Organometallics **2001,** *20,* 3087−3096

A New Family of Chiral Chelating Diamines with Transition-Metal Stereocenters: Synthesis, Structure, and Reactivity of the Enantiomerically Pure Dirhenium-Substituted 1,2-Diamine $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2N(CH_3)CH_2CH_2(H_3C)NCH_2)(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)$

Luke J. Alvey,[1a] Olivier Delacroix,[1b] Carsten Wallner,[1b] Oliver Meyer,[1a]
Frank Hampel,[1b] Slawomir Szafert,[1a,c] Tadeusz Lis,[1c] and J. A. Gladysz*,[1a,b]

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112,
Institut für Organische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg,
Henkestrasse 42, 91054 Erlangen, Germany, and Department of Chemistry,
University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

Received February 26, 2001

Reaction of enantiopure (*S*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ ((*S*)-**1**) with $Ph_3C^+BF_4^-$ (1 equiv) and then the *N*,*N*′-dimethyl 1,2-diamine $HN(CH_3)CH_2CH_2(H_3C)NH$ (0.5 equiv) gives the diammonium salt $(S_{Re}S_{Re})$-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2NH(CH_3)CH_2CH_2(H_3C)HNCH_2)(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)]^{2+}(BF_4^-)_2$ (94%) as a mixture of Re/N configurational diastereomers. Reaction with *t*-BuOK yields the title compound $(S_{Re}S_{Re})$-**4** (66%) as an air-stable orange powder. Reaction with $(PhCN)_2PdCl_2$ gives a single diastereomer of a chelate complex, $(S_{Re}R_NR_NS_{Re})$-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2N(CH_3)CH_2CH_2(H_3C)NCH_2)(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)]PdCl_2$ (80%), the configuration and approximate C_2 symmetry of which has been established crystallographically. Racemic **1**, $Ph_3C^+BF_4^-$ (1 equiv), and the *N*,*N*′-dimethyl 1,2-diamine $HN(CH_2CH_3)CH_2CH_2(H_3CCH_2)NH$ (1 equiv) give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2NH(CH_2CH_3)CH_2CH_2NH(CH_2CH_3))]^+BF_4^-$, and the crystal structure of the $S_{Re}S_N,R_{Re}R_N$ diastereomer is determined. The $ReCH_2N$ conformations of the preceding compounds, and their influence upon the diastereoselectivities, are analyzed in detail.

Introduction

Chiral 1,2-diamines see extensive use in enantioselective organic synthesis and catalysis.[2] They serve as building blocks for recoverable chiral auxiliaries[2,3] and as ligands in metal catalysis.[2,4] They are further employed in the resolution of enantiomers[2] and as components of chiral NMR shift reagents.[5] Despite their many successful applications, the search continues for chiral 1,2-diamines with improved performance characteristics. As is typical throughout the field of enantioselective synthesis, research teams are reaching into nearly every corner of the natural and unnatural chiral pools for new-generation systems.[6]

For example, the use of metal catalysts containing ferrocene-based chelate ligands with *planar* and/or other chirality elements has grown rapidly over the past decade.[7] These systems have proven highly effective, practical, and robust. Thus, chiral diamines with ferrocenyl units are receiving increasing attention.[8,9] This

---

(1) (a) University of Utah. (b) Universität Erlangen-Nürnberg (permanent address of corresponding author). (c) University of Wrocław.

(2) Recent reviews: (a) Fache, F.; Schulz, E.; Tommasino, M. L.; Lemaire, M. *Chem. Rev.* **2000**, *100*, 2159. (b) Lucet, D.; Le Gall, T.; Mioskowski, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 2580; *Angew. Chem.* **1998**, *110*, 2724.

(3) Additional lead references from the year 2000: (a) Li, X.; Schenkel, L. B.; Kozlowski, M. C. *Org. Lett.* **2000**, *2*, 875. (b) Wiberg, K. B.; Bailey, W. F. *Tetrahedron Lett.* **2000**, *41*, 9365. (c) Barrett, S.; O'Brien, P.; Steffens, H. C.; Towers, T. D.; Voith, M. *Tetrahedron* **2000**, *56*, 9633.

(4) Additional lead references from the years 1999−2001: (a) Mimoun, H.; de Saint Laumer, J. Y.; Giannini, L.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 6158. (b) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40; *Angew. Chem.* **2001**, *113*, 41. (c) Burk, M. J.; Hems, W.; Herzberg, D.; Malan, C.; Zanotti-Gerosa, A. *Org. Lett.* **2000**, *2*, 4173. (d) Malkov, A. V.; Spoor, P.; Vinader, V.; Kocovský, P. *Tetrahedron Lett.* **2001**, *42*, 509. (e) Catalysis not requiring a metal: Leclerc, E.; Mangeney, P.; Henryon, V. *Tetrahedron: Asymmetry* **2000**, *11*, 3471.

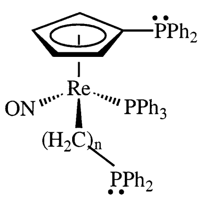
(5) (a) Kido, J.; Okamoto, Y.; Brittain, H. G. *J. Org. Chem.* **1991**, *56*, 1412. (b) Devitt, P. G.; Mitchell, M. C.; Weetman, J. M.; Taylor, R. J.; Kee, T. P. *Tetrahedron: Asymmetry* **1995**, *6*, 2039. (c) Hulst, R.; Koen de Vries, N.; Feringa, B. L. *Tetrahedron: Asymmetry* **1994**, *5*, 699.

(6) Representative new syntheses from the year 2000: (a) Busacca, C. A.; Campbell, S.; Dong, Y.; Grossbach, D.; Ridges, M.; Smith, L.; Spinelli, E. *J. Org. Chem.* **2000**, *65*, 4753. (b) Rivas, F. M.; Riaz, U.; Diver, S. T. *Tetrahedron: Asymmetry* **2000**, *11*, 1703. (c) Roland, S.; Mangeney, P. *Eur. J. Org. Chem.* **2000**, 611. (d) Alexakis, A.; Tomassini, A.; Chouillet, C.; Roland, S.; Mangeney, P.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 4093; *Angew. Chem.* **2000**, *112*, 4259. (e) Yamauchi, T.; Higashiyama, K.; Kubo, H.; Ohmiya, S. *Tetrahedron: Asymmetry* **2000**, *11*, 3003. (f) Mitchell, J. M.; Finney, N. S. *Tetrahedron Lett.* **2000**, *41*, 8431. (g) Martelli, G.; Morri, S.; Savoia, D. *Tetrahedron* **2000**, *56*, 8367. (h) Markidis, T.; Kokotos, G. *J. Org. Chem.* **2001**, *66*, 1919.

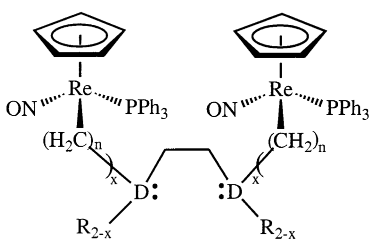
(7) (a) Togni, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1475; *Angew. Chem.* **1996**, *108*, 1581. (b) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377. (c) Togni, A.; Bieler, N.; Burckhardt, U.; Köllner, C.; Pioda, G.; Schneider, R.; Schnyder, A. *Pure Appl. Chem.* **1999**, *71*, 1531.

10.1021/om010153a CCC: $20.00
Publication on Web 06/05/2001

led us to speculate that chelate ligands that contain a metal-based *center* of chirality—e.g., a nonplanar spectator moiety of general formula M(A)(B)(C)(D)[10]—might also provide efficient and perhaps superior stereogenesis. We recently detailed a long-term study of diphosphines that contain such a chiral rhenium species as part of the chelate backbone, as shown in **A**.[11] These afforded excellent rhodium enantioselective hydrogenation catalysts, and we sought to extend this concept to other donor atoms and architectural motifs.



A



B

x = 1, 2

We wondered whether one could easily prepare 1,2-diamines that contain chiral-at-metal fragments as part of the nonchelating, N-alkyl substituents—for example, a $L_nMCH_2NRCH_2CH_2NR'R''$ species or a symmetrically substituted analogue such as **B**. The latter features the 18-valence-electron rhenium fragment $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$, for which many derivatives are readily available in enantiomerically pure form.[12,13] Only alkoxide and amide adducts are configurationally labile (the mechanistic basis for which is known in detail).[14] Therefore, a methylene or similar spacer group between the rhenium and diamine nitrogen is desirable. It has furthermore been shown that the β-thio-substituted complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SCH_3)$ is a much stronger Lewis base than its organic counterpart CH_3SCH_3.[15] Hence, we expected that similar β-amino rhenium species would give thermodynamically stronger metal−nitrogen bonds.

In this paper, we report the efficient synthesis of such a chelating diamine, featuring a methyl and a methylenerhenium substituent on each terminus and therefore capable of C_2 symmetry. A square-planar palladium derivative is isolated and the crystal structure determined. Geometric features are carefully analyzed, particularly with respect to the high nitrogen diastereoselectivity that accompanies chelation. Supporting reactions and model compounds are described, including a crystallographically characterized 1:1 rhenium−diamine adduct that establishes a higher Brønsted basicity for methylenerhenium- vs proton-substituted amines.[16]

Results

Diamine Synthesis. Both enantiomers of the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) can be obtained in >99% ee from commercial $Re_2(CO)_{10}$ in a routine series of steps.[12] Reactions with trityl salts $Ph_3C^+X^-$ give the methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+X^-$ ($\mathbf{2}^+X^-$).[17] The methylidene ligand is electrophilic and is attacked by a variety of carbon,[17−19] nitrogen,[18] phosphorus,[11b] and sulfur[15] nucleophiles. In all cases investigated, this occurs with overall retention at rhenium.[11b,17a,19] Hence, the route to the title compound in Scheme 1 was envisioned.

Accordingly, (*S*)-**1**[20,21] and $Ph_3C^+BF_4^-$ were combined in CH_2Cl_2 at −80 °C to generate (*S*)-$\mathbf{2}^+BF_4^-$. Then 0.5 equiv of the inexpensive disecondary *N,N′*-dimethyl 1,2-diamine $HN(CH_3)CH_2CH_2(H_3C)NH$ was added. Workup gave the ditertiary diammonium salt $(S_{Re}S_{Re})$-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2NH(CH_3)CH_2CH_2(H_3C)HNCH_2)(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)]^{2+}(BF_4^-)_2$ ($(S_{Re}S_{Re})$-$\mathbf{3}^{2+}(BF_4^-)_2$) in 94% yield after crystallization as an air-stable bright yellow powder. The complex $(S_{Re}S_{Re})$-$\mathbf{3}^{2+}(BF_4^-)_2$, and all new compounds below, were characterized by microanalysis and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. Data are summarized in the Experimental Section.

The diprotonated diamine $(S_{Re}S_{Re})$-$\mathbf{3}^{2+}(BF_4^-)_2$ contains two rhenium and two nitrogen stereocenters. The former are set by the precursor (*S*)-**1**. The trivalent nitrogen atoms of the precursor diamine are of course rapidly inverting, thereby interconverting *meso* and *rac* diastereomers. In the absence of a kinetic or thermodynamic resolution, three diastereomers of $\mathbf{3}^{2+}(BF_4^-)_2$ would be expected: $S_{Re}S_NS_NS_{Re}$, $S_{Re}S_NR_NS_{Re}$ (which is

---

(8) (a) Spescha, M.; Duffy, N. W.; Robinson, B. H.; Simpson, J. *Organometallics* **1994**, *13*, 4895. (b) Crameri, Y.; Foricher, J.; Scalone, M.; Schmid, R. *Tetrahedron: Asymmetry* **1997**, *8*, 3617. (c) Woltersdorf, M.; Kranich, R.; Schmalz, H.-G. *Tetrahedron* **1997**, *53*, 7219. (d) Schwink, L.; Knochel, P. *Chem. Eur. J.* **1998**, *4*, 950. (e) Schwink, L.; Ireland, T.; Püntener, K.; Knochel, P. *Tetrahedron: Asymmetry* **1998**, *9*, 1143. (f) Song, J.-H.; Cho, D.-J.; Jeon, S.-J.; Kim, Y.-H.; Kim, T.-J.; Jeong, J.-H. *Inorg. Chem.* **1999**, *38*, 893. (g) Delacroix, O.; Picart-Goetgheluck, S.; Maciejewski, L.; Brocard, J.; Nowogrocki, G. *Synlett* **2001**, 29.

(9) (a) Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270. (b) Rios, R.; Liang, J.; Lo, M. M.-C.; Fu, G. C. *J. Chem. Soc., Chem. Commun.* **2000**, 377. (c) Related studies with monoamines: Fu, G. C. *Acc. Chem. Res.* **2000**, *33*, 412.

(10) Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1194; *Angew. Chem.* **1999**, *111*, 1248.

(11) (a) Zwick, B. D.; Arif, A. M.; Patton, A. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 910; *Angew. Chem.* **1987**, *99*, 921. (b) Kromm, K.; Zwick, B. D.; Meyer, O.; Hampel, F.; Gladysz, J. A. *Chem. Eur. J.* **2001**, *7*, 2015.

(12) Agbossou, F.; O'Connor, E. J.; Garner, C. M.; Quirós Méndez, N.; Fernández, J. M.; Patton, A. T.; Ramsden, J. A.; Gladysz, J. A. *Inorg. Synth.* **1992**, *29*, 211.

(13) (a) Dewey, M. A.; Stark, G. A.; Gladysz, J. A. *Organometallics* **1996**, *15*, 4798 and references therein. (b) Saura-Llamas, I.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 2136.

(14) Dewey, M. A.; Zhou, Y.; Liu, Y.; Gladysz, J. A. *Organometallics* **1993**, 12, 3924.

(15) McCormick, F. B.; Gleason, W. B.; Zhao, X.; Heah, P. C.; Gladysz, J. A. *Organometallics* **1986**, *5*, 1778.

(16) (a) Some of this work is taken from: Alvey, L. J. Ph.D. Thesis, University of Utah, 1999. (b) See also: Wallner, C. Diplom Thesis, University of Erlangen-Nürnberg, 1999.

(17) (a) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204. (b) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

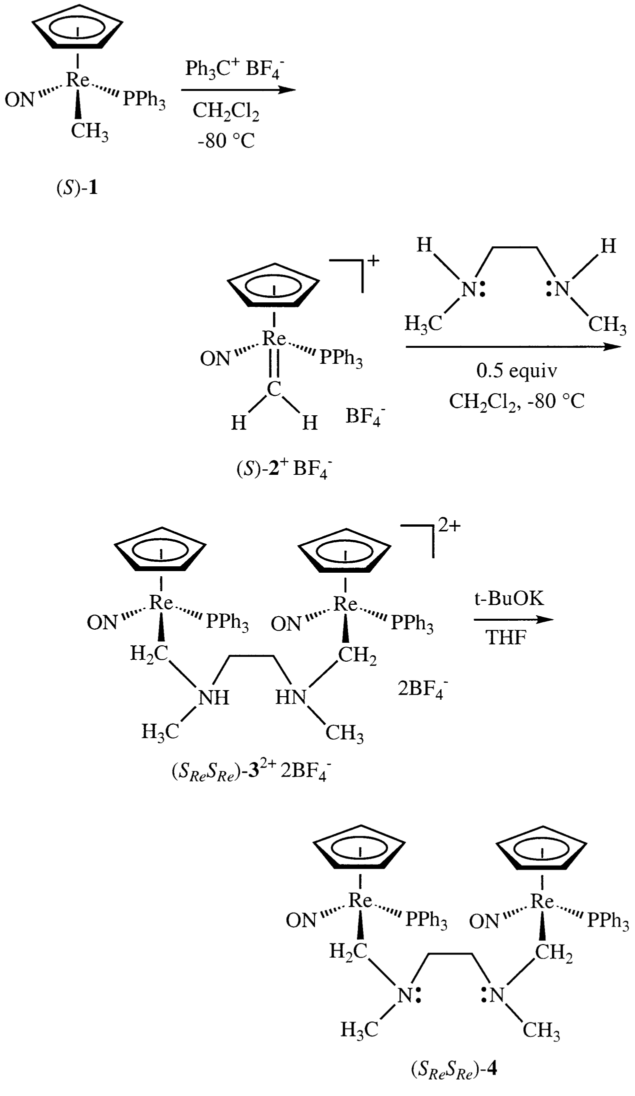
(18) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(19) O'Connor, E. J.; Kobayashi, M.; Floss, H. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 4837.

(20) The absolute configurations at rhenium are assigned according to a modified Cahn−Ingold−Prelog priority rule. The cyclopentadienyl ligand is considered a pseudoatom of atomic number 30. This gives the following sequence: $\eta^5\text{-}C_5H_5 > PPh_3 > NO > CH_2N > CH_3$. See: Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1.

(21) The nonracemic complexes in this study were first synthesized with a rhenium configuration opposite to that used in most previous studies. Although both enantiomers were eventually prepared, all characterization data are from the former series. To facilitate comparisons and analyses, the abstract, Results, and Discussion sections are narrated from the standpoint of the latter (customary) series (including schemes and figures). The compound configurations in the Experimental Section correspond to the work as it was actually conducted. One consequence deserves emphasis: the structures in Figures 1 and 2 are the enantiomers of those crystallographically determined.

Scheme 1. Synthesis of a Dirhenium-Substituted 1,2-Diamine



identical with $S_{\mathrm{Re}}R_{\mathrm{N}}S_{\mathrm{N}}S_{\mathrm{Re}}$), and $S_{\mathrm{Re}}R_{\mathrm{N}}R_{\mathrm{N}}S_{\mathrm{Re}}$. Accordingly, ^{31}P NMR spectra showed three signals (CD$_3$CN, δ 22.6, 22.1, 21.9; ca. 31:32:37), and ^{1}H NMR spectra showed four cyclopentadienyl signals (CD$_3$CN, δ 5.31, 5.30, 5.28, 5.23; ca. 32:10:30:28). No attempt was made to deconvolute or assign these resonances.

As depicted in Scheme 1, ($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-**3**$^{2+}$(BF$_4^-$)$_2$ and *t*-BuOK (2 equiv) were combined in THF. Workup gave the target diamine ($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-($\eta^5$-C$_5H_5$)Re(NO)(PPh$_3$)(CH$_2$N(CH$_3$)CH$_2CH_2$(H$_3$C)NCH$_2$)(Ph$_3$P)(ON)Re($\eta^5$-C$_5H_5$) (($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-**4**) in 66% yield as an air-stable orange powder.[21] This compound can be regarded as a dirhenium derivative of tetramethylethylenediamine (a dirhena-TMEDA). Since the nitrogen stereocenters are again trivalent, rapid inversion would be expected. Accordingly, only one ^{31}P NMR signal (δ 26.8) and one cyclopentadienyl ^{1}H NMR signal (δ 4.98) were observed, even in spectra recorded at −80 °C. In solution, ($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-**4** gradually decomposed over a period of several weeks. The IR spectrum of ($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-**4** showed a strong ν_{NO} band at slightly lower frequency than that of ($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-**3**$^{2+}$(BF$_4^-$)$_2$ (1630 vs 1647 cm^{-1}) and a broad, weak :NCH$_3$-derived ν_{CH} band (2774 cm^{-1}).[22] As expected, the diastereotopic ReCH$_2$ protons gave separate ^{1}H NMR signals (δ 4.18, br d, $^2J_{\mathrm{HH}} = 11.7$ Hz; δ 3.74, dd, $^2J_{\mathrm{HH}} = 11.7$, $^3J_{\mathrm{HP}} = 7.2$ Hz). The chemical shift/coupling constant pattern (downfield proton with near-zero $^3J_{\mathrm{HP}}$ value, upfield proton with larger $^3J_{\mathrm{HP}}$ value) differed from that of most neutral and cationic complexes with Re−CH$_2$X linkages.[23] However, exceptions are known, especially when X is a nitrogen or oxygen atom (e.g., pyridine or methoxide adducts).[18]

Palladium Chelate. We next sought to prepare a chelate derivative of ($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-**4**, preferably of a metal fragment used extensively in catalysis. A dichloropalladium adduct of TMEDA has been reported,[24] as well as many related compounds.[25] Note that chelation gives tetravalent nitrogen stereocenters that, in the absence of dissociation, will have high inversion barriers. As shown in Scheme 2, three rhenium/nitrogen diastereomers are possible. On the basis of both preparative[26,27] and computational[28] precedent, we expected to find the bulky rhenium moieties on opposite sides of the square-planar palladium. Not so obvious to every casual reader is that two diastereomers fit this criterion ($S_{\mathrm{Re}}R_{\mathrm{N}}R_{\mathrm{N}}S_{\mathrm{Re}}$ and $S_{\mathrm{Re}}S_{\mathrm{N}}S_{\mathrm{N}}S_{\mathrm{Re}}$).

The diamine ($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-**4** and (PhCN)$_2$PdCl$_2$ were combined in THF (Scheme 2). A precipitative workup gave the target chelate **5** in 80% yield as an air-stable orange powder.[21] Only one ^{31}P NMR signal (δ 24.8) and one cyclopentadienyl ^{1}H NMR signal (δ 5.06) were observed, even in spectra recorded at −90 °C, suggesting very high diastereomeric purity. The ReCH$_2$ protons gave ^{1}H NMR signals with the more usual chemical shift/coupling constant pattern (see above; δ 4.92, dd, $^2J_{\mathrm{HH}} = 12.3$, $^3J_{\mathrm{HP}} = 11.4$ Hz; δ 4.78, d, $^2J_{\mathrm{HH}} = 12.3$ Hz). The IR spectrum showed a strong ν_{NO} band (1636 cm^{-1}), and in accord with precedent for palladium and other metal chelates, the :NCH$_3$-based ν_{CH} band present for ($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-**4** had disappeared.[24]

Orange prisms of a CHCl$_3$ trisolvate were grown, and X-ray data were obtained as outlined in Table 1. Refinement, described in the Experimental Section, showed that the $S_{\mathrm{Re}}R_{\mathrm{N}}R_{\mathrm{N}}S_{\mathrm{Re}}$ diastereomer had formed.[21] An ORTEP drawing is given in Figure 1, and selected bond lengths, bond angles, and torsion angles are listed in Table 2. The unit cell was gigantic, especially in

---

(22) (a) Braunholtz, J. T.; Ebsworth, E. A. V.; Mann, F. G.; Sheppard, N. *J. Chem. Soc.* **1958**, 2780. (b) Baldwin, D. A.; Leigh, G. J. *J. Chem. Soc. A* **1968**, 1431.

(23) (a) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109. (b) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Am. Chem. Soc.* **1987**, *109*, 5711.

(24) Mann, F. G.; Watson, H. R. *J. Chem. Soc.* **1958**, 2772.

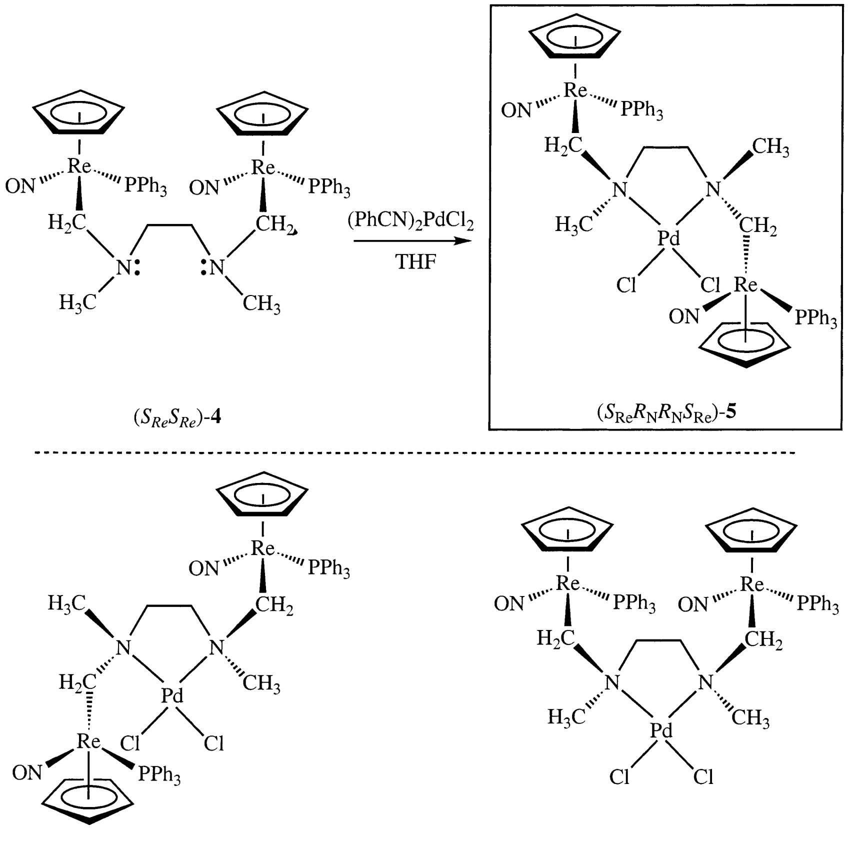
(25) (a) Abu-Surrah, A. S.; Fawzi, R.; Steimann, M.; Rieger, B. *J. Organomet. Chem.* **1996**, *512*, 243. (b) Robinson, D. J.; Kennard, C. H. L. *J. Chem. Soc. A* **1970**, 1008. (c) Haszeldine, R. N.; Young, J. C. *Proc. Chem. Soc., London* **1959**, 394. (d) Iball, J.; MacDougall, M.; Scrimgeour, S. *Acta Crystallogr.* **1975**, *B31*, 1672. (e) Ito, T.; Marumo, F.; Saito, Y. *Acta Crystallogr.* **1971**, *B27*, 1695. (f) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

(26) Lead references to a research team with many relevant papers on group 10−11 1,2-diamine complexes: (a) De Renzi, A.; Di Blasio, B.; Saporito, A.; Scalone, M.; Vitagliano, A. *Inorg. Chem.* **1980**, *19*, 960. (b) Albano, V. G.; Demartin, F.; De Renzi, A.; Morelli, G. *Inorg. Chim. Acta* **1988**, *149*, 253. (c) Cucciolito, M. E.; Jama, M. A.; Giordano, F.; Vitagliano, A.; De Felice, V. *Organometallics* **1995**, *14*, 1152. (d) Cavallo, L.; Cucciolito, M. E.; De Martino, A.; Giordano, F.; Orabona, I.; Vitagliano, A. *Chem. Eur. J.* **2000**, *6*, 1127.

(27) (a) Becker, J. J.; White, P. S.; Gagné, M. R. *Inorg. Chem.* **1999**, *38*, 798. (b) Zhang, X.; Zhu, Q.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 8093.

(28) Bernard, M.; Delbecq, F.; Sautet, P.; Fache, F.; Lemaire, M. *Organometallics* **2000**, *19*, 5715.

Scheme 2. Formation of a Palladium Chelate of ($S_{\rm Re}S_{\rm Re}$)-4: Possible Diastereomers



($S_{Re}S_{Re}$)-**4**

($S_{\rm Re}R_{\rm N}R_{\rm N}S_{\rm Re}$)-**5**

($S_{\rm Re}S_{\rm N}S_{\rm N}S_{\rm Re}$)-**5**

($S_{\rm Re}R_{\rm N}S_{\rm N}S_{\rm Re}$)-**5**

comparison to those of the >100 existing crystal structures of chiral rhenium complexes: eight molecules of ($S_{\rm Re}R_{\rm N}R_{\rm N}S_{\rm Re}$)-**5** and 24 of $CHCl_3$. This complicated the refinement, and consequently, the esd values associated with the metrical parameters are greater than normal. Nonetheless, the data unequivocally establish structure, relative and absolute configurations, and conformation.

The most striking feature of Figure 1 is the approximate C_2 symmetry axis passing through palladium. Neglecting minor differences in bond lengths and angles, this exchanges the two chlorine atoms, the amine nitrogen atoms, the chelate carbon atoms, and rhenium moieties. Both nitrogen stereocenters adopt *R* configurations in response to rhenium stereocenters of *S* configuration. As with other 1,2-diamine chelates, the five-membered ring is puckered (a λ or left-hand helical conformation in Figure 1),[29] with the C3−C30 bond at a −63.1° angle to the N1−Pd−N2 plane. The $PdCl_2$ bond lengths and angles (2.299(7)/2.334(8) Å, 90.2(3)°) are very close to those of three other crystallographically characterized 1,2-diamine adducts (2.283(1)−2.30(1) Å, 91.47(4)−90.7(3)°).[25a−c] The Pd−N bond lengths and angles (2.06(2)/2.07(2) Å; 85.9(9)°) are also very close (2.082(3)−2.09(2) Å, 85.70(12)−85.1(9)°).

Figure 2 shows a Newman-type projection of ($S_{\rm Re}R_{\rm N}R_{\rm N}S_{\rm Re}$)-**5** down the C1−Re1 bond.[21] The rhenium is formally octahedral, as analyzed in many previous papers. The chelate nitrogen is *roughly* anti to the bulky PPh_3 ligand, as quantified by a P−Re−C−N torsion angle of 142(2)° (at Re2, 147(5)°). Analogous solid-state conformations are found for all other complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2X)]^{n+}(X'^-)_n$.[11b,15,30] This directs the X group into the least congested interstice, between the smaller nitrosyl and cyclopentadienyl ligands.[23] The deviation from an idealized anti P−Re−C−X conformation renders one diastereotopic $ReCH_2$ proton roughly orthogonal to phosphorus (occupying the interstice between the cyclopentadienyl and PPh_3 ligands) and the other syn. Experiments have established a Karplus-type $^3J_{\rm HP}$ relationship, such that the ^{1}H NMR signal with the smaller coupling can be assigned to the "orthogonal" proton.[23]

A number of complexes are known in which the atom β to rhenium bears three sterically differentiated substituents (L/M/S). The conformations about the $ReCH_2$−X(L)(M)(S)[30b−c] or ReD−C(L)(M)(S)[13,31] linkages have also been analyzed (D = non-carbon ligating atom). Typically, the largest group (L) exhibits a torsion angle near 180°, such that the Re−C and X−L or Re−D and C−L bonds are roughly anti to each other. This feature is evident in ($S_{\rm Re}R_{\rm N}R_{\rm N}S_{\rm Re}$)-**5**, which has a large β-palladium moiety and Re−C−N−Pd torsion angles of 165.8(11)/158.9(13)°. As illustrated by the stylized representation **C** in Figure 2, these torsion angle relation-

---

[29] House, D. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 2, p 23.

[30] (a) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204. (b) Meyer, O.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1995**, *14*, 1844. (c) Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *J. Chem. Soc., Dalton Trans.* **1995**, 1857.

[31] Otto, M.; Boone, B. J.; Arif, A. M.; Gladysz, J. A. *J. Chem. Soc., Dalton Trans.* **2001**, 1218.

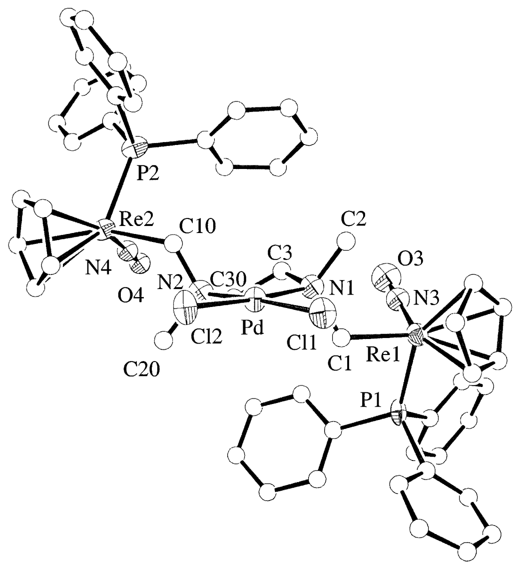


Figure 1. Molecular structure of ($R_{Re}S_NS_NR_{Re}$)-**5**.[21]

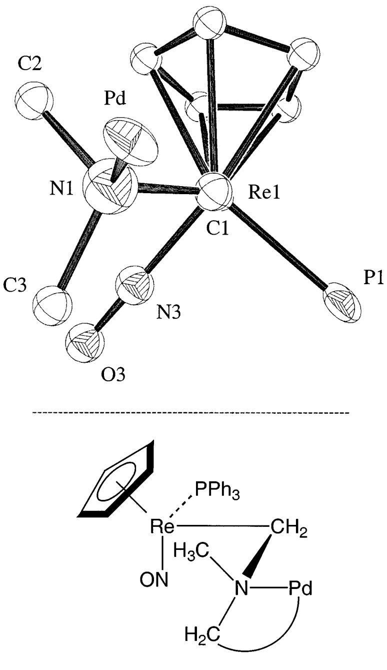
Table 1. Summary of Crystallographic Data

	($S_{Re}R_NR_NS_{Re}$)-**5**·3CHCl$_3$[21]	($R_{Re}R_N$,$S_{Re}S_N$)-**6**$^+$BF$_4^-$·CH$_2$Cl$_2$
formula	$C_{55}H_{57}Cl_{11}$-$N_4O_2P_2PdRe_2$	$C_{61}H_{78}B_2Cl_2F_8$-$N_6O_2P_2Re_2$[a]
fw	1736.74	1606.15
collecn temp (K)	85(2)	173(2)
diffractometer	KUMA KM4	Nonius KappaCCD
cryst syst	tetragonal	triclinic
space group	$P4_12_12$	$P\bar{1}$
cell dimens		
a, Å	20.096(4)	9.45120(10)
b, Å	20.096(4)	13.8930(2)
c, Å	33.398(17)	26.6314(4)
V, Å^3	13 488(8)	3281.34(8)
Z	8	2
d$_{calcd}$, g/cm^3	1.711(1)	1.626
d_{obsd}, g/cm^3 (CCl$_4$/CH$_2$I$_2$, 22 °C)	1.72	-
cryst dimens, mm	0.35 × 0.20 × 0.20	0.20 × 0.10 × 0.10
no. of rflns measd	9926	26 057
range/indices (h, k, l)	−15 to +15; 0−22; 0−34	−12 to +12; −18 to +18; −30 to +34
θ limit, deg	2.27−23.05	1.54−27.49
total no. of unique data	7509	15 034
no. of obsd data, $I > 2\sigma(I)$	3954	9148
abs coeff, mm^{-1}	4.368	3.885
min transmissn, %	30.2	51.05
max transmissn, %	43.6	69.74
no. of variables	406	780
no. of restraints	0	21
goodness of fit	1.030	0.957
$R_{int} = \sum\|F_o^2 - F_o^2(\text{mean})\|/\sum[F_o^2]$	0.1254	0.0644
R1 $= \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.1500; 0.0644[a]	0.1132; 0.0487[a]
wR2 $= (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$	0.1744; 0.1509[a]	0.1301; 0.1052[a]
$\Delta\rho$ (max), e/Å^3	1.381	1.787

[a] All; observed.

ships lead to a “W”-shaped conformational preference for the P−Re−C−X−L or P−Re-D−C−L units. This will play a key role in analyzing the diastereoselectivity of chelate formation (see Discussion).

Other Reactions. The synthesis of ($S_{Re}S_{Re}$)-**3**$^{2+}$(BF$_4^-$)$_2$ in Scheme 1 gives a mixture of diastereomers. We wondered if other approaches might give more enriched samples. Thus, ($S_{Re}S_{Re}$)-**3**$^{2+}$(BF$_4^-$)$_2$ and triethylamine (0.3 equiv) were combined in CD$_3$CN in an NMR tube.[21] The added base was expected to be weaker than the diconjugate base ($S_{Re}S_{Re}$)-**4** but sufficiently



C

Figure 2. Partial views of the structure of ($R_{Re}S_NS_NR_{Re}$)-**5**.[21]

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in ($S_{Re}R_NR_NS_{Re}$)-5·3CHCl$_3$[21]

Pd−N1	2.05(2)	Pd−N2	2.07(2)
Pd−Cl1	2.303(7)	Pd−Cl2	2.337(7)
N1−C3	1.57(3)	N2−C30	1.46(3)
C3−C30	1.44(3)		
Cl1−Pd−Cl2	90.1(3)	N1−Pd−N2	86.2(9)
N1−Pd−Cl1	91.8(7)	N2−Pd−Cl2	92.1(6)
N1−Pd−Cl2	175.7(7)	N2−Pd−Cl1	176.1(7)
C3−N1−Pd	105.0(15)	C30−N2−Pd	104.4(16)
C30−C3−N1	107(2)	C3−C30−N2	114(2)
Re1−C1	2.19(2)	Re2−C10	2.17(3)
Re1−P1	2.325(7)	Re2−P2	2.327(8)
Re1−N3	1.86(2)	Re2−N4	1.70(2)
N3−O3	1.07(2)	N4−O4	1.26(3)
C1−Re1−P1	88.4(6)	C10−Re2−P2	89.4(8)
P1−Re1−N3	90.9(7)	P2−Re2−N4	92.2(8)
N3−Re1−C1	101.0(9)	N4−Re2−C10	98.3(11)
N1−C1−Re1	123.8(17)	N2−C10−Re2	119.0(19)
N1−C1	1.45(3)	N2−C10	1.51(4)
N1−C2	1.52(3)	N2−C20	1.49(3)
C1−N1−Pd	113.1(17)	C10−N2−Pd	109.5(17)
C2−N1−Pd	106.5(15)	C20−N2−Pd	108.6(16)
C1−N1−C2	112.2(19)	C10−N2−C20	115(2)
C1−N1−C3	109(2)	C10−N2−C30	113(2)
C2−N1−C3	111(2)	C20−N2−C30	106(2)
N1−C3−C30−N2	−54.8(30)		
N3−Re1−C1−N1	51.8(21)		
N4−Re2−C10−N2	54.7(23)		
P1−Re1−C1−N1	142.2(20)		
P2−Re2−C10−N2	147.5(21)		
Pd−N1−C1−Re1	165.8(11)		
Pd−N2−C10−Re2	158.9(13)		
C2−N1−C1−Re1	45.0(28)		
C20−N2−C10−Re2	36.7(31)		
C3−N1−C1−Re1	−77.6(23)		
C30−N2−C10−Re2	−86.2(24)		

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in $(R_{\mathrm{Re}}R_{\mathrm{N}},S_{\mathrm{Re}}S_{\mathrm{N}})-6^+BF_4^-$·CH$_2Cl_2$[a]

Re1−C50	2.160(6)/2.158(7)	N2−C53	1.514(8)/1.473(9)
Re1−P1	2.3555(18)/2.354(2)	N2−C50	1.545(8)/1.538(9)
Re1−N1	1.763(6)/1.743(6)	N2−C51	1.505(9)/1.504(10)
N1−O1	1.212(7)/1.214(7)	N3−C54	1.454(9)/1.472(10)
C53−C54	1.501(10)/1.509(11)	N3−C55	1.419(11)/1.429(9)
C50−Re1−P1	88.99(18)/90.2(2)	C50−N2−C53	113.3(5)/112.9(6)
N1−Re1−P1	91.27(19)/89.2(2)	C54−C53−N2	114.9(6)/110.4(6)
N1−Re1−C50	98.4(3)/96.3(3)	C51−N2−C53	112.9(5)/112.8(6)
N2−C50−Re1	115.6(4)/114.2(5)	C53−C54−N3	108.5(6)/107.8(7)
C50−N2−C51	111.1(5)/115.0(6)	C55−N3−C54	116.0(7)/113.6(7)
N1−Re1−C50−N2	56.9(5)/66.9(5)	N2−C53−C54−N3	−171.8(6)/−48.8(9)
P1−Re1−C50−N2	148.0(4)/156.1(5)	C50−N2−C53−C54	66.9(8)/−84.7(8)
C51−N2−C50−Re1	−88.3(6)/−71.7(7)	C51−N2−C53−C54	−60.6(8)/142.9(8)
C53−N2−C50−Re1	143.3(4)/157.0(5)	C50−N2−C51−C52	174.6(6)/−63.8(9)
H2A−N2−C50−Re1	−26.1/−42.4		

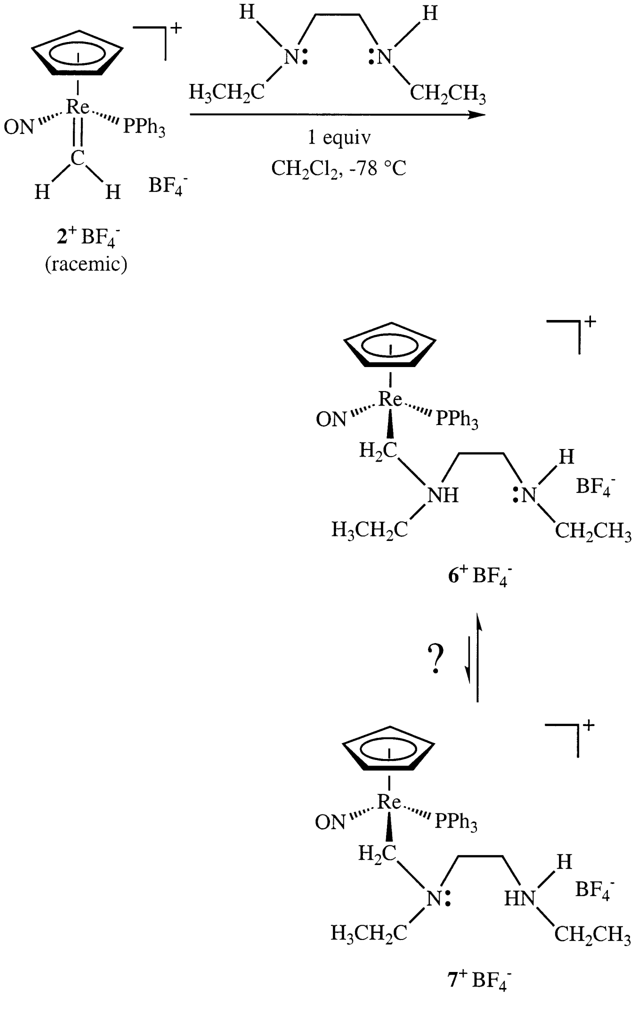
[a] The slash (/) separates data for the two independent cations.

strong for proton exchange and diastereomer equilibration. Accordingly, the ^{31}P NMR spectrum collapsed to one broad signal, and the ^{1}H NMR spectrum gave one broad cyclopentadienyl signal (δ 5.26). The volatiles were removed, and the residue was reprecipitated to return $(S_{\mathrm{Re}}S_{\mathrm{Re}})$-**3**$^{2+}(\mathrm{BF_4}^-)_2$ as a mixture of diastereomers (^{31}P NMR δ 22.6, 22.1, 21.9; ca. 33:35:32) in nearly the same ratio as the starting sample (31:32:37).

Another strategy would be to attempt a synthesis under kinetic control. Thus, $(S_{\mathrm{Re}}S_{\mathrm{Re}})$-**4** and the strong acid HBF$_4$·OEt$_2$ (2 equiv) were combined in THF at −80 °C in a NMR tube.[21] The ^{31}P NMR spectrum showed several signals, and the resulting $(S_{\mathrm{Re}}S_{\mathrm{Re}})$-**3**$^{2+}(\mathrm{BF_4}^-)_2$ was isolated and analyzed by NMR (CD$_3$CN). The ^{31}P spectrum showed four peaks (δ 22.6, 22.5, 22.1, 21.9; ca. 21:21:21:37) and the ^{1}H spectrum four cyclopentadienyl peaks (δ 5.31, 5.30, 5.28, 5.23; ca. 21:21:37:21). Hence, all attempts to obtain diastereomerically enriched $(S_{\mathrm{Re}}S_{\mathrm{Re}})$-**3**$^{2+}(\mathrm{BF_4}^-)_2$ were unsuccessful.

In the course of the preceding efforts, reactions of methylidene complex **1** and other types of amines were attempted, normally in search of model compounds or data. One experiment used racemic **1** and the *N,N′*-diethyl analogue of the original diamine, HN(CH$_2$CH$_3$)CH$_2$CH$_2$(H$_3$CH$_2$C)NH. Although the initial conditions were directed at the synthesis of a homologue of $(S_{\mathrm{Re}}S_{\mathrm{Re}})$-**3**$^{2+}(\mathrm{BF_4}^-)_2$, a crystalline byproduct was obtained, the 1:1 adduct [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_2$NH(CH$_2$CH$_3$)CH$_2$CH$_2$NH(CH$_2$CH$_3$))]$^+$BF$_4^-$ (**6**$^+$BF$_4^-$). Hence, the reaction was conducted with the proper stoichiometry as shown in Scheme 3, and the crude tertiary ammonium salt **6**$^+$BF$_4^-$ was isolated in 92% yield. The microanalysis fit the molecular formula.

Scheme 3. Synthesis of a 1:1 Rhenium 1,2-Diamine Adduct



The ^{1}H NMR spectrum showed three cyclopentadienyl signals in a 63:22:15 ratio (δ 5.28, 5.32, 5.55), and traces of additional components (≤2% each) were seen by ^{31}P NMR. Two signals might be due to rhenium−nitrogen diastereomers. Another possibility would be a tautomer, the secondary ammonium salt **7**$^+$BF$_4^-$ (Scheme 3). The equilibrium **6**$^+$BF$_4^-$/**7**$^+$BF$_4^-$ is of particular interest, since it reflects the relative Brønsted basicities of two nitrogen atoms that differ in a single substituent (ReCH$_2$ vs H). The ^{1}H NMR couplings were not well enough resolved to establish the location of the ammonium proton. However, other data strongly suggest that **6**$^+$BF$_4^-$ dominates in solution. For example, the cyclopentadienyl ^{1}H NMR chemical signals of the two major species (δ 5.28, 5.32) are much closer to those of dicationic $(S_{\mathrm{Re}}S_{\mathrm{Re}})$-**3**$^{2+}(\mathrm{BF_4}^-)_2$ than those of neutral $(S_{\mathrm{Re}}S_{\mathrm{Re}})$-**4** ($\delta$ 5.31−5.23 vs 4.98). The ^{31}P NMR signals and IR ν_{CO} values show similar trends.

Crystallization gave a dichloromethane solvate (75%), and X-ray data were collected (Table 1). Refinement showed two independent cations in the unit cell. Key metrical parameters are given in Table 3. As shown in Figure 3 (top, bottom), both cations were $S_{\mathrm{Re}}S_{\mathrm{N}},R_{\mathrm{Re}}R_{\mathrm{N}}$ diastereomers of **6**$^+$BF$_4^-$, differing in the conformations

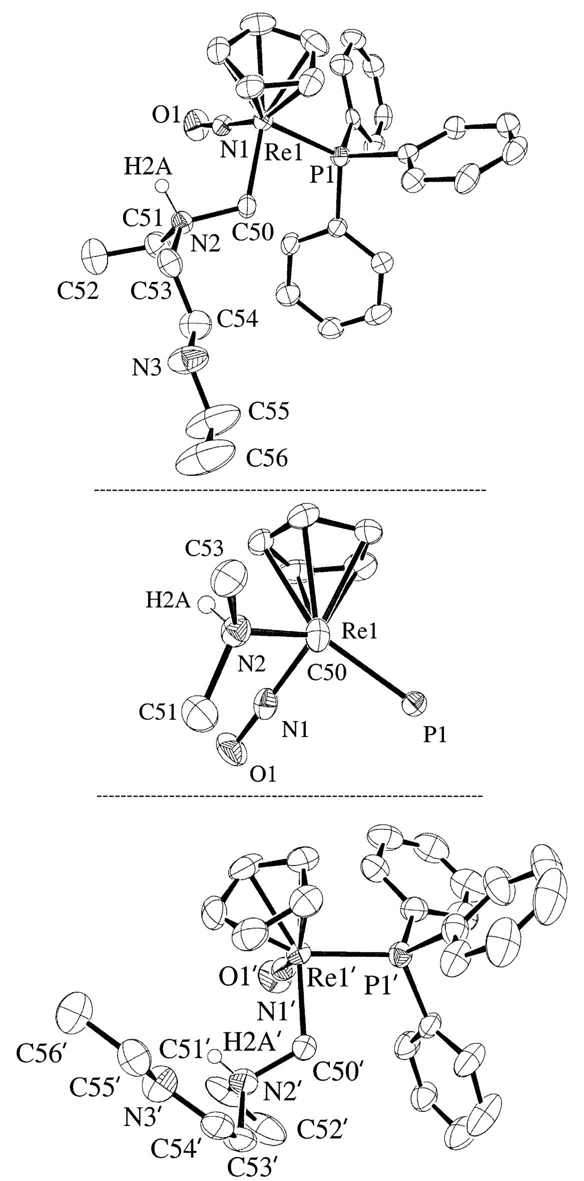


Figure 3. Structures of the cations of $(R_{Re}R_N,S_{Re}S_N)$-$\mathbf{6}^+BF_4^-$: (top) first independent cation; (middle) Newman projection (partial) down the C−Re bond; (bottom) second independent cation.

of the $ReCH_2N$−alkyl groups. The ammonium proton electron density was located in each, confirming the absence of the tautomer $\mathbf{7}^+BF_4^-$. As a check, the $N-CH_2CH_3$ bond lengths were compared. Those at the nitrogen β to rhenium (1.505(9)/1.504(10) Å) were significantly longer than at the nitrogen ϵ to rhenium (1.419(11)/1.429(9) Å). The former values are typical for tertiary ammonium salts, whereas tertiary and secondary amines exhibit shorter nitrogen−carbon bonds (average values in the Cambridge Structural Database: 1.502 and 1.469 Å).[32]

The cations in Figure 3 are depicted with calculated ammonium proton positions. In the first, the closest $ReCH_2NH-BF_4^-$ contact (2.095 Å) is much shorter than in the second (3.870 Å). On the other hand, the second has a short $ReCH_2NH-N$ contact (2.158 Å, with N2′/N3′ = 2.727 Å). The conformation of the $CH_2CH_2NHCH_2CH_3$ group in the first cation precludes a similar interaction. Such 2.1−2.2 Å distances are typical of weak ammonium hydrogen bonds,[33] something that each cation finds a separate means of achieving. Since both cations exhibit similar $Re-CH_2$ conformations, only the Newman projection of the first is given (middle, Figure 3). This shows that $(S_{Re}S_N,R_{Re}R_N)$-$\mathbf{6}^+BF_4^-$ has a $Re-CH_2$ conformation similar to that of $(S_{Re}R_NR_NS_{Re})$-**5** (Figure 2, top), with P−Re−C−N torsion angles of 148.0(4)/156.1(4)° as compared to 142(2)/147(5)°. With respect to the $ReCH_2-N$ conformation, the largest group on nitrogen ($CH_2CH_2NHCH_2CH_3$) is roughly anti to the $Re-CH_2$ bond, as indicated by torsion angles of 143.3(4)/157.0(5)°. This is again similar to $(S_{Re}R_NR_NS_{Re})$-**5** (Figure 2, bottom), in which the analogous $Re-CH_2-N-Pd$ torsion angles are 165.8(11)/158.9(13)°.

When crystalline $(S_{Re}S_N,R_{Re}R_N)$-$\mathbf{6}^+BF_4^-\cdot CH_2Cl_2$ was dissolved, two cyclopentadienyl ^1H NMR signals (δ 5.28, 5.32; 69:31) and one ^{31}P NMR signal were observed. The tautomer $\mathbf{7}^+BF_4^-$ has a configurationally labile nitrogen stereocenter and can only give one set of signals. The ^1H NMR signals therefore represent either two diastereomers of $\mathbf{6}^+BF_4^-$ or $\mathbf{7}^+BF_4^-$ and one diastereomer of $\mathbf{6}^+BF_4^-$. We have prepared other pairs of $ReCH_2N^+HRR'/ReCH_2NRR'$ compounds and always find widely separated ^{31}P and cyclopentadienyl ^1H NMR signals.[34] We therefore conclude, as further supported by chemical shift arguments above, that the signals represent diastereomers of $\mathbf{6}^+BF_4^-$. This in turn indicates that (1) $\mathbf{6}^+BF_4^-$ is more stable than $\mathbf{7}^+BF_4^-$ and (2) the diastereomers of $\mathbf{6}^+BF_4^-$ rapidly equilibrate in solution, quite possibly via $\mathbf{7}^+BF_4^-$.

Discussion

The very high diastereoselectivity with which the chelate complex $(S_{Re}R_NR_NS_{Re})$-**5** forms represents one of the most interesting aspects of the preceding data. Since different nitrogen-based diastereomers of such metal 1,2-diamine catalysts would logically give different enantioselectivities, this point is analyzed first. Here, the configurationally labile alkoxide and amido complexes mentioned in the Introduction, $(\eta^5-C_5H_5)Re(NO)(PPh_3)(OCHRR')$ and $(\eta^5-C_5H_5)Re(NO)(PPh_3)(N(R'')CHRR')$, are relevant. They undergo epimerization at both rhenium and carbon, and thermodynamic diastereomer ratios are easily obtained. The direction of equilibrium can be rationalized by the model shown in Scheme 4, in which both diastereomers (**D** and **E**) are viewed in W-type conformations with respect to phosphorus, rhenium, oxygen/nitrogen, carbon, and the largest group on carbon. As noted in the torsion angle analyses above, this directs the largest groups anti about the Re−O/N and O/N−C bonds.

In the less stable diastereomer (**E**), a slight destabilizing interaction between the medium-sized carbon substituent and the cyclopentadienyl ligand can be identified. In the more stable diastereomer (**D**), the medium-sized carbon substituent is aligned with the

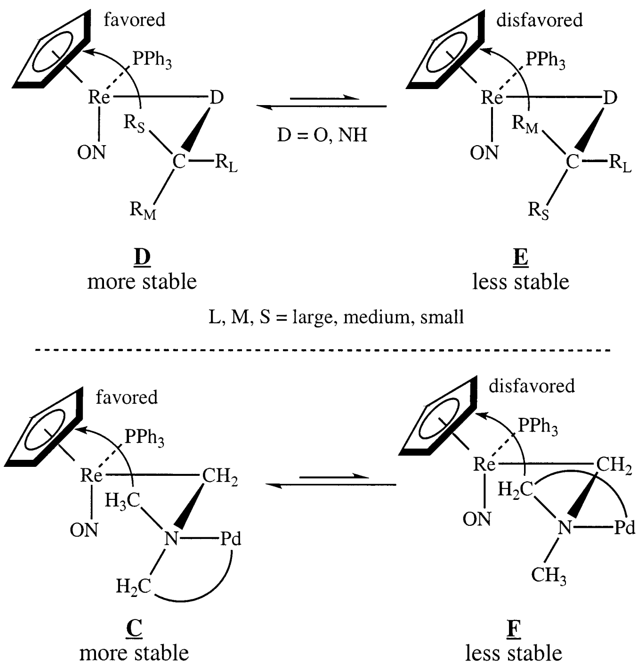
---

(32) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1 (compare the last five entries on page S9 with entries 2−5 on page S10).

(33) (a) Dewey, M. A.; Knight, D. A.; Klein, D. P.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1991**, *30*, 4995. (b) Amoroso, A. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1997**, *16*, 6032.

(34) Prommesberger, M. Unpublished research reports, University of Erlangen-Nürnberg.

Scheme 4. Models for Relative Stabilities of Diastereomers



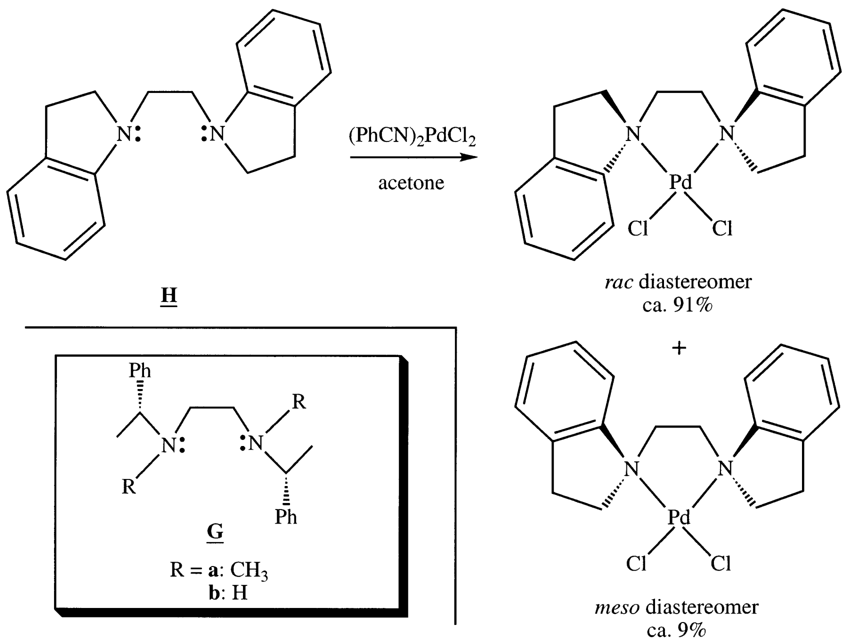
small nitrosyl ligand. Although such compounds certainly adopt an ensemble of conformations in solution, this simple explanation has rationalized all data to date. Our new results with $6^+BF_4^-$ also indirectly support this model. First, the diastereomers rapidly equilibrate in solution. Second, the two independent cations in Figure 3 ($S_{Re}S_N,R_{Re}R_N$) both correspond to diastereomer **D** (D = CH$_2$ and nitrogen in place of C_β). Although this cannot be taken as a proof of the dominant diastereomer in solution, it is always the more probable case, and even more so here, since nature would have to perpetrate the same deception twice.

In the same sense, the observed chelate diastereomer ($S_{Re}R_NR_NS_{Re}$)-**5** and the alternative ($S_{Re}S_NS_NS_{Re}$)-**5** can be represented as **C** and **F** in Scheme 4. The palladium is clearly the largest group on nitrogen and methyl the smallest. In **F**, a destabilizing interaction between the chelate backbone and the cyclopentadienyl ligand is present. Thus, ($S_{Re}R_NR_NS_{Re}$)-**5** can be viewed as a "doubly matched" diastereomer, whereas ($S_{Re}S_NS_NS_{Re}$)-**5** is doubly mismatched. Since we have no evidence that chelate formation is under thermodynamic control, the diastereoselectivity might be a function of similar interactions in transition states. Regardless, this model constitutes a very plausible mechanism for 1,3-chirality transfer from rhenium to nitrogen. One corollary is that the corresponding *N*,*N'*-diethyl chelate (i.e., the same diamine used for $6^+BF_4^-$) would have a greater tendency to give other diastereomers, since the ethyl group will be closer in effective size to the chelate backbone.

Purely organic chiral 1,2-diamines that contain carbon stereocenters in the nonchelating *N*-alkyl substituents are known. One example is **G-a** (Scheme 5),[26a,b] which, like ($S_{Re}S_{Re}$)-**4**, has tertiary nitrogen stereocenters. Enantiomerically pure **G-a** has a carefully characterized coordination chemistry. To our knowledge chelate diastereomers have never been observed—despite possibilities analogous to those of ($S_{Re}S_{Re}$)-**4** in Scheme 2. As would be expected, structurally characterized complexes always have the larger CH(CH$_3$)Ph groups on opposite sides of the chelate plane. Interestingly, the related disecondary diamine **G-b** gives all three possible PtCl$_2$ chelate isomers.[35] Scheme 5 also shows a 1,2-diamine with only nitrogen stereocenters (**H**).[25a] When this ligand chelates PdCl$_2$, *rac* and *meso* diastereomers can be detected. The major *rac* diastereomer has been crystallized and structurally characterized. More importantly, NMR spectra show no trace of the *meso* diastereomer. Hence, we believe that the diastereomers of chelate **5** (Scheme 2) are also slow to equilibrate in solution.

From the standpoint of concept and design in new chiral diamines for enantioselective synthesis, the representative ferrocene-containing examples in Figure 4

Scheme 5. Other Chelating 1,2-Diamines and Palladium Complexes



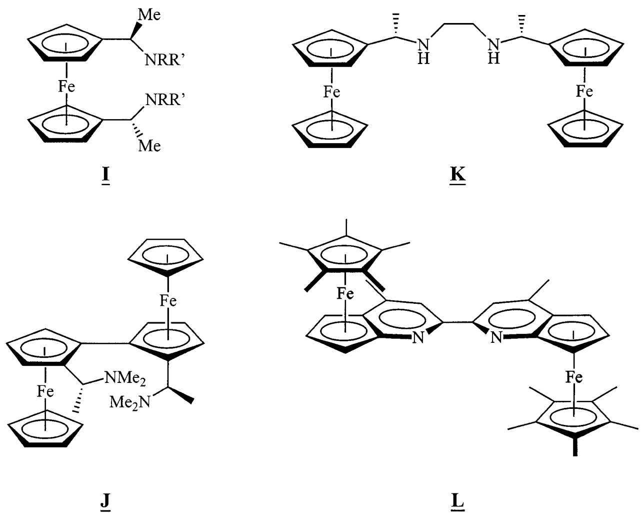


Figure 4. Representative ferrocenes containing chiral diamines.

are offered for comparison. These place the ferrocene units *endocyclic* to the chelate backbone (**I**),[8d,e] *exocyclic* to the chelate backbone (**J**),[8a] within the N-alkyl substituents (**K**),[8c] or in other motifs (**L**).[9a,b] Both **J** and **L** contain planar chirality elements. To our knowledge, no other transition-metal fragments, chiral or otherwise, have been similarly applied as architectural units in chiral diamines. In view of the tremendous breath of transition-metal fragments available, and the intrinsic diversity elements within, we find this oversight surprising. The conversion of commercial $Re_2(CO)_{10}$ to the nonracemic methyl complex (*S*)-**1** and then ($S_{\mathrm{Re}}S_{\mathrm{Re}}$)-**4** requires nine steps and proceeds in 37% overall yield. This is not as efficient as the synthesis of **I** (four steps from ferrocene, 76%) but compares favorably with that of **L** (six steps from a tetrasubstituted pyridine, 10%).

Chiral diamines that are unsymmetrically substituted or have chirality elements only on one terminus are also highly effective in certain enantioselective reactions.[2,36] Thus, possible applications of $\mathbf{6}^+BF_4^-$ (Scheme 3) or its conjugate base should not be overlooked. However, within the context of this study, this half-protonated diamine is more important for the physical insight provided. As noted above, the lower stability of the tautomer $\mathbf{7}^+BF_4^-$ shows that the Brønsted basicity of a $ReCH_2$-substituted amine is much greater than that of an analogous hydrogen-substituted amine. In other words, a (η^5-C_5H_5)Re(NO)(PPh_3)CH_2− substituent is a much stronger electron donor than hydrogen toward nitrogen.

In summary, this study has described a very efficient synthesis of a new and architecturally novel chiral 1,2-diamine capable of C_2 symmetry. It is the first 1,2-diamine in which the chirality is derived from a metal as opposed to a carbon stereocenter. It readily forms chelates with very high diastereoselectivity, and the rhenium fragment confers a unique combination electronic and steric properties. Applications in enantioselective organic catalysis and other extensions of this work will be reported in due course.

Experimental Section

General Considerations. All reactions were conducted under dry inert atmospheres. Analytical data were recorded on standard instruments, most of which were listed in a previous paper.[37] Rather than enumerate the many small differences between the two locations in which synthetic work was conducted, readers are referred to two dissertations.[16] Chemicals were treated as follows: $CHCl_3$, distilled from P_2O_5; CH_2Cl_2 and ethyl acetate, distilled from CaH_2; toluene, hexane, benzene, ether, and THF, distilled from Na/benzophenone; C_6D_6, CD_2Cl_2, and CD_3CN (Cambridge) and *t*-BuOK (Aldrich), used as received; $HN(R)CH_2CH_2(R)NH$ (Aldrich), dried and distilled from KOH (R = CH_3) or dried over 4 Å molecular sieves (R = CH_2CH_3); $Ph_3C^+BF_4^-$ (Fluka), recrystallized from CH_2Cl_2/ethyl acetate.[38]

($R_{\mathrm{Re}}R_{\mathrm{Re}}$)-[($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($CH_2NH(CH_3)CH_2CH_2$($H_3C$)$HNCH_2$)($Ph_3P$)(ON)Re($\eta^5$-$C_5H_5$)]$^{2+}$($BF_4^-$)$_2$ (($R_{\mathrm{Re}}R_{\mathrm{Re}}$)-$\mathbf{3}^{2+}$($BF_4^-$)$_2$).[21] A Schlenk flask was charged with (*R*)-**1** (0.7131 g, 1.276 mmol)[12] and CH_2Cl_2 (20 mL) and cooled to −80 °C (acetone/CO_2 @ 1300 m). A second Schlenk flask was charged with $Ph_3C^+BF_4^-$ (0.4226 g, 1.280 mmol) and CH_2Cl_2 (20 mL) and cooled to −80 °C. The solution in the second Schlenk flask was added to the first, dropwise via cannula over 30 min, to generate (*R*)-$\mathbf{2}^+BF_4^-$.[17,18] After 10 min, $HN(CH_3)CH_2CH_2(H_3C)NH$ (0.068 mL, 0.64 mmol) was added. After 8 h, the cold bath was removed and the mixture warmed to room temperature. The sample was filtered (glass frit) and reduced to 10 mL under vacuum (10 mmHg). Benzene (40 mL) was added and the sample kept at −10 °C for 12 h. The yellow microcrystals were collected by filtration, washed with hexane (5 mL), and dried by oil pump vacuum to give ($R_{\mathrm{Re}}R_{\mathrm{Re}}$)-$\mathbf{3}^{2+}$($BF_4^-$)$_2$ (0.8243 g, 0.5986 mmol, 94%). Anal. Calcd for $C_{52}H_{56}B_2F_8N_4O_2P_2Re_2$: C, 45.36; H, 4.10. Found: C, 45.36; H, 4.17. IR (cm^{-1}, KBr): ν_{NH} 3548 s br, ν_{NO} 1647 s. NMR (δ, CD_3CN): ^{1}H 7.60−7.12 (m, 6Ph), 6.05−5.80 (br s, 2NH), 5.31, 5.30, 5.28, 5.23 (4s, $2C_5H_5$; ca. 32:10:30:28), 4.54−4.32 (m, 2H of $ReCH_2$), 4.10−3.88 (m, 2H of $ReCH_2$), 3.60−3.48 (m, 2H of $2NCH_2$), 3.40−3.06 (m, 2H of $2NCH_2$), 2.81, 2.75, 2.70 (3d, J_{HH} = 5.1, $2NCH_3$; ca. 34:37:29); ^{31}P{^{1}H} 22.6, 22.1, 21.9 (3s; ca. 31:32:37).

($R_{\mathrm{Re}}R_{\mathrm{Re}}$)-($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($CH_2N(CH_3)CH_2CH_2$($H_3C$)$NCH_2$)($Ph_3P$)(ON)Re($\eta^5$-$C_5H_5$) (($R_{\mathrm{Re}}R_{\mathrm{Re}}$)-4).[21] A Schlenk flask was charged with ($R_{\mathrm{Re}}R_{\mathrm{Re}}$)-$\mathbf{3}^{2+}$($BF_4^-$)$_2$ (0.9270 g, 0.6730 mmol) and THF (20 mL). Then *t*-BuOK (1.35 mL, 1.0 M in THF, 1.35 mmol) was added. After 30 min, solvent was removed by oil pump vacuum. Toluene (10 mL) was added, and the mixture was filtered through a medium-porosity glass frit. Heptane (30 mL) was added to the filtrate and the sample kept at −10 °C for 12 h. The orange precipitate was collected by filtration and dried by oil pump vacuum to give ($R_{\mathrm{Re}}R_{\mathrm{Re}}$)-**4** (0.5236 g, 0.04462 mmol, 66%): mp 97.8 °C (DSC), 101 °C dec (capillary). Anal. Calcd for $C_{52}H_{54}N_4O_2P_2Re_2$: C, 51.99; H, 4.53. Found: C, 51.88; H, 4.69. IR (cm^{-1}, C_6H_6): ν_{CH} (:NCH_3)[22] 2774 w br, ν_{NO} 1630 s (KBr, 1624). MS (positive FAB, 3-NBA/C_6H_6, *m/z*): 1199 (45.8), 1200 (27.2), 1201 (M$^+$, 100), 1202 (55.6), 1203 (76.7), 1204 (38.7), 1205 (12.2), 1206 (3.5). NMR (δ, C_6D_6): ^{1}H 7.59−7.51 (m, 12H of 6Ph), 7.07−6.95 (m, 18H of 6Ph), 4.98 (s, $2C_5H_5$), 4.18 (br d, J_{HH} = 11.7, $w_{1/2}$ = 5.3 Hz, 2ReC*H*H′), 3.74 (dd, $^1J_{\mathrm{HH}}$ = 11.7, $w_{1/2}$ = 2.8 Hz, $^3J_{\mathrm{HP}}$ = 7.2, 2ReCH*H*′), 3.20 (m, 2NC*H*H′), 2.65 (s, $2NCH_3$), 2.50 (m, 2NH*H*′); ^{13}C{^{1}H} 137.7 (d, J_{CP} = 50.1, *i*-Ph), 134.3 (d, J_{CP} = 10.9, *o*-Ph), 130.3 (s, *p*-Ph), 128.8 (s, *m*-Ph), 91.5 (s, C_5H_5), 60.2 (s, NCH_2), 47.1 (s, NCH_3), 31.2 (d, $ReCH_2$); ^{31}P{^{1}H} 26.8 (s).

---

(35) Fanizzi, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chem.* **1988**, *27*, 2422.

(36) (a) Södergren, M. J.; Andeersson, P. G. *J. Am. Chem. Soc.* **1998**, *120*, 10760 and reviews cited therein. (b) Fehr, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2567; *Angew. Chem.* **1996**, *108*, 2726.

(37) Alvey, L. J.; Meier, R.; Soós, T.; Bernatis, P.; Gladysz, J. A. *Eur. J. Inorg. Chem.* **2000**, 1975.

(38) Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956.

($R_{Re}S_NS_NR_{Re}$)-[(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2N(CH_3)$-$CH_2CH_2(H_3C)NCH_2$)(Ph_3P)(ON)Re(η^5-C_5H_5)]$PdCl_2$ (($R_{Re}S_N$-S_NR_{Re})-5).[21] A Schlenk flask was charged with ($R_{Re}R_{Re}$)-**4** (0.1339 g, 0.1114 mmol) and THF (10 mL). A second Schlenk flask was charged with $(PhCN)_2PdCl_2$ (0.0427 g, 0.1113 mmol)[39] and THF (10 mL). The second solution was added to the first via cannula. After 30 min, the solvent was removed by oil pump vacuum. Benzene (20 mL) was added. The sample was filtered (medium-porosity glass frit) and added to hexane (50 mL). The pale orange precipitate was collected by filtration and dried by oil pump vacuum to give ($R_{Re}S_NS_NR_{Re}$)-**5** (0.1223 g, 0.0887 mmol, 80%): mp 156 °C dec (capillary). Anal. Calcd for $C_{52}H_{54}N_4O_2P_2Re_2$: C, 45.30; H, 3.95. Found: C, 45.09; H, 4.01. IR (cm^{-1}, C_6H_6/KBr): ν_{NO} 1636/1634 s. NMR (δ, CD_2Cl_2): ^1H 7.55−7.30 (m, 6Ph), 5.06 (s, $2C_5H_5$), 4.92 (dd, $^2J_{HH} = 12.3$, $^3J_{HP} = 11.4$, $w_{1/2} = 2.7$ Hz, 2ReC*H*H′), 4.78 (br d, $^2J_{HH} = 12.3$, $w_{1/2} = 2.4$ Hz, 2ReCH*H*′), 2.33 (s, $2NCH_3$), 1.49 (d, $J_{HH} = 9.9$, 2NC*H*H′), 1.14 (d, $J_{HH} = 9.6$, 2NH*H*′); $^{13}C\{^1H\}$ 136.3 (d, $J_{CP} = 53.0$, *i*-Ph), 134.2 (d, $J_{CP} = 10.4$, *o*-Ph), 131.2 (s, *p*-Ph), 129.2 (d, $J_{CP} = 10.3$, *m*-Ph), 91.6 (s, C_5H_5), 61.8 (s, NCH_2), 54.9 (s, NCH_3), 31.0 (d, $ReCH_2$); $^{31}P\{^1H\}$ 24.8 (s).

Vapor diffusion of hexane into a $CHCl_3$ solution of ($R_{Re}S_NS_NR_{Re}$)-**5** (3 days) gave orange prisms of ($R_{Re}S_NS_NR_{Re}$)-**5**·$3CHCl_3$ that were used for X-ray crystallography (below).

[(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2NH(CH_2CH_3)CH_2CH_2NH(CH_2CH_3)$)]$^+BF_4^-$ ($6^+BF_4^-$). Racemic $\mathbf{2}^+BF_4^-$ was generated from racemic **1** (0.303 g, 0.542 mmol)[12] in CH_2Cl_2 (15 mL) and $Ph_3C^+BF_4^-$ (0.197 g, 0.597 mmol) in CH_2Cl_2 (5 mL) analogously to the procedure for (*R*)-$\mathbf{2}^+BF_4^-$ above. After 10 min, $HN(CH_2CH_3)CH_2CH_2(H_3CH_2C)NH$ (0.039 mL, 0.27 mmol) was added. The solution turned bright yellow. After 1.5 h, the cold bath was removed and the mixture warmed to room temperature. Hexane (40 mL) was added. The yellow precipitate was isolated by filtration and dissolved in CH_2Cl_2 (10 mL). An ether layer (40 mL) was added. After 2 h, the yellow powder was collected by filtration and dried by oil pump vacuum to give crude $\mathbf{6}^+BF_4^-$ (0.379 g, 0.498 mmol, 92%; see text for analysis of isomers). Anal. Calcd for $C_{30}H_{38}BF_4N_3OPRe$: C, 47.37; H, 5.03. Found: C, 46.99; H, 5.10. IR (cm^{-1}, KBr): ν_{NH} 3552 w br, ν_{NO} 1640 (C_6H_6 1644) vs. NMR (δ, CD_2Cl_2): ^1H 7.49−7.47 (m, 6H of 3Ph), 7.36−7.34 (m, 9H of 3Ph), 5.55, 5.32, 5.28 (3s, C_5H_5; ca. 15:22:63), 4.31 (d, $J_{HH} = 13.2$, ReC*H*H′), 3.9−3.7 (br m, 3H), 3.41 (m, 1H), 3.3−3.2 (br m, 2H), 3.05 (s, 1H), 2.95−2.80 (br m, 3H), 2.71−2.61 (br m, 2H), 1.23, 1.13 (2 pseudo-t, $J_{HH} = 7.1$, 6H, $2CH_3$; ca. 78:22); $^{13}C\{^1H\}$ (partial) 134.7 (d, $J_{CP} = 53.3$, *i*-Ph), 133.6 (d, $J_{CP} = 9.2$, *o*-Ph), 131.2 (s, *p*-Ph), 129.2 (d, $J_{CP} = 11.0$, *m*-Ph), 94.8, 91.4, 91.0 (3s, C_5H_5); $^{31}P\{^1H\}$ 21.9, 21.8, 21.2 (major), 20.5, 20.3 (5s).

The yellow powder was dissolved in CH_2Cl_2 (10 mL) and layered with benzene (40 mL). After 4 days, yellow cubic crystals were collected by filtration, washed with hexane, and dried by oil pump vacuum to give ($R_{Re}R_N$,$S_{Re}S_N$)-$\mathbf{6}^+BF_4^-\cdot CH_2Cl_2$ (0.316 g, 0.406 mmol, 75%). Anal. Calcd for $C_{30}H_{38}BF_4N_3OPRe\cdot CH_2Cl_2$: C, 44.03; H, 4.77. Found: C, 44.22; H, 4.81. NMR (δ, CD_2Cl_2): ^1H 7.49−7.47 (m, 6H of 3Ph), 7.36−7.34 (m, 9H of 3Ph), 5.32, 5.28 (2s, C_5H_5; 31:69), 4.31 (d, $J_{HH} = 13.2$, 1H of ReC*H*H′), 3.9−3.7 (br m, 3H), 3.41 (m, 1H), 3.3−3.2 (br m, 2H), 3.05 (s, 1H), 2.95−2.80 (br m, 3H), 2.71−2.61 (br m, 2H), 1.23, 1.13 (2 pseudo-t, $J_{HH} = 7.1$, 6H, CH_3 12:88); $^{13}C\{^1H\}$ 134.7 (d, $J_{CP} = 53.3$, *i*-Ph), 133.6 (d, $J_{CP} = 9.2$, *o*-Ph), 131.2 (s, *p*-Ph), 129.2 (d, $J_{CP} = 11.0$, *m*-Ph), 91.0 (s, C_5H_5), 55.9 (s, $^+NCH_2CH_2N$:),[40] 48.9 (s, $^+NCH_2CH_3$),[40] 44.1 (s, $^+NCH_2CH_2N$:),[40] 43.6 (s, :NCH_2CH_3),[40] 26.5 (s, $ReCH_2$), 15.3 (s, :NCH_2CH_3),[40] 7.6 (s, $^+NCH_2CH_3$);[40] $^{31}P\{^1H\}$ 21.2.

Crystallography. Crystals were obtained as described above and data collected as outlined in Table 1. Standard reflections showed no crystal decay.

Cell parameters of ($R_{Re}S_NS_NR_{Re}$)-**5**·$3CHCl_3$ were determined from 80 reflections with 15° < 2θ < 23°. The space group was determined from systematic absences and subsequent least-squares refinement. Lorentz, polarization, and absorption (numerical via SHELX76[41]) corrections were applied. The structure was solved by standard heavy-atom techniques with SHELXS and refined with SHELX-93.[42] Rhenium, palladium, and chlorine atoms were refined with anisotropic thermal parameters. Other atoms were refined isotropically, with the cyclopentadienyl, phenyl, and NO moieties as rigid groups. There were four $CHCl_3$ positions per palladium, but two were half-occupied, giving a tris(solvate). Hydrogen atom positions were calculated and added to the structure factor calculations but were not refined. The absolute configuration was confirmed by Flack's parameter (0.023(18)).[43]

Cell parameters of ($R_{Re}R_N$,$S_{Re}S_N$)-$\mathbf{6}^+BF_4^-\cdot CH_2Cl_2$ were determined and refined from 71 466 reflections. Lorentz, polarization, and absorption[44] corrections were applied. The structure was solved by direct methods and showed two independent molecules in the unit cell. The parameters were refined with all data by full-matrix least-squares on F^2 using SHELXL-93.[42] Non-hydrogen atoms were refined with anisotropic thermal parameters. The electron density for the ammonium hydrogens was located (N2, N2′), but for refinements all hydrogen atoms were fixed in idealized positions. Both BF_4^- anions showed partial disorder of one fluorine atom (F3,F3a and F3′,F3b), which could be resolved with a occupation ratio of 55:45. Scattering factors for both structures, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[45]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG; GL 300-1/4 and postdoctoral fellowship, O.M.) and the US NIH for support and Johnson Matthey PMC for a loan of palladium.

Supporting Information Available: Tables of bond lengths and angles, atomic coordinates, and anisotropic displacement parameters for ($R_{Re}S_NS_NR_{Re}$)-**5**·$3CHCl_3$ and ($R_{Re}R_N$,$S_{Re}S_N$)-$\mathbf{6}^+BF_4^-\cdot CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010153A

---

(39) Anderson, G. K.; Lin, M. *Inorg. Synth.* **1990**, *28*, 60.

(40) These assignments were made based upon chemical shifts predicted by ChemNMR-Pro (Cambridge Software).

(41) Sheldrick, G. M. SHELX-76; University of Cambridge, Cambridge, U.K., 1976.

(42) (a) Sheldrick, G. M. SHELX-93, Program for Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1993. (b) Sheldrick, G. M. SHELXL-93. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1993; pp 175−189.

(43) Flack, H. D. *Acta Crystallogr,* **1981**, *A37*, 734. Limiting values are 0 for the correct structure and +1 for the inverted structure.

(44) (a) "Collect" Data Collection Software; Nonius BV, 1998. (b) Otwinowski, Z.; Minor, W. "Scalepack" Data Processing Software. In *Methods Enzymol.* **1997**, *276* (Macromolecular Crystallography, Part A), 307.

(45) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974.