CH$_3$)]$^+$TfO$^-$ (3b). Complex **1** (0.390 g, 0.699 mmol), toluene (10 mL), HOTf (0.0619 mL, 0.699 mmol), and CH_3NH_2 (g) were combined in a procedure analogous to that given for **3a**. A similar workup gave **3b** as a bright yellow powder (0.491 g, 0.678 mmol, 97%), mp 208–210 °C. Anal. Calcd for $C_{25}H_{25}F_3N_2O_4PReS$: C, 41.49; H, 3.48. Found: C, 41.26; H, 3.41.

(+)-(*S*)-3b. Complex (+)-(*S*)-**1** (1.001 g, 1.80 mmol),[18,41] toluene (25 mL), HOTf (0.0159 mL, 1.80 mmol), and CH_3NH_2 (g) were combined in a procedure analogous to that given for **3b**. A similar workup gave (+)-(*S*)-**3b** as a yellow powder (1.029 g, 1.42 mmol, 79%): mp 207–209 °C; $[\alpha]^{25}_{589}$ 422 ± 10° (*c* 0.85 mg/mL).[19] Anal. Calcd for $C_{25}H_{25}F_3N_2O_4PReS$: C, 41.49; H, 3.48. Found: C, 41.42; H, 3.49.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(NH$_2$CH$_2$Si(CH$_3$)$_3$)]$^+$TfO$^-$ (3c). Complex **1** (0.512 g, 0.917 mmol), toluene (10 mL), and HOTf (0.0812 mL, 0.917 mmol) were combined in a procedure analogous to that given for **3a**. After 5 min, $(CH_3)_3SiCH_2NH_2$ (0.369 mL, 2.75 mmol) was added via syringe with stirring. The bath was removed, and the mixture was allowed to warm to room temperaure. Some product precipitated. After 2 h, hexane (50 mL) was added with stirring to complete precipitation. The resulting yellow powder was collected as above to give **3c** (0.640 g, 0.807 mmol, 88%), mp 186–189 °C. Anal. Calcd for $C_{28}H_{33}F_3N_2O_4PReSSi$: C, 42.25; H, 4.18. Found: C, 42.54; H, 4.21.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(NH$_2$C$_6$H$_5$)]$^+$TfO$^-$ (3d). Complex **1** (0.141 g, 0.252 mmol), toluene (10 mL), HOTf (0.0223 mL, 0.252 mmol), and $C_6H_5NH_2$ (0.229 mL, 2.52 mmol) were combined in a procedure analogous to that given for **3c**. A similar workup gave **3d** as an orange powder (0.184 g, 0.234 mmol, 93%), mp 201–202 °C. Anal. Calcd for $C_{30}H_{27}F_3N_2O_4PReS$: C, 45.86; H, 3.46. Found: C, 45.84; H, 3.48.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(NH$_2$CH(CH$_3$)$_2$)]$^+$TfO$^-$ (3e). Complex **1** (0.123 g, 0.218 mmol), toluene (10 mL), HOTf (0.0193 mL, 0.218 mmol), and $(CH_3)_2CHNH_2$ (0.186 mL, 2.18 mmol) were combined in a procedure analogous to that given for **3c**. A similar workup gave **3e** as an orange powder (0.155 g, 0.205 mmol, 94%), mp 215–216 °C. Anal. Calcd for $C_{27}H_{29}F_3N_2O_4PReS$: C, 43.14; H, 3.89. Found: C, 43.20; H, 3.92.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(NH(CH$_3$)$_2$)]$^+$TfO$^-$ (3f). Complex **1** (0.512 g, 0.917 mmol), toluene (25 mL), HOTf (0.0811 mL, 0.917 mmol), and $(CH_3)_2NH$ (g) were combined in a procedure analogous to that given for **3a**. A similar workup gave **3f** as a yellow powder (0.669 g, 0.909 mmol, 99%), mp 200–202 °C. Anal. Calcd for $C_{26}H_{27}F_3N_2O_4PReS$: C, 42.33; H, 3.69. Found: C, 42.40; H, 3.72.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(NH(CH$_2$C$_6$H$_5$)$_2$)]$^+$TfO$^-$ (3g). Complex **1** (0.553 g, 0.990 mmol), toluene (25 mL), HOTf (0.0876 mL, 0.990 mmol), and $(C_6H_5CH_2)_2NH$ (0.952 mL, 4.95 mmol) were combined in a procedure analogous to that given for **3c**. The mixture was refluxed for 10 h. A similar workup gave **3g** as an orange powder (0.482 g, 0.542 mmol, 55%), mp 201–202 °C. Crystallization from CH_2Cl_2/pentane gave **3g**·CH_2Cl_2. Anal. Calcd for $C_{38}H_{35}F_3N_2O_4PReS{\cdot}CH_2Cl_2$: C, 48.05; H, 3.83; Cl, 7.27. Found: C, 47.81; H, 3.88; Cl, 7.02.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(NHCH$_2$CH$_2$CH$_2$CH$_2$)]$^+$TfO$^-$ (3h). Complex **1** (0.544 g, 0.974 mmol), toluene (25 mL), HOTf (0.0861 mL, 0.974 mmol), and pyrrolidine (0.407 mL, 4.87 mmol) were combined in a procedure analogous to that given for **3c**. A similar workup gave **3h** as a yellow powder (0.718 g, 0.945 mmol, 97%), mp 199–201 °C. Anal. Calcd for $C_{28}H_{29}F_3N_2O_4PReS$: C, 44.03; H, 3.83. Found: C, 44.10; H, 3.87.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(N(CH$_3$)$_3$)]$^+$TfO$^-$ (3i). Complex **1** (0.214 g, 0.383 mmol), toluene (10 mL), HOTf (0.0339 mL, 0.383 mmol), and $(CH_3)_3N$ (g) were combined in a procedure analogous to that given for **3a**. A similar workup gave **3i** as a yellow powder (0.184 g, 0.333 mmol, 87%), mp 187–189 °C. Anal. Calcd for $C_{27}H_{29}F_3N_2O_4PReS$: C, 43.14; H, 3.89. Found: C, 43.40; H, 3.71.

(η^5-C_5H_5)Re(NO)(PPh$_3$)(N$_3$) (5). A Schlenk flask was charged with **1** (0.125 g, 0.224 mmol), C_6H_5Cl (2.5 mL), and a stir bar and cooled to −45 °C. Then $HBF_4{\cdot}OEt_2$ (0.033 mL, 0.26 mmol) was added with stirring to generate [(η^5-C_5H_5)Re(NO)(PPh$_3$)(ClC_6H_5)]$^+BF_4^-$.[5b] After 25 min, solid PPN^+ N_3^- (0.349 g, 0.601 mmol)[22] was added. After 15 min, the cold bath was removed, and the mixture was allowed to warm to room temperature. After 3.5 h, solvent was removed under vacuum. The residue was extracted with benzene, and the extract was poured onto a 5-cm plug of Florisil. The plug was eluted with benzene, and the eluate was concentrated to ca. 3 mL by rotary evaporation. Hexane was added with stirring. An orange powder precipitated, which was collected by filtration and dried under vacuum to give **5** (0.088 g, 0.150 mmol, 67%), mp 159–163 °C dec. IR (cm^{-1}, KBr): ν_{NNN} 2038 vs; ν_{NO} 1635 vs. ^1H NMR (δ, CD_2Cl_2): 7.49–7.37 (m, 15 H), 5.29 (s, 5 H). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2): 134.7 (d, J_{CP} = 53.2 Hz, *i*-PPh$_3$), 134.1 (d, J_{CP} = 11.0 Hz, *o*-PPh$_3$), 131.1 (d, J_{CP} = 2.2 Hz, *p*-PPh$_3$), 129.0 (d, J_{CP} = 10.8 Hz, *m*-PPh$_3$), 91.4 (s, C_5H_5). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2): 17.0 (s). Anal. Calcd for $C_{23}H_{20}N_4OPRe$: C, 47.17; H, 3.44; N, 9.57. Found. C, 47.44; H, 3.47; N, 9.31.

Reactions of 3a,b,f and (+)-(*S*)-3b with $(CH_3CH_2)_4N^+CN^-$. The following procedure is representative. A Schlenk flask was charged with (+)-(*S*)-**3b** (0.053 g, 0.074 mmol), CH_2Cl_2 (2 mL), and a stir bar. Then solid $(CH_3CH_2)_4N^+CN^-$ (0.014 g, 0.088 mmol) was added. The mixture was stirred for 1 h, and the solvent was removed under oil pump vacuum. The residue was extracted with THF and the extract chromatographed on a 2-cm silica gel column (2.5 g, THF). Solvent was removed from a yellow band by rotary evaporation. This gave (+)-(*S*)-**4** as a yellow powder (0.021 g, 0.038 mmol, 51%): mp 191–193 °C, $[\alpha]^{25}_{589}$ 179 ± 4° (*c* 1.08 mg/mL).[19] Spectroscopic properties were identical to those of the racemate.[5a] A sample was precipitated from CH_2Cl_2/hexane, washed with hexane, and dried under oil pump vacuum. Anal. Calcd for $C_{24}H_{20}N_2OPRe$: C, 50.61; H, 3.54; N, 4.92. Found: C, 50.47; H, 3.59; N, 4.90.

Reactions of 3a,b,f with PPN^+ N_3^-. The following procedure is representative. A Schlenk flask was charged with **3b** (0.0087 g, 0.012 mmol), THF (3 mL), and a stir bar. Then solid $PPN^+N_3^-$ (0.007 g, 0.012 mmol) was added. The mixture was stirred for 3 h, and the solvent was removed under oil pump vacuum. The residue was extracted with benzene, and the extract was filtered through a plug of Florisil. The plug was eluted with benzene, and heptane was added to the eluate. The solution was concentrated to ca. 3 mL by rotary evaporation. An orange powder precipitated, which was collected by filtration and dried under oil pump vacuum to give **5** (0.0069 g, 0.012 mmol, 98%).

Crystal Structure of 3f. An orange prism of **3f** was grown from layered acetone/hexane, and mounted for data collection on a Syntex $P\bar{1}$ diffractometer. Cell constants (Table II) were obtained from 25 reflections with 20° < 2θ < 34°. The space group was determined from systematic absences (*h0l*, *h* + *l* = 2*n*; 0*k*0, *k* = 2*n*) and subsequent least-squares refinement. Standard reflections showed no decay during data collection. Lorentz and polarization corrections and an empirical

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absorption correction based upon a series of Ψ scans were applied to the data. The structure was solved by standard heavy-atom techniques with the SDP-VAX package.[42] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom H21 was located and refined with fixed isotropic thermal parameters. The remaining hydrogen atom positions were calculated and added to the structure factor calculations but not refined. Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[43]

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Supplementary Material Available: ^{1}H NMR spectra of **4** in the presence of (+)-Eu(hfc)$_3$ (Figure 2) and tables of additional crystallographic data, bond lengths and angles, hydrogen atom parameters, and anisotropic thermal parameters for **3f** (6 pages); a table of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

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Catalytic Asymmetric Hydrogenation of Imines. Use of Rhodium(I)/Phosphine Complexes and Characterization of Rhodium(I)/Imine Complexes

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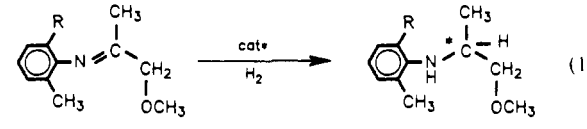
An in situ Rh^I(P-P) catalyst formed from [Rh(NBD)Cl]$_2$ and cycphos (P-P = 1,2-bis(diphenylphosphino)-1-cyclohexylethane) effects asymmetric hydrogenation of some commercially important and model imines in 1:1 benzene/methanol under 1000-1500 psig H_2 from -25 to +25 °C; a maximum of 91% ee is obtained for ArC(Me)=NCH$_2$Ph (Ar = 4-MeOC$_6$H$_4$) in the presence of iodide cocatalyst at -25 °C. Two [Rh(diphos)(imine)$_2$]BF$_4$ complexes have been isolated (diphos = 1,2-bis(diphenylphosphino)ethane): imine **8** = 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (complex **11**) or imine **4** with Ar = 2-MeOC$_6$H$_4$ (complex **16**). Complex **11** crystallizes in the triclinic system, space group $P\bar{1}$, with a = 12.564 (1) Å, b = 21.446 (2) Å, c = 10.521 (1) Å, α = 100.655 (9)°, β = 110.539 (8)°, γ = 79.102 (7)°, and Z = 2, the structure refining to R = 6.8% and R_w = 8.2% for 5881 reflections; the η^1-imines bind via nitrogen in a syn arrangement at the essentially square-planar Rh, while in solution an anti isomer is also evident. Other species [Rh(diphos)(η^1-imine)(MeOH)]$^+$ and Rh(P-P)Cl(η^1-imine), where P-P = diphos or chiral bis(tertiary phosphines), have been characterized in solution, and Rh(diop)(Cl) (**8**) has been isolated (diop = 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane). Complexes [Rh(diphos)(imine)]$^+$ containing a chelated imine (via the nitrogen lone pair and oxygen of a methoxy functionality) exist, but chelation is not essential for effective asymmetric induction. The catalytic hydrogenations appear to occur via an unsaturate route; a plausible intermediate is Rh(P-P)(X)(MeOH)(imine), where X = halide and the alcohol facilitates η^2-(C=N) binding.

Introduction

Although much is known about the asymmetric reduction of alkenes and ketones by dihydrogen, a reaction catalyzed by chiral metal complexes,[1] the analogous hydrogenation of imines has received much less attention.[2,3] Rhodium(I) and iridium(I) derivatives of chiral bis(tertiary phosphines) are the catalysts of choice for the few asymmetric imine reductions studied to date,[2,3] and the present work is concerned with extending our knowledge of the rhodium systems.

Our work in this area began with a search for a catalyst for the asymmetric reduction of the commercially important imines **1** (eq 1).[3a-c] Only the Z form of the E/Z mixture is shown.



(1)

1a R=CH$_3$
b R=C$_2$H$_5$

Optical yields of up to 69% were achieved by using low-temperature, H_2 pressure of >1000 psig, a solvent mixture of MeOH/benzene (or toluene), and a particular chiral bidentate phosphine, cycphos ($Ph_2PCH(C_6H_{11})CH_2PPh_2$), in conjunction with the [Rh(NBD)Cl]$_2$ precursor.[3a-c,4,5] The optimum conditions

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(4) Cycphos = $Ph_2PCH(C_6H_{11})CH_2PPh_2$, norphos = $Ph_2PCHCHCH{=}CHCH(CH_2)CHPPh_2$, chiraphos = $Ph_2PCH(CH_3)CH(CH_3)PPh_2$, skewphos = $Ph_2PCH(CH_3)CH_2CH(CH_3)PPh_2$, diphos = $Ph_2PCH_2CH_2PPh_2$, DPPP = $Ph_2P(CH_2)_3PPh_2$, diop = $Ph_2PCH_2CHOCMe_2OCHCH_2PPh_2$.

(5) Norphos is also effective as a ligand.[3b]

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