National de la Recherche Scientifique of Belgium for financial support. J.F.D. is Chercheur Qualifié at this institution.

Registry No. $Na^+(EuDOTA \cdot H_2O)^- \cdot 4H_2O$, 88083-35-6.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters, hydrogen atom coordinates, polyhedral edge lengths and polyhedral angles, and packing bond distances and corresponding angles (Tables SI-SV) (18 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6, and Nicolet Instrument Corporation, Fremont, California 94539

Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes. X-ray Structure of $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(CH_3)C_6H_4CH_3][BF_4]$ and ^1H NMR Study of Stereoisomerism of the Organohydrazido(1-) Ligand in Complexes of This Type

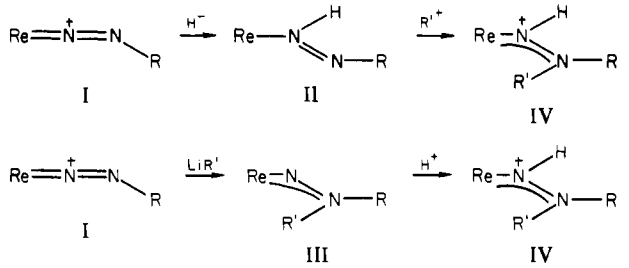
CARLOS F. BARRIENTOS-PENNA,[1a] CHARLES F. CAMPANA,[1b] FREDERICK W. B. EINSTEIN,[1a] TERRY JONES,[1a] DEREK SUTTON,*[1a] and ALAN S. TRACEY[1a]

Received March 10, 1983

The organohydrazido(1-) complexes $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NHNRR')][BF_4]$ (where R = C_6H_4X; X = *p*-Me, *p*-OMe, or *p*-NEt_2; R' = Me, *n*-Bu, or Ph) have been synthesized either by protonation of the corresponding organohydrazido(2-) complex $(\eta^5\text{-}C_5H_5)Re(CO)_2(NNRR')$ or by action of LiR' on the corresponding aryldiazene complex $(\eta^5\text{-}C_5H_5)Re(CO)_2(NHNR)$. The complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(Me)C_6H_4Me]][BF_4]$ crystallizes in the space group $P2_1/c$ of the monoclinic system, with a = 10.060 (5) Å, b = 9.549 (3) Å, c = 18.193 (4) Å, β = 93.32 (3)°, and Z = 4. The calculated and measured densities are 2.015 and 2.02 (2) g cm^{-3}, respectively. On the basis of 1850 observed, three-dimensional, X-ray-counter measured intensities, with $F \geq 3\sigma(F)$ in the range $3° \leq 2\theta \leq 45°$ (Mo Kα), the structure was solved and refined by full-matrix, least-squares methods to R = 0.043 and R_w = 0.050, with anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms, including that of the NH group, were located and refined. Selected dimensions are Re-N(1) = 1.949 (9) Å, N(1)-N(2) = 1.32 (1) Å, Re-N(1)-N(2) = 139.1 (7)°, N(1)-N(2)-C(Me) = 115.7 (9)°, N(1)-N(2)-C(tol) = 121.6 (8)° and C(Me)-N(2)-C(tol) = 121.9 (9)°. In $CDCl_3$ solution, the ^1H NMR spectra of these organohydrazido(1-) complex cations exhibit resonances attributable to two stereoisomers in equilibrium. An analysis of the nuclear Overhauser effect (NOE), saturation transfer, and variable-temperature ^1H NMR spectra for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(Me)C_6H_4OMe]][BF_4]$ indicates that the stereoisomers interconvert by rotation about the N-N bond with an activation energy of 17.4 ± 0.5 kcal mol^{-1} and differ in ground-state energy by 0.39 ± 0.03 kcal mol^{-1} at 294 K. The more stable stereoisomer has essentially the same orientation of the organohydrazido(1-) ligand that is observed in the crystal structure.

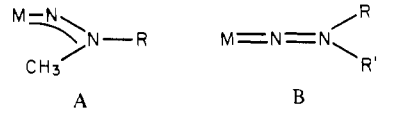
Introduction

Work described in a previous publication[2] and extended in this paper has shown that the aryldiazenido ligand (N_2R; R = aryl) in rhenium complex cations of composition $[CpRe(CO)_2(N_2R)]^+$ (I) (Cp = η^5-C_5H_5) is capable of transformation to give, first, aryldiazene (II) or substituted arylhydrazido(2-) (III) intermediates and, then, the substituted arylhydrazido(1-) derivatives (IV). This transformation is notable since it models a possible sequence of steps $M\text{-}N_2H \rightarrow M\text{-}N_2H_2 \rightarrow M\text{-}N_2H_3$ for the reduction and protonation of dinitrogen on a transition metal, M, though this sequence may not necessarily be followed in biological nitrogen fixation.[3]



Characterization of the structures and dynamics of such model intermediates as I-IV can potentially provide information about the electron distribution and bonding in the metal-diazo complex at each stage and help to establish the salient features that must exist in a given intermediate for it to undergo the next step in the transformation sequence.

In the previous paper,[2] we demonstrated that the arylmethylhydrazido(2-)-N^1 ligand in $CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]$ exhibited an unusual *bent* metal-ligand skeleton (A), rather than the linear skeleton (B) that has been commonly encountered in previously determined metal-hydrazido(2-) structures.[4] We attributed this to a difference in the electronic requirements of the metal in the two types.



As a consequence of this bent geometry, the hydrazido(2-) ligand of type A in these rhenium complexes is capable of protonation at the inner nitrogen atom N^1 to generate cations $[CpRe(CO)_2[NHN(CH_3)R]]^+$ that contain organohydrazido(1-) ligands. This paper deals with the structural characterization of examples of these rhenium hydrazido(1-) complexes, by using X-ray analysis to provide a comparison with the present hydrazido(2-) complexes[2] and ^1H NMR

(1) (a) Simon Fraser University. (b) Nicolet Instrument Corp.
(2) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578.
(3) Chatt, J.; Richards, R. L. "New Trends in the Chemistry of Nitrogen Fixation"; Chatt, J., da Câmara Pina, L. M., Richards, R. L., Eds.; Academic Press: London, 1980.
(4) Chatt, J.; Crichton, B. A. L.; Dilworth, J. R.; Dahlstrom, P. L.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1041.

0020-1669/84/1323-0363$01.50/0

spectroscopy to determine the nature of their stereoisomerism in solution.

Experimental Section

The general experimental details of the synthetic techniques used and some preparative methods have been described previously.[2] Only those preparations that have not been described before or for which improved methods have been found are included here.

$CpRe(CO)_2[p\text{-}NN(Ph)C_6H_4OMe]$. An excess of PhLi (1.95 M in cyclohexane–diethyl ether 1:1) was added to a solution of $[CpRe(CO)_2(p\text{-}NNC_6H_4OMe)][BF_4]$ (60 mg) in CH_2Cl_2 (5 mL) and the mixture stirred at room temperature for 30 min under N_2. The solution quickly became dark red-orange. Chromatography on Florisil with hexane as an eluent gave yellow $CpRe(CO)_2(N_2)$[2] and then elution with CH_2Cl_2 gave yellow-orange $CpRe(CO)(COPh)(p\text{-}NNC_6H_4OMe)$: IR ($CH_2Cl_2$) 1949 vs[5] ($\nu$(CO)), 1644 s br cm^{-1} (benzoyl + ν(NN)); ^1H NMR ($(CD_3)_2CO$) δ 7.32 s br (Ph), 7.26 d, 7.04 d (4 H, C_6H_4), 6.05 s (5 H, Cp), 3.87 s (3 H, OMe). Finally, a dark red band was eluted with acetone, which was $CpRe(CO)_2[p\text{-}NN(Ph)C_6H_4OMe]$: IR ($CH_2Cl_2$) 1948 vs, 1867 vs cm^{-1} (ν(CO)); ^1H NMR ($(CD_3)_2CO$) δ 7.65–6.90 m br (Ph), 7.27 d, 7.01 d (4 H, C_6H_4), 5.97 s (5 H, Cp), 3.86 s (3 H, OMe); mass spectrum, *m/e* (based on Re^{185} and Re^{187}) 518, 520 (M^+), 490, 492 ($M - CO^+$). As reported previously,[2] the reaction in hexane–CH_2Cl_2 does not yield this compound.

$CpRe(CO)_2[p\text{-}NN(n\text{-}Bu)C_6H_4OMe]$. An excess of *n*-BuLi (2.4 M in hexane) was added to a solution of $[CpRe(CO)_2(p\text{-}NNC_6H_4OMe)][BF_4]$ (60 mg) in CH_2Cl_2 (5 mL) and the mixture stirred for 30 min under N_2. The solution rapidly became deep red, and the IR showed the presence of the desired hydrazido(2–) complex, together with a small amount of $CpRe(CO)_2(N_2)$,[2] but the complete absence of any monocarbonyl product. Hexane was added to precipitate $LiBF_4$, which was filtered off, and the solution evaporated to give $CpRe(CO)_2[p\text{-}NN(n\text{-}Bu)C_6H_4OMe]$ as a dark red microcrystalline solid in nearly quantitative yield: IR (CH_2Cl_2) 1935 vs, 1855 vs cm^{-1} (ν(CO)); ^1H NMR ($CDCl_3$, −30 °C) δ 7.18 d, 6.85 d (4 H, C_6H_4), 5.87 s (5 H, Cp), 4.34 t (2 H, NCH_2), 3.83 s (3 H, OMe), 1.92–1.16 m br (4 H, $(CH_2)_2$), 0.98 t (3 H, CH_3); mass spectrum, *m/e* 498, 500 (M^+), 470, 472 ($M - CO^+$).

$CpRe(CO)_2[p\text{-}NN(n\text{-}Bu)C_6H_4NEt_2]$. This was carried out similar to the above. The color changed from dark green to dark red-orange, and the IR spectrum of the solution showed the presence of the desired product and a very small amount of $CpRe(CO)_2(N_2)$. Evaporation of the hexane afforded the product as a dark red microcrystalline solid in near quantitative yield: IR (CH_2Cl_2) 1933 vs, 1852 vs cm^{-1} (ν(CO)); ^1H NMR ($CDCl_3$, −30 °C) δ 7.11 d, 6.57 d (4 H, C_6H_4), 5.82 s (5 H, Cp), 4.34 t (2 H, $NCH_2(n\text{-}Bu)$), 3.35 q (4 H, $CH_2(Et)$), 1.92–1.04 m br (4 H, $(CH_2)_2$), 1.15 t (6 H, $CH_3(Et)$), 0.97 t (3 H, $CH_3(n\text{-}Bu)$); mass spectrum, *m/e* 539, 541 (M^+), 511, 513 ($M - CO^+$). As reported previously,[2] reaction in 1:1 acetone–hexane produced only a monocarbonyl complex, tentatively identified as $CpRe(CO)(CO\text{-}n\text{-}Bu)(p\text{-}N_2C_6H_4NEt_2)$.

$CpRe(CO)_2(p\text{-}NHNC_6H_4OMe)$. The following method is preferred to that used previously.[2] A stoichiometric amount of $NaBH_4$ was added to $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ in methanol at 0 °C, and the resultant mixture stirred for 15 min under N_2. A rapid reaction took place, with gas evolution, and the color changed from red to deep orange. Solvent was removed under vacuum, and the deep orange solid was carefully treated with diethyl ether without stirring so as to redissolve the desired product but leave behind poorly soluble impurities and $NaBF_4$. Evaporation gave the product as a microcrystalline deep red solid in near quantitative yield. $CpRe(CO)_2(NHNC_6H_5)$ was synthesized similarly as an air-sensitive dark red-orange microcrystalline solid.

$[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]][BF_4]$. This was prepared from $CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]$ and HBF_4, as reported previously,[2] or from the aryldiazene complex and $[(CH_3)_3O][BF_4]$ as follows. To a solution of $CpRe(CO)_2(p\text{-}NHNC_6H_4OMe)$ in CH_2Cl_2 (5 mL) was added a stoichiometric amount of $[(CH_3)_3O][BF_4]$ dissolved in CH_2Cl_2 and the mixture stirred at room temperature. A rapid reaction occurred, with the color changing from bright orange to deep red. An IR spectrum of this solution showed the presence of the hydrazido(1–) complexes $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]][BF_4]$, $[CpRe(CO)_2[p\text{-}NHNHC_6H_4OMe]][BF_4]$, and other unidentified compounds.

Evaporation of the solvent and extraction of the residue by $CHCl_3$ afforded essentially the former complex, contaminated with some of the latter. It was identified by IR and ^1H NMR spectroscopy. $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]][BF_4]$ could be synthesized similarly.

$[CpRe(CO)_2[p\text{-}NHN(Ph)C_6H_4OMe]][BF_4]$ was synthesized similarly[2] from HBF_4 and $CpRe(CO)_2[p\text{-}NN(Ph)C_6H_4OMe]$. IR ($CH_2Cl_2$): 2010 vs, 1943 vs cm^{-1} (ν(CO)); ^1H NMR ($CDCl_3$, −30 °C) δ 16.25 s (NH), 7.30 m br (C_6H_4 + Ph), 6.18 s (Cp), 3.82 s (OMe) [conformer 1]; 16.52 s (NH), 7.30 m br (C_6H_4 + Ph), 6.15 s (Cp), 3.92 s (OMe) [conformer 2].

$[CpRe(CO)_2[p\text{-}NHN(n\text{-}Bu)C_6H_4OMe]][BF_4]$ was synthesized similarly[2] from HBF_4 and $CpRe(CO)_2[p\text{-}NN(n\text{-}Bu)C_6H_4OMe]$. IR ($CH_2Cl_2$): 2007 vs, 1937 vs cm^{-1} (ν(CO)). ^1H NMR ($CDCl_3$, −30 °C) δ 16.12 s (NH), 7.36 d, 7.10 d (C_6H_4), 6.04 s (Cp), 3.92 s (OMe), 3.74 t (NCH_2), 1.16 m br ($(CH_2)_2$), 0.90 t (CH_3) [conformer 1]; 15.62 s (NH), 6.16 s (Cp), 3.88 s (OMe) [conformer 2 (*n*-Bu and C_6H_4 resonances obscured by those of conformer 1)].

X-ray Structure Determination for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]][BF_4]$. A deep red crystal suitable for data collection, from a sample synthesized in the manner reported previously,[2] was mounted in a Lindemann glass capillary. Precession and Weissenberg photographs were used to determine the space group and approximate unit cell dimensions. Accurate cell dimensions were determined by least-squares refinement of 10 accurately centered reflections (2θ = 15.7–24.0°; λ(MoKα) = 0.71069 Å). Data were collected on a Nicolet R3m/E diffractometer system, equipped with a graphite monochromator and a scintillation counter with pulse height discrimination. The ω-scan method was used, with a scan width of 1.0° corrected for dispersion. Stationary-crystal, stationary-counter background counts were taken for 50% of the scan time at each scan limit. The intensity of each reflection was premeasured so as to determine a suitable scan speed for its accurate measurement (speeds varied from 9.8–29.3°/min). Intensity measurement of two standards every 100 reflections showed no evidence of crystal deterioration and no instability in the detection system. Intensities ($2\theta \leq 45°$) were measured for 2609 reflections, of which 1850 unique reflections were classed as observed [$F \geq 3\sigma(F)$]. Relevant data are listed in Table I.

Table I. Summary of Crystal Data and Data Collection Conditions

compd	$[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]][BF_4]$
formula	$C_{15}H_{16}ReF_4O_2N_2B$
space group	$P2_1/c$
a, Å	10.060 (5)
b, Å	9.549 (3)
c, Å	18.193 (4)
β, deg	93.32 (3)
V, Å^3	1744.74
Z	4
d_{obsd}, g cm^{-3}	2.02 (2)
d_{calcd}, g cm^{-3}	2.015
cryst dimens, mm	0.40 × 0.33 × 0.20
temp, °C	24
radiation	Mo Kα (λ = 0.71069 Å)
μ, cm^{-1}	71.08
scan speeds, deg min^{-1}	9.8–29.3
scan width, deg	1.0 + dispersion
measd reflcns ($3° < 2\theta < 45°$)	2609
obsd reflcns ($F \geq 3\sigma(F)$)	1850
R	0.043
R_w	0.050

The Re atom was located by conventional Patterson synthesis. All remaining non-hydrogen atoms and some hydrogen atoms were located in subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically, the BF_4^- anion being constrained to a regular tetrahedral geometry. The hydrogen atoms were initially included as fixed contributions in their calculated positions but, in the latter stages of refinement, were allowed to "ride" on their parent carbon or nitrogen atoms [C–H = 0.960 Å; N–H = 0.960 Å; U_{iso}(H) $\propto U_{ij}$(parent)].

The final difference map was clean, apart from a large positive peak (1.2 e Å^{-3}) in the vicinity of the BF_4^- anion. Full-matrix

(5) This ν(CO) value was previously reported incorrectly as 1962 cm^{-1} in ref 2.

Table II. Atom Coordinates (×10⁴) and Temperature Factors (10³Å²) for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]][BF_4]$

atom	x	y	z	U_{eq}[a]
Re	1885 (1)	958 (1)	1745 (1)	47 (1)
N(1)	3342 (9)	1443 (10)	1131 (4)	49 (3)
N(2)	3553 (9)	1634 (10)	430 (4)	54 (3)
C(1)	571 (12)	2130 (14)	1281 (7)	60 (5)
O(1)	−258 (10)	2811 (12)	1016 (6)	96 (4)
C(2)	1007 (14)	−464 (15)	1159 (8)	72 (5)
O(2)	426 (11)	−1310 (11)	847 (7)	107 (5)
C(3)	2417 (13)	1312 (16)	−94 (7)	76 (5)
C(11)	4693 (11)	2323 (11)	209 (5)	49 (4)
C(12)	5277 (12)	3350 (14)	643 (6)	58 (5)
C(13)	6384 (14)	4045 (14)	430 (6)	70 (5)
C(14)	6910 (13)	3745 (12)	−245 (6)	61 (5)
C(15)	6299 (13)	2745 (14)	−661 (6)	67 (5)
C(16)	5214 (12)	1999 (14)	−452 (6)	61 (5)
C(4)	8082 (14)	4569 (16)	−492 (8)	84 (6)
C(21)	1886 (14)	−384 (14)	2781 (7)	73 (5)
C(22)	3148 (13)	168 (16)	2744 (6)	69 (5)
C(23)	3037 (14)	1651 (14)	2804 (5)	62 (5)
C(24)	1712 (16)	1963 (16)	2866 (6)	74 (6)
C(25)	962 (14)	702 (17)	2853 (6)	82 (6)
B	6704 (6)	684 (6)	2268 (3)	27 (4)
F(1)	6376 (8)	−183 (8)	2784 (4)	118 (4)
F(2)	5900 (9)	1762 (9)	2251 (5)	145 (6)
F(3)	6609 (16)	46 (11)	1630 (4)	289 (14)
F(4)	7928 (8)	1111 (11)	2405 (8)	241 (10)

[a] Equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized U tensor.

least-squares refinement for 227 variables gave final agreement factors of $R = 0.043$ and $R_w = 0.050$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$. Lorentz, polarization, and absorption corrections have been made. The absorption correction was empirical and based upon the ψ scans of 14 reflections with 2θ values in the range 4.5–32.4°.

A weighting scheme, utilizing weights of the form $w = 1/\sigma^2(F_o) + gF^2$ (where $g = 0.001$), was implemented as a result of an analysis of the data set as a function of F_o, 2θ, and Miller indices. Scattering factors were those for neutral atoms, taken from ref 6.

The computer programs used were those of the SHELXTL suite.[7] Final positional and thermal parameters are given in Table II and selected bond lengths and interbond angles in Table III. Anisotropic temperature factors (Table A), hydrogen atom coordinates and temperature factors (Table B), and a list of observed and calculated structure factors (Table C) are available as supplementary material.

^{1}H NMR Spectroscopy. Spectra were obtained for solutions in $CDCl_3$ by using either a Varian XL-100 instrument, operating at 100 MHz in the FT mode, or a Bruker WM-400 FT instrument, operating at 400 MHz. Nuclear Overhauser effect (NOE) experiments on $[CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]][BF_4]$ were done at ambient temperature and saturation-transfer experiments at 273, 290, 297, and 305 K, by using the Bruker instrument. Since both are well-known experiments,[8] they will not be discussed further, except to state that the time used for NOE buildup was 10 s and the delays used to obtain the rates of saturation transfer were 0.05, 0.10, 0.25, 0.50, 0.75, 1.00, 2.00, 3.00, 5.00, and 7.50 s. All spectra were obtained by using an 8-kHz spectral width. Four hundred difference spectra (i.e., 800 total spectra) were acquired in each of the NOE experiments and 36 spectra for the saturation-transfer experiments. The temperature of coalescence of the cyclopentadienyl resonances was measured by using the XL-100 since the smaller (by a factor of 4) proton chemical shift range (in Hz) for this instrument, compared to the Bruker instrument, allowed coalescence to be observed within the usable temperature range of $CDCl_3$. The temperature range for observations was −60 to +60 °C, and throughout the range +40 to +60 °C, a spectrum was recorded for each degree increment in temperature.

(6) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(7) Sheldrick, G. M. "SHELXTL, Program for Crystal Structure Determination"; University of Cambridge, Cambridge, England, 1980; Revision 2.5.
(8) Martin, M. L.; Martin, G. J.; Delpeuch, J. J. "Practical NMR Spectroscopy"; Heydon & Son Ltd.: London, 1980.

Table III. Bond Parameters for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]][BF_4]$

	(a) Bond Lengths (Å)		
Re-C(1)	1.89 (1)	B-F(2)	1.31 (1)
Re-C(2)	1.91 (1)	B-F(3)	1.31 (1)
Re-C(21)	2.28 (1)	B-F(4)	1.31 (1)
Re-C(22)	2.29 (1)	C(21)-C(22)	1.38 (2)
Re-C(23)	2.29 (1)	C(22)-C(23)	1.43 (2)
Re-C(24)	2.27 (1)	C(23)-C(24)	1.38 (2)
Re-C(25)	2.28 (1)	C(24)-C(25)	1.42 (2)
Re-N(1)	1.949 (9)	C(25)-C(21)	1.40 (2)
Re-CR[a]	1.945	C(11)-C(12)	1.37 (2)
N(1)-N(2)	1.32 (1)	C(12)-C(13)	1.37 (2)
N(2)-C(3)	1.48 (2)	C(13)-C(14)	1.40 (2)
N(2)-C(11)	1.40 (1)	C(14)-C(15)	1.35 (2)
C(1)-O(1)	1.14 (2)	C(15)-C(16)	1.38 (2)
C(2)-O(2)	1.13 (2)	C(16)-C(11)	1.37 (2)
B-F(1)	1.31 (1)	C(14)-C(4)	1.51 (2)
	(b) Bond Angles (deg)		
C(1)-Re-C(2)	83.3 (6)	F(2)-B-F(4)	109.5 (7)
C(1)-Re-N(1)	97.6 (5)	F(3)-B-F(4)	109.5 (10)
C(1)-Re-CR[a]	122.4	Re-N(1)-N(2)	139.1 (7)
C(2)-Re-N(1)	100.8 (5)	N(1)-N(2)-C(3)	115.7 (9)
C(2)-Re-CR[a]	122.7	N(1)-N(2)-C(11)	121.6 (8)
N(1)-Re-CR[a]	121.5	C(3)-N(2)-C(11)	121.9 (9)
Re-C(1)-O(1)	177 (1)	N(2)-C(11)-C(12)	120 (1)
Re-C(2)-O(2)	175 (1)	N(2)-C(11)-C(16)	120 (1)
C(21)-C(22)-C(23)	107 (1)	C(12)-C(11)-C(16)	120 (1)
C(22)-C(23)-C(24)	108 (1)	C(11)-C(12)-C(13)	121 (1)
C(23)-C(24)-C(25)	109 (1)	C(12)-C(13)-C(14)	120 (1)
C(24)-C(25)-C(21)	106 (1)	C(13)-C(14)-C(15)	117 (1)
C(25)-C(21)-C(22)	110 (1)	C(13)-C(14)-C(4)	120 (1)
F(1)-B-F(2)	109.5 (7)	C(4)-C(14)-C(15)	123 (1)
F(1)-B-F(3)	109.4 (8)	C(14)-C(15)-C(16)	124 (1)
F(1)-B-F(4)	109.5 (8)	C(15)-C(16)-C(11)	118 (1)
F(2)-B-F(3)	109.4 (8)		

[a] CR denotes the centroid of the Cp ring.

Results and Discussion

Synthesis. Previously,[2] we reported the synthesis and characterization of some arylmethylhydrazido(2−)-N^1 complexes, e.g. $CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]$, from the reaction of CH_3Li with a suspension of the corresponding aryldiazenido complex in hexane:

$$[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4] \xrightarrow[\text{hexane}]{CH_3Li} CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe] + LiBF_4$$

Reactions of the more bulky nucleophiles, PhLi or *n*-BuLi, then appeared not to generate corresponding hydrazido(2−) complexes, but we can now report that, by a small change in the solvent (i.e., essentially carrying out the reaction in CH_2Cl_2), we have been able to observe the formation of these hydrazido(2−) complexes in solution and, subsequently, to isolate them:

$$[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4] \xrightarrow[CH_2Cl_2]{PhLi} CpRe(CO)_2[p\text{-}NN(Ph)C_6H_4OMe] + LiBF_4$$

Indeed, the effects of solvent on the products of the reaction, in the case of *n*-BuLi, seem quite remarkable: acetone–hexane produced only a monocarbonyl product, tentatively identified[2] as $CpRe(CO)(CO\text{-}n\text{-}Bu)(p\text{-}N_2C_6H_4NEt_2)$, whereas CH_2Cl_2 gives the hydrazido(2−) complex in high yield, evidently with complete exclusion of the monocarbonyl compound.

As in the case of the methyl analogue,[2] solutions of these new *n*-butyl- and phenylhydrazido(2−) complexes in CH_2Cl_2 or $CHCl_3$ are protonated by HBF_4 in Et_2O to give the corresponding organohydrazido(1−) complex cations:

$$CpRe(CO)_2[p\text{-}NN(n\text{-}Bu)C_6H_4OMe] \xrightarrow[CH_2Cl_2]{HBF_4} [CpRe(CO)_2[p\text{-}NHN(n\text{-}Bu)C_6H_4OMe]][BF_4]$$

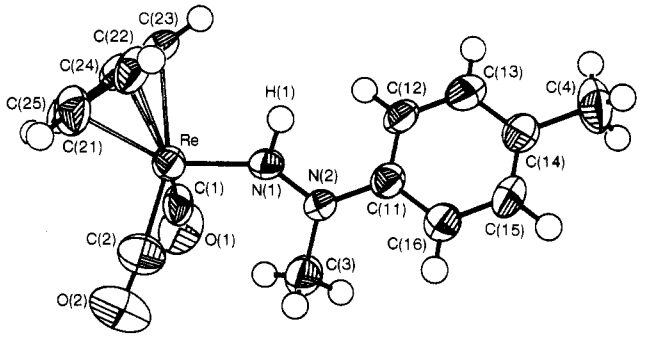


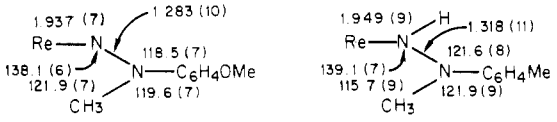
Figure 1. Perspective view of the cation in $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]][BF_4]$, with atom numbering.

We therefore expect that, in all cases, the hydrazido(2–) ligands are closely related structurally to that determined by X-rays in the methyl analogue, i.e., to be bent at N(1), since they display similar spectroscopic and chemical properties. An alternative synthetic route to the organohydrazido(1–) complex cations is methylation (at N(2)) of the aryldiazene complex using methylating agents such as $[(CH_3)_3O][BF_4]$ or CH_3OSO_2F:

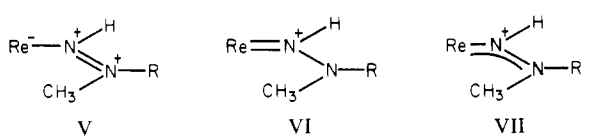
$$CpRe(CO)_2(p\text{-}NHNC_6H_4OMe) \xrightarrow{[(CH_3)_3O][BF_4]} [CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]][BF_4]$$

This procedure is less ideal due to side products such as $CpRe(CO)_2[p\text{-}NHN(H)C_6H_4OMe]][BF_4]$ (from traces of HBF_4) and $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (due to hydride abstraction from the diazene).

X-ray Structure of $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]][BF_4]$. The structure was solved with the intention of determining (i) the effect, if any, that protonation at the inner nitrogen atom N(1) has on the metrical details, compared with those of the parent hydrazido(2–) complex of previously determined[2] structure (note, however, a minor change in the aryl group from $-C_6H_4OMe$ to $-C_6H_4Me$ here) and (ii) the conformation of the arylmethylhydrazido(1–)-N^1 ligand (cf. the existence of two conformers in solution, as discussed later). A perspective view of the cation is shown in Figure 1. The esd's are a little larger than those for the unprotonated structure, but with this in mind, the protonation seems to have resulted in remarkably little change in the structural dimensions of the hydrazido ligand, as can be seen from the following comparison:



While the N–N bond may have lengthened, it is (at 1.32 Å) still much shorter than typical values of N–N single bonds (which are near 1.43 Å)[9] and indicates the retention of significant multiple-bond character in this bond. At the same time, the Re–N bond (1.949 (9) Å) is also short enough to indicate that this has some multiple-bond character as well, so the hydrazido(1–) ligand may perhaps best be represented by VII, intermediate between formal valence structures V and



V VI VII

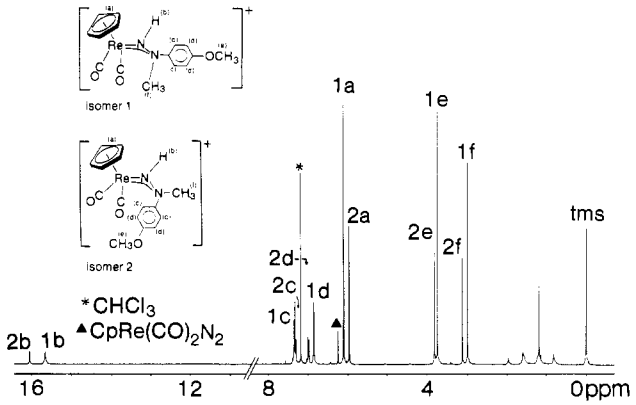
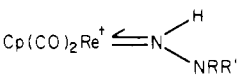


Figure 2. ^1H NMR spectrum (400 MHz) of $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]][BF_4]$ in $CDCl_3$ at ambient temperature, showing resonances from isomer 1 and isomer 2.

VI, very like the situation for the parent hydrazido(2–) complex.[2] A simple representation such as VIII can be written



VIII

for electron-counting purposes, where the NHNRR′ group[10,11] is seen to contribute three electrons to complete an 18-electron count for the metal. The number of examples of well-characterized organohydrazido(1–) complexes is not large and both "end-on" (η^1) and "side-on" (η^2, cyclic) arrangements of this ligand have been found. The two structurally determined examples having η^2 coordination are $[Cp_2W(NH_2NPh)][BF_4]$[9] and $[Mo(NNMePh)(NHNMePh)(S_2CNMe_2)_2][BPh_4]$.[12] Some others such as $CpMo(NO)I(NRNR'R'')$ (where R = H, alkyl; R′ = H, alkyl, aryl; R′ = alkyl, aryl) are believed to have η^2 coordination, but no X-ray confirmation has been obtained;[13,14] however, the phenylhydrazine complex $[CpMo(NO)I(NH_2NHPh)][BF_4]$ obtained by protonation of $CpMO(NO)I(NHNHPh)$ has been shown by X-ray analysis to have η^2 coordination of the phenylhydrazine ligand.[13] Other than the example in this paper, we known of only three other hydrazido(1–) complexes that have been shown crystallographically to be η^1 bound. These are the (dimethylpyrazolyl)borate complexes $Mo[HB(Me_2C_3N_2H)_3](NO)I(NHNMePh)$[14,15] and $Mo[HB(Me_2C_3N_2H)_3](NO)I(NHNMe_2)$[14] and the ortho-metalated arylhydrazido(1–) complex $[Ir(NHNHC_6H_3NO_2)(CO)(PPh_3)_2][BF_4]$.[16] In all cases, the ligand,[10] whether η^1 or η^2 bonded, is acting as a 3e donor. The factors that control whether an η^1 or η^2 coordination mode is adopted by organohydrazido(1–) ligands are not presently clear. Presumably, steric considerations are contributory, but in the present example it does not seem convincing to argue that the η^2 mode is sterically unfavorable for $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]]^+$ when it is ob-

(9) Cowie, M.; Gauthier, M. D. *Inorg. Chem.* **1980**, *19*, 3142. Carroll, J. A.; Sutton, D.; Cowie, M.; Gauthier, M. D. *J. Chem. Soc., Chem. Commun.* **1979**, 1058.

(10) Throughout this paper we have conformed to the IUPAC recommendation[11] of naming the NHNRR′ ligand "hydrazido(1–)"; however, for many purposes, including electron counting, it is simpler to consider the ligand to be neutral (compare C_5H_5).

(11) *IUPAC Inf. Bull.* **1978**, 151.

(12) Chatt, J.; Dilworth, J. R.; Dahlstrom, P. L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 786.

(13) Frisch, P. D.; Hunt, M. M.; Kita, W. G.; McCleverty, J. A.; Rae, A. E.; Seddon, D.; Swann, D.; Williams, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1819.

(14) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1983**, 71. McCleverty, J. A., private communication.

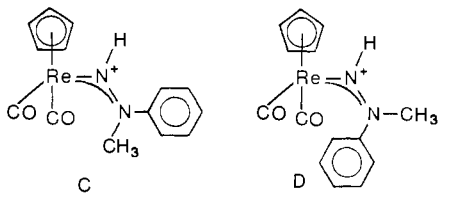
(15) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Organomet. Chem.* **1979**, *168*, C1.

(16) Carroll, J. A.; Cobbledick, R. E.; Einstein, F. W. B.; Farrell, N.; Sutton, D.; Vogel, P. L. *Inorg. Chem.* **1977**, *16*, 2462.

served in the somewhat similar complexes $[Cp_2W(NH_2NPh)]^+$ and $[CpMo(NO)I(NH_2NHPh)]^+$ and in the evidently more crowded $[Mo(NNMePh)(NHNMePh)(S_2CNMe_2)_2]^+$.

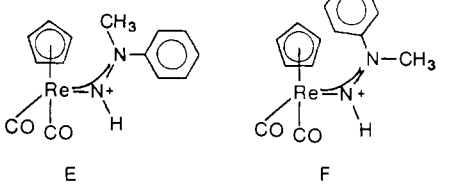
^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of each of the organohydrazido(1−) complexes $[CpRe(CO)_2(NHNRR')]^+$ in $CDCl_3$ at ambient temperature exhibits two sets of resonances assignable to two stereoisomers (see Figure 2). The pairs of lines from corresponding protons in each stereoisomer coalesce as the temperature is increased, confirming that these stereoisomers are interconverting by a process that becomes rapid on the NMR time scale above ambient temperature. By contrast, spectra from $(CD_3)_2CO$ solution contain only a single set of lines in the temperature range −60 to +60 °C.

The X-ray structure determination has shown that the arylmethylhydrazido(1−)-N^1 ligand has the conformation (C)



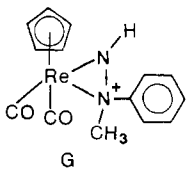
C

D



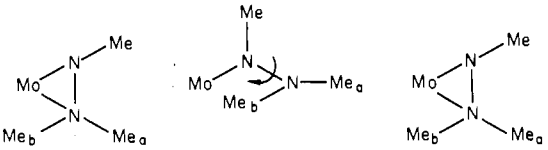
E

F



G

with the H and CH_3 groups trans, and it is possible (but it cannot be assumed) that this is the structure of one of the stereoisomers in solution also. If we restrict ourselves to only η^1 coordination of the hydrazido(1−) ligand, the other candidate geometries are D, E, and F. In addition, however, we should bear in mind the possibility of η^2-coordination of the organohydrazido(1−) ligand in structures such as G and related stereoisomers. As well as this occurring in the known examples of η^2 coordination cited above, it is important to note in the present context that it has been suggested to be the geometry in the complex $CpMo(NO)I(MeNNMe_2)$, for which two NMe_2 methyl resonances are observed at −70 °C that collapse to a single line at ambient. This methyl site averaging was interpreted as resulting from a ring-opening...N–N rotation...ring-closure mechanism,[13] with an activation energy of ca. 59 kJ mol^{-1}.



Note, however, that this site-averaging does not *require* an η^2-coordination mode to be present, and by way of comparison, the $NHNMe_2$ ligand in the related pyrazolylborate complex $Mo[HB(Me_2C_3N_2H)_3](NO)I(NHNMe_2)$, which is known to be η^1 in the crystal by X-ray analysis, also undergoes methyl site averaging in $CDCl_3$ with a lower activation energy (ca. 40 kJ mol^{-1}),[14] suggested to be due to a simple N–N-bond rotation in the η^1 ligand without the η^2 geometry becoming involved at all.

So as to try to provide an unambiguous interpretation of the mechanism operating in the present organohydrazido(1−) complexes, we have examined the NMR of the methylarylhydrazido(1−) complex $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]]^+$ in some detail. The activation energy ΔG^* determined from the coalescence temperature (328 K) and ν_∞ (7.55 Hz) for the Cp resonances was 17.4 ± 0.2 kcal mol^{-1} (72.9 kJ mol^{-1}). From the proportion of the two components (2:1) at room temperature, the ground-state energy difference, ΔE, between the two stereoisomers was calculated to be 0.39 ± 0.03 kcal mol^{-1}. This value was confirmed by obtaining the ratios at lower temperatures and comparing them with those expected from this ΔE value.

Since, in the determination of the activation energy, the coalescence point was estimated from transitions of unequal intensity, it was decided also to measure interconversion rates directly from a saturation-transfer experiment. Briefly, this is a useful consequence of the NOE experiment (described below) in that, if the site of irradiation is involved in chemical exchange, saturation can be transferred as exchange occurs. This is the basis of the saturation-transfer experiments described by Forsén and Hoffman[17] from which exchange kinetics are obtained. This procedure has recently been reviewed.[8] In this case, the resonance corresponding to the Cp group in one stereoisomer was irradiated and the intensity of the Cp peak of the second stereoisomer was determined as a function of time. The rate of interconversion was determined at four temperatures, and the results gave an activation energy $\Delta G^* = 17.5 \pm 0.3$ kcal mol^{-1} in very good agreement with the value obtained from the coalescence temperature.

For determining the identity of each stereoisomer a particularly useful NMR experiment is nuclear Overhauser effect (NOE) difference spectroscopy. One spectrum is accumulated while simultaneously saturating irradiation is applied at the transition of interest. From this spectrum is subtracted a second spectrum for which the irradiation frequency is moved to a region free from any transitions. The resultant difference spectrum shows a large negative peak corresponding to the first irradiation frequency and positive peaks for any resonances that are enhanced by the NOE. The magnitude of the enhancement provides information concerning internuclear distances and, in the case of ^{1}H NMR, is only expected to be significant for protons that have reasonably short intramolecular nonbonded contacts with the irradiated one.[18]

Interpretation of the NOE results must take into account NH exchange between the stereoisomers (and with trace water), which occurs during the irradiation period required for NOE buildup (10 s). Thus, for example, irradiation at NH (isomer 1) alone results in magnetization transfer to NH (isomer 2), and therefore, there is observed NOE enhancement of appropriate protons in isomer 1 *and* isomer 2 in the difference spectrum (Figure 3). Fortunately, an internal referencing is possible; the difference spectrum thus shows negative peaks due to NH (isomer 1) and NH (isomer 2) whose relative intensities may then be individually compared to the relative intensities of the NOE-enhanced peaks of neighboring protons in each isomer.

Let isomer 1 (its stereochemistry to be determined) be the dominant isomer at ambient temperature. From the relative

(17) Forsén, S.; Hoffman, R. A. *J. Chem. Phys.* **1968**, *39*, 2892.
(18) Noggle, J. H.; Schirmer, R. E. "The Nuclear Overhauser Effect. Chemical Applications"; Academic Press: New York, 1971.

Table IV. Relative Intensities of Peaks in the ^{1}H NMR NOE-Difference Spectra for $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]][BF_4]$[a]

irradiation position	NH intensities[b,c]		NOE-enhanced intensities[b,c]				
	NH(2)	NH(1)	C_6H_4 (ortho position)[d]	Cp(1)	Cp(2)	NMe(1)	NMe(2)
NH(2)	4.8	1.3[e]	1.0[f]	1.0	0.67	0.60	0.33
NH(1)	2.3[e]	1.5	1.0[f]	0.81	0.52	0.33	0.17

[a] In $CDCl_3$ at ambient temperature. [b] Determined from relative peak heights: NH(1), Cp(1), and NMe(1) are resonances for isomer 1; NH(2) etc., for isomer 2. [c] All resonances are ordered in increasing field from left to right for comparison with Figures 2 and 3. [d] Resonances from isomers 1 and 2 are superimposed and cannot be individually determined. [e] Due to magnetization transfer. [f] Normalized to 1.0.

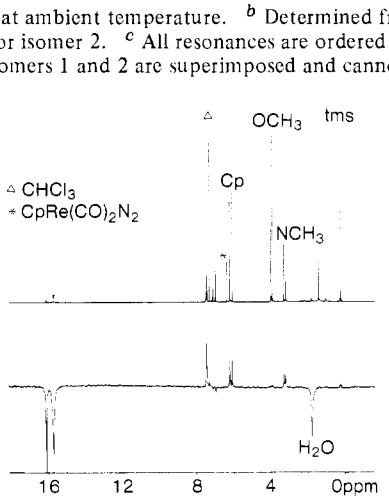


Figure 3. ^{1}H NMR spectrum and ^{1}H NMR NOE-difference spectrum of $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]][BF_4]$ in $CDCl_3$. Irradiation is at NH(1), arrow, resulting in negative peaks for NH(1), NH(2), and H_2O and NOE enhancement of ortho aromatic, Cp, and NMe resonances.

intensities in the spectrum (Figure 2), it is associated with the Cp(1), NH(1), aromatic, $NCH_3(1)$, and $OCH_3(1)$ resonances labeled thus and isomer 2 with the corresponding alternate set. Note that isomer 1 has its NH resonance upfield of that of isomer 2. Irradiation at the separate NH(1) and NH(2) positions[19] results in NOE enhancement of Cp, aromatic (ortho position), and NCH_3 resonances only. Observed relative intensities are given in Table IV, and a typical difference spectrum is shown in Figure 3. Various comparisons of interest are as follows. (i) There is no correlation between the enhancement of the aromatic protons with the enhancement of either the Cp or the NMe groups. (ii) Neither is there any correlation between the enhancements of the Cp and NMe groups.[20] (iii) However, there is a clear correlation between the intensities of NH(2) and NMe(2), establishing that these groups are cis in isomer 2.[21,22] (iv) A similar correlation between the intensities of NH(1) and the aromatic ortho protons establishes that these are cis in isomer 1.[23] (v) There is no correlation between the intensities of either NH(1) or NH(2) individually or with the Cp(1) or Cp(2) resonances, which means that the Cp groups are enhanced by the presence of an NOE in both structures, a conclusion in agreement with the lack of correlation observed in i and ii. Indeed, further analysis of the integrated intensities shows that the enhancements of Cp(1) and Cp(2) by NH(1) are approximately equal to those produced by NH(2). This means that the distance from the NH proton to the Cp group in the two stereoisomers is roughly the same.

If we restrict consideration for the moment only to the η^1 structures C–F, these NOE results conclusively show that isomer 1 has structure C (which is also the solid-state structure and thermodynamically the more stable one in $CDCl_3$ solution), while isomer 2 has structure D, related to C by rotation about the N–N bond. The tentative proposal made previously[2] that interconversion involved rotation about the Re–N bond is ruled out by the NOE results. Further, NOE experiments allow us to rule out of consideration the η^2 (cyclic) structures such as G since irradiation of the Cp resonances produced no NOE enhancement of either the NMe or aromatic resonances, or vice versa. Since it has already been established that an NOE occurs between the Cp and the bound (α) NH group, an NOE would also be expected between the Cp and one or the other of these groups if the β-nitrogen atom were also coordinated to the metal, to give a cyclic structure.

In summary, then, the NOE experiments conclusively establish that the interconverting stereoisomers in $CDCl_3$ solution are C and D, involving only η^1 coordination of the organohydrazido(1–) ligand and rotation about the N–N bond. The measured $\Delta G^{\ddagger}$ (17.5 kcal mol^{-1}) falls in the range established for restricted rotation about a partial double bond, and the relatively small ΔE (0.39 kcal mol^{-1}) is reasonable for two stereoisomers differing only by such a rotation. The single set of resonances observed for this compound in $(CD_3)_2CO$ are from isomer 1. In an NOE experiment, irradiation of NH produced enhancement of Cp and ortho aromatic protons but not those of the NMe group, while irradiation of the Cp resonance gave no enhancement of either the aromatic or NMe protons.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada, through operating grants to F.W.B.E., D.S., and A.S.T. Nicolet Instrument Corp. is thanked for the use of their X-ray facilities and the University of Concepcion, Concepcion, Chile, for a leave of absence to C.F.B.-P.

Registry No. $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]][BF_4]$, 81028-57-1; $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]][BF_4]$, 81028-59-3; $[CpRe(CO)_2[p\text{-}NHN(n\text{-}Bu)C_6H_4OMe]][BF_4]$, 87984-96-1; $[CpRe(CO)_2[p\text{-}NHN(Ph)C_6H_4OMe]][BF_4]$, 87984-94-9; $[CpRe(CO)_2(p\text{-}NNC_6H_4OMe)][BF_4]$, 81028-27-5; $CpRe(CO)_2(N_2)$, 36543-62-1; $CpRe(CO)(COPh)(p\text{-}NNC_6H_4OMe)$, 81028-62-8; $CpRe(CO)_2[p\text{-}NN(Ph)C_6H_4OMe]$, 87984-87-0; $CpRe(CO)_2[p\text{-}NN(n\text{-}Bu)C_6H_4OMe]$, 87984-88-1; $CpRe(CO)_2[p\text{-}NN(n\text{-}Bu)C_6H_4NEt_2]$, 87984-89-2; $CpRe(CO)_2(p\text{-}NHNC_6H_4OMe)$, 81028-46-8; $CpRe(CO)_2(NHNC_6H_5)$, 87984-90-5; $CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]$, 81028-50-4; $[CpRe(CO)_2[p\text{-}NHNHC_6H_4OMe]][BF_4]$, 87984-92-7.

Supplementary Material Available: Anisotropic temperature factors (Table A), hydrogen atom coordinates and temperature factors (Table B), and observed and calculated structure factors (Table C) for $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]][BF_4]$ (13 pages). Ordering information is given on any current masthead page.

(19) NH(1) and NH(2) are used here to designate the NH resonances of isomers 1 and 2, respectively, in the spectrum.
(20) this is more evident if the intensities are normalized to Cp(1) = 1.0, giving the following values for irradiated NH(2) and NH(1), respectively: (Cp(1)) 1.0, 1.0; (Cp(2)) 0.67, 0.65; (NMe(1)) 0.60, 0.41; (NMe(2)) 0.33, 0.21.
(21) Normalizing the NH(2) intensities to 1.0 makes this more evident in the following values for irradiated NH(2) and NH(1), respectively: (NH(2)) 1, 1; (NH(1)) 0.28, 0.62; (aromatic) 0.21, 0.43; (Cp(1)) 0.21, 0.35; (Cp(2)) 0.14, 0.22; (NMe(1)) 0.13, 0.14; (NMe(2)) 0.07, 0.07.
(22) There is also a correlation with the NMe(1) intensity that shows that NOE enhancement is transferred to NMe(1) as a result of the interconversion process.
(23) Normalizing the NH(1) intensities to 1.0 makes this more evident in the following values for irradiated NH(2) and NH(1), respectively: (NH(1)) 1, 1; (aromatic) 0.75, 0.69; (Cp(1)) 0.75, 0.56; (Cp(2)) 0.50, 0.35; (NMe(1)) 0.45, 0.23; (NMe(2)) 0.25, 0.12.