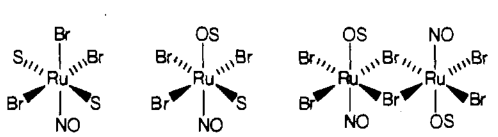
distances are around 2.5 Å, which is a typical value.[1,21-23] The Ru-Br bond trans to NO in $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$ is not shortened, as is observed for the Ru-Cl bond in other nitrosyl chloro complexes.[24] The ν(NO) stretching frequency decreases in the order Cl > Br > I. The reason for the absence of Ru-Br bond shortening may be because of the difficulty of the larger Br atom getting close to the central metal atom. For the three complexes $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$, $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$, and $[Ru(NO)Br_3(Et_2SO)]_2$, the distance of the approximately linear Br-Ru-Br system is relatively constant at 4.99, 5.01, and 5.01 Å respectively. The Ru-S and Ru-O bond lengths are typical of reported values.[1,17,19,20,23,25-27] As in the dimeric compound the S-O bond in $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ of 1.543 (8) Å is similar to that found in other O-bonded sulfoxides. The S-O bond is shorter in S-bonded sulfoxides.[17,27]

The significant difference between the two complexes $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$ and $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ is that the two sulfides are trans to each other in the first compound and the sulfide and sulfoxide are cis in the second compound. The complex $[Ru(NO)Br_3(Et_2S)_2]$ is expected to have the same stereochemistry as $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$, based on an earlier ^1H NMR study.[2] Since the mixed sulfide/sulfoxide complex is derived from $[Ru(NO)Br_3(Et_2S)_2]$, the difference in the arrangement of the sulfur-containing ligands in the two compounds may be due to the influence of the nitrosyl ligand. It is likely that the nitrosyl achieves better bonding (particularly Ru-NO π-back-bonding) when trans to oxygen than when trans to bromine. Unfortunately the disorder involving the NO ligand in $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$ prevents one from obtaining an accurate Ru-N distance. Even so the Ru-N distance is longer (1.787 (9) Å) when NO is trans to the bromine in the bis(dipropyl)sulfide) complex than when it is trans to oxygen (1.72 (1) Å) in the sulfide/sulfoxide complex.

The stereochemical relationship between the two complexes whose structures have been determined and that of the dimer[1] is represented diagrammatically as follows:



It is suggested that the overall process is that one diethyl sulfide ligand is oxidized to sulfoxide, which then recoordinates trans to the NO. Then two molecules of the sulfide/sulfoxide complex condense together with elimination of Et_2S (and its oxidation to Et_2SO and Et_2SO_2) and production of the dimer.

Conclusion. The photochemical oxidation reaction of the complex $[Ru(NO)Br_3(Et_2S)_2]$ requires radiation, dioxygen, and an electron donor (e.g. ethanol or sulfide). The reaction is considered as taking place in three steps. The first is the photochemical dissociation of some NO from the complex and the consequential oxidation of Ru(II) to Ru(III). An electron donor is also required in the reaction, but it does not depend on the presence of dioxygen. The second step is the oxidation of the sulfide, which requires both dioxygen and the liberated NO. Each reagent by itself does not achieve the oxidation. Radiation is unnecessary at this step, as is the electron donor. The third step is the condensation of two of the mixed sulfide/sulfoxide complexes to give the dimeric compound. The low solubility of the dimer and the continuing oxidation of the sulfide to sulfoxide and sulfone assists in this latter process.

Acknowledgment. The authors acknowledge grants from the New Zealand University Grants Committee and the University of Canterbury for the purchase of equipment.

Registry No. $Ru(NO)Cl_3(i\text{-}Bu_2S)_2$, 105502-33-8; $Ru(NO)Br_3(n\text{-}PrPhS)_2$, 105502-34-9; $Ru(NO)Br_3(n\text{-}Bu_2S)_2$, 105502-35-0; $Ru(NO)Br_3(n\text{-}BuPhS)_2$, 105502-36-1; $Ru(NO)Br_3(i\text{-}Bu_2S)_2$, 105502-37-2; $Ru(NO)I_3(Et_2S)_2$, 105502-38-3; $Ru(NO)Br_3(Et_2S)(Et_2SO)$, 105502-39-4; $[Ru(NO)Cl_3(Et_2SO)]_2$, 105502-40-7; $[Ru(NO)I_3(Et_2SO)]_2$, 105502-41-8; $Ru(NO)Br_3(Me_2SO)_2$, 105517-96-2; $Ru(NO)Br_3(Et_2SO)_2$, 105517-97-3; $Ru(NO)Br_3(Et_2S)_2$, 61567-06-4; $Ru(NO)Br_3(n\text{-}Pr_2S)_2$, 61567-08-6; $[Ru(NO)Br_3(Et_2SO)]_2$, 59492-73-8; $Ru(NO)Cl_3(Me_2SO)_2$, 39734-03-7; $RuBr_3(NO)$, 68171-32-4; $RuBr_3(n\text{-}PrPhS)_3$, 32663-17-5; $RuBr_3(i\text{-}Bu_2S)_3$, 105502-42-9; Et_2S, 352-93-2; NO_2, 10102-44-0; $Ru(NO)Br_3(EtPhS)_2$, 61567-07-5; O_2, 7782-44-7.

Supplementary Material Available: Tables of root-mean-square amplitudes of vibration along the principal axes of their thermal ellipsoids for $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$, hydrogen atom coordinates and temperature factors and anisotropic thermal parameters of non-hydrogen atoms for $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$, and additional bond angles for both compounds (5 pages); tables of observed and calculated structure factors for both compounds (19 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Structural Isomers of the Rhenium Azobenzene Complex $CpRe(CO)_2(N_2Ph_2)$

Frederick W. B. Einstein, Derek Sutton,* and Kenneth G. Tyers

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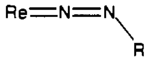
The azobenzene complexes $CpRe(CO)_2(N_2R_2)$ [**1**-**3**, Cp = η-C_5H_5; R = Ph (**1**), p-C_6H_4Me (**2**), p-C_6H_4F (**3**)] have been synthesized from $CpRe(CO)_2(THF)$ and the respective *trans*-azobenzene in hexane. The single-crystal X-ray structure determination for **1** reveals it to be isomer **1a** in which the azobenzene is bound "side-on" to the rhenium as η^2-*trans*-N_2Ph_2 with unequal Re-N bond lengths [Re-N(1) = 2.048 (12) Å, Re-N(2) = 2.136 (11) Å] and N(1)-N(2) = 1.415 (17) Å. The angle between the normals to the two N(1)-N(2)-C(phenyl) planes is 43°. Crystal data for **1a**: space group $P2_1$, a = 8.3151 (14) Å, b = 11.2138 (17) Å, c = 9.5111 (22) Å, β = 105.75(2)°, V = 853.5 Å^3, Z = 2, d_{obsd} = 2.02 (1) g cm^{-3}, d_{calcd} = 1.905 g cm^{-3}, R_F = 0.0244, R_{wF} = 0.0271. In solution, **1**-**3** each exist as two principal isomers, a and b, with distinguishable IR ν(CO) absorptions and ^1H NMR Cp resonances. These isomers are deduced to involve the azobenzene ligand bound in cyclic (η^2, a) and acyclic (η^1, b) forms, respectively. Analysis of the ^1H and ^{13}C NMR spectra, using variable-temperature and saturation-transfer experiments, indicates that the η^1-isomer (b) undergoes coordination site exchange between N(1) and N(2) and exchanges with the η^2-isomer (a) and that the η^2-isomer undergoes further fluxional behavior with a low activation barrier. This probably involves inversion at the nitrogen atoms.

Introduction

Part of the current work in our laboratory is directed at determining the structural, stereochemical, and chemical properties of complexes of molecules with unsaturated N-N moieties. These include complexes of dinitrogen (N_2), as well as diazenide (N_2H), diazene (HN=NH), and hydrazide (NNH_2 or $NHNH_2$), or their organic derivatives. We are trying to establish what possible changes in the coordination mode can occur as a dinitrogen ligand is transformed on a metal center, through visualized intermediates of the diazenide, diazene, or hydrazide type by successive chemical steps. The CpRe(CO)$_2$ fragment and its counterpart Cp*Re(CO)$_2$ (Cp = η-C$_5$H$_5$, Cp* = η-C$_5$Me$_5$) provide good systems with which to study this since not only are the dinitrogen complexes CpRe(CO)$_2$(N$_2$)[1] and Cp*Re(CO)$_2$(N$_2$)[2] known (I) but also are representative examples of each of the organodiazenide (II),[3,4] -diazene (III),[5] and -hydrazide (IV, V)[5,6] derivatives.

$\mathrm{Re{-}N{\equiv}N}$

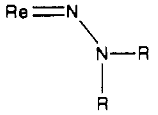
I



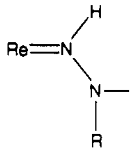
II

$\mathrm{Re{-}NHNR}$

III

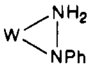


IV

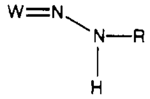


V

The hydrazide structures, shown as IV and V, have been established crystallographically for CpRe(CO)$_2$[*p*-NN(CH$_3$)C$_6$H$_4$OMe] and [CpRe(CO)$_2${*p*-NHN(CH$_3$)C$_6$H$_4$Me}][BF$_4$], respectively.[5,6] Most interestingly, the acyclic (η^1) structure (V) contrasts with the cyclic (η^2) structure (VI) that we had previously observed for a similar ligand in the related tungsten complex [Cp$_2$W(NH$_2$NPh)][BF$_4$],[7] whose precursor [Cp$_2$WH{NN(H)Ph}][BF$_4$][8] nevertheless has an acyclic structure (VII) like that of IV.

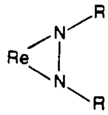


VI

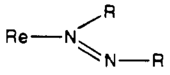


VII

Rather little evidence is presently available by which to establish with certainty the structure of the rhenium–aryldiazene moiety (III). It occurs in CpRe(CO)$_2$(*p*-NHNC$_6$H$_4$OMe),[5] but this compound has not been crystallized. By comparison with the structures of other monoaryldiazene complexes,[9] an η^1-NHNR structure has been assumed but this requires confirmation and may well not be correct. So in order to address this question, in an attempt to obtain structural information on a related rhenium–aryldiazene complex that can be crystallized, we have synthesized the 1,2-diphenyldiazene (azobenzene) complex CpRe(CO)$_2$(N$_2$Ph$_2$) and have determined its crystal structure and spectroscopic behavior in solution. We find that the rhenium–azobenzene arrangement is cyclic (η^2) (VIII) in the crystal, but in organic solvents this structure is in equilibrium with the acyclic (η^1) form (IX) and the latter is also undergoing coordination site exchange of the nitrogen atoms.



VIII



IX

Experimental Section

General Methods. Solvents were dried by appropriate procedures (THF using sodium and benzophenone) and were distilled under nitrogen. Reactions were conducted under nitrogen by using typical Schlenk techniques. CpRe(CO)$_2$(THF) was synthesized and isolated as described previously.[5] Azobenzene was purchased from Eastman Kodak. Azotoluene was synthesized by the reduction of *p*-nitrotoluene with Co$_2$(CO)$_8$,[10] and *p,p'*-difluoroazobenzene was similarly synthesized from *p*-fluoronitrobenzene. *cis*-Azobenzene was made by irradiating azobenzene in hexane with a 200-W high-pressure Hanovia quartz-mercury lamp, followed by chromatography. IR spectra were measured on a Perkin-Elmer 983 spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded by M. M. Tracey of this department on a Bruker WM-400 spectrometer at 400 or 100 MHz. Mass spectra were recorded on a Hewlett-Packard 5985 instrument by G. Owen, and microanalytical data were obtained by M. K. Yang of the SFU microanalytical service.

Preparation of CpRe(CO)$_2$(N$_2$Ph$_2$) (1). In a typical reaction, excess azobenzene was added to a hexane solution of CpRe(CO)$_2$(THF) (100 mg, 0.26 mmol) and stirred vigorously for 6 h. Chromatography on Florisil and eluting with hexane yielded first excess azobenzene, and then, with 1:1 hexane-CH$_2$Cl$_2$, brown CpRe(CO)$_2$(N$_2$Ph$_2$) was isolated. This was recrystallized from hexane–CHCl$_3$. IR (hexane): 2006 m, 1939 m (**1a**) cm^{-1}; 1947 s, 1980 s (**1b**) cm^{-1} (ν(CO)). IR (KBr): 2001 s, 1928 m, 1900 m cm^{-1}. ^{1}H NMR (acetone-d_6) δ 7.57 (app (apparent) t, J = 8 Hz, meta, isomer b), 7.45–7.40 (overlapping app t's, meta and para, isomer b), 7.32 (app t, J = 8 Hz, para, isomer b), 7.24 (d, J = 8 Hz, ortho, isomer b), 7.13 (d, J = 8 Hz, ortho, isomer b), 5.72 (s, Cp of isomer a, minor isomer), 4.95 (s, Cp of isomer b, major isomer). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 202.1 (CO, isomer b), 166.8, 158.6 (ipso, isomer b), 129.4, 127.8 (ortho, isomer b), 127.7, 127.0 (meta, isomer b), 121.3, 117.7 (para, isomer b), 93.4 (Cp, isomer a, minor isomer), 85.8 (Cp, isomer b, major isomer). Mass spectrum: m/z (based on ^{185}Re and ^{187}Re), 489, 491 (M$^+$), 461, 463 (M$^+$ – CO), 433, 435 (M$^+$ – 2CO). Anal. Calcd for **1**: C, 46.62; H, 3.09; N, 5.72. Found: C, 46.81; H, 3.11; N, 5.80.

Preparation of CpRe(CO)$_2${N$_2$(C$_6$H$_4$Me-*p*)$_2$} (2). This was prepared in a fashion identical with that used for **1**, with azotoluene used to replace azobenzene. IR (hexane): 2004 w, 1945 s, 1887 s cm^{-1} (ν(CO)). ^{1}H NMR (acetone-d_6): δ 7.29 (d, J = 8 Hz, meta, isomer b), 7.21 (d, J = 8 Hz, meta, isomer b), 7.13 (d, J = 8 Hz, ortho, isomer b), 7.03 (d, J = 8 Hz, ortho, isomer b), 5.68 (s, Cp, isomer a, minor isomer, very weak), 4.92 (s, Cp, isomer b, major isomer), 2.40, 2.38 (Me, isomer b). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 202.4 (CO), 156.7, 151.1 (ipso), 141.1, 138.0 (para), 129.9, 129.7, 128.2, 122.7, 121.2, 117.8 (aromatics), 85.6 (Cp), 29.7 (CH$_3$), 21.4 (CH$_3$). Mass spectra: m/z (based on ^{185}Re and ^{187}Re), 516, 518 (M$^+$), 488, 490 (M$^+$ – CO), 460, 462 (M$^+$ – 2CO). Anal. Calcd for **2**: C, 48.73; H, 3.70; N, 5.41. Found: C, 48.84; H, 3.80; N, 5.48.

Preparation of CpRe(CO)$_2${N$_2$(C$_6$H$_4$F-*p*)$_2$} (3). This was prepared in an identical fashion, with *p,p'*-difluoroazobenzene used in place of azobenzene. IR (hexane): 2008 s, 1941 s (**3a**) cm^{-1}; 1950 s, 1893 s (**3b**) cm^{-1} (ν(CO)). ^{1}H NMR (CDCl$_3$): δ 6.8–7.4 (complex, C$_6$H$_4$, isomers a and b), 5.83 (s, Cp, isomer a, minor isomer), 5.05 (s, Cp, isomer b, major isomer). ^{13}C{^{1}H} (CDCl$_3$): δ 202.2 (CO, isomer b), 161.2 (d, $^1J_{\mathrm{CF}}$ = 246 Hz, para, isomer b), 154.07 (ipso, isomer b), 130.0 (d, $^1J_{\mathrm{CF}}$ = 223 Hz, para, isomer b), 123.08 (d, $^3J_{\mathrm{CF}}$ = 8.4 Hz, ortho, isomer b), 119.49 (d, $^3J_{\mathrm{CF}}$ = 8.5 Hz, ortho, isomer b), 116.43 (d, $^2J_{\mathrm{CF}}$ = 22.6 Hz, meta, isomer b), 114.52 (d, $^2J_{\mathrm{CF}}$ = 22.7 Hz, meta, isomer b), 93.4 (s, Cp, isomer a, minor isomer), 86.8 (s, Cp, isomer b, major isomer). Mass spectrum: m/z (based on ^{185}Re and ^{187}Re), 524, 526 (M$^+$), 496, 498 (M$^+$ – CO), 468, 470 (M$^+$ – 2CO).

X-ray Structure Determination for CpRe(CO)$_2$(η^2-N$_2$Ph$_2$) (1a). A small orange crystal recrystallized from hexane–CHCl$_3$ and suitable for data collection was mounted on the end of a glass fiber. Accurate cell dimensions were determined from the least-squares refinement of 25 accurately centered reflections (2θ = 21.4–28.8°). Data were collected on an Enraf-Nonius CAD-4 diffractometer, equipped with a graphite monochromator. The ω–2θ scan method was used with scan width and scan speeds as listed in the summary of crystal data in Table I. Two standards were monitored every hour of X-ray beam time and showed only random variations. Intensities of 1180 reflections ($3° \le 2\theta \le 45°$) were measured in the quadrant $+h,+k,\pm l$. The data were corrected for Lorentz, polarization, and absorption effects (empirical method; ψ scans, μ(Mo Kα) = 72.3 cm^{-1}) and 991 reflections were counted as observed with $I \ge 3\sigma(I)$.

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Table I. Summary of Crystal Data and Data Collection Conditions for $CpRe(CO)_2(\eta^2\text{-}N_2Ph_2)$ (**1a**)

compd	$(\eta^5\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-}N_2Ph_2)$
formula	$C_{19}H_{15}N_2O_2Re$
space group	$P2_1$
a, Å	8.3151 (14)
b, Å	11.2138 (17)
c, Å	9.5111 (22)
β, deg	105.75 (2)
V, Å^3	853.5
Z	2
d_{obsd}, g cm^{-3}	2.02 (1)
d_{calcd}, g cm^{-3}	1.905
crystal dimens, mm	0.08 × 0.11 × 0.13
temp, °C	21
radiation	Mo Kα (graphite monochromated)
μ, cm^{-1}	72.3
transmission factors	0.492–0.992 (empirical)
scan speed, deg min^{-1}	0.5–4.0
scan width, deg	0.6 + dispersion
no. of measd reflcns ($3° \leq 2\theta \leq 45°$)	1180
no. of obsd. reflcns ($I \geq 3\sigma(I)$)	991
no. of variables	131
R_F	0.0244
R_{wF}	0.0271
goodness-of-fit	1.55
extinction	0.473×10^{-6}

Table II. Positional Parameters ($\times 10^4$) for $CpRe(CO)_2(\eta^2\text{-}N_2Ph_2)$ (**1a**)

atom	x	y	z	B_{eq}, Å^2
Re	429.8 (6)	2500	2932.8 (5)	2.63 (6)
N(1)	1616 (1)	1306 (1)	1927 (1)	3.2 (6)
N(2)	2834 (1)	2157 (1)	2615 (1)	2.9 (6)
C(1)	1826 (2)	3245 (1)	4740 (2)	4.2 (8)
O(1)	2698 (2)	3613 (1)	5805 (1)	8.3 (8)
C(2)	71 (2)	1441 (2)	4237 (2)	5.4 (10)
O(2)	−300 (2)	740 (1)	5032 (2)	8.3 (9)
C(3)	1936 (2)	143 (1)	2484 (2)	3.0 (3)
C(4)	614 (2)	−637 (2)	2225 (2)	4.4 (3)
C(5)	900 (2)	−1826 (2)	2705 (2)	5.6 (4)
C(6)	2445 (2)	−2225 (2)	3466 (2)	5.7 (4)
C(7)	3731 (2)	−1404 (2)	3773 (2)	5.8 (4)
C(8)	3608 (2)	−254 (2)	3269 (2)	4.0 (3)
C(9)	3310 (2)	2941 (1)	1622 (1)	3.4 (3)
C(10)	3287 (1)	2590 (1)	215 (1)	3.8 (2)
C(11)	3907 (2)	3397 (2)	−652 (2)	4.2 (3)
C(12)	4559 (2)	4500 (2)	−102 (2)	5.0 (4)
C(13)	4611 (2)	4830 (2)	1308 (2)	5.1 (4)
C(14)	3974 (2)	4060 (2)	2177 (2)	4.7 (4)
C(15)	8313 (1)	2736 (2)	779 (1)	3.5 (3)
C(16)	7635 (2)	2791 (2)	1917 (1)	4.3 (3)
C(17)	8249 (2)	3826 (2)	2716 (2)	4.7 (4)
C(18)	9466 (2)	4375 (2)	2013 (2)	4.5 (3)
C(19)	9374 (2)	3658 (1)	822 (2)	3.8 (3)

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $CpRe(CO)_2(\eta^2\text{-}N_2Ph_2)$ (**1a**)

	Bond Lengths		
Re–N(1)	2.048 (12)	N(1)–N(2)	1.415 (17)
Re–N(2)	2.136 (11)	N(1)–C(3)	1.406 (20)
Re–C(1)	1.979 (18)	N(2)–C(9)	1.424 (18)
Re–C(2)	1.800 (21)	C(1)–O(1)	1.150 (23)
Re–Cp(center)	1.988 (15)	C(2)–O(2)	1.189 (26)
	Bond Angles		
Re–N(1)–N(2)	73.6 (7)	N(2)–Re–C(1)	81.3 (5)
Re–N(2)–N(1)	66.9 (6)	N(1)–N(2)–C(9)	113.7 (10)
Re–N(1)–C(3)	119.7 (9)	N(2)–N(1)–C(3)	114.4 (10)
Re–N(2)–C(9)	115.0 (8)	Re–C(1)–O(1)	175.6 (14)
N(1)–Re–N(2)	39.5 (4)	Re–C(2)–O(2)	174.6 (19)
N(1)–Re–C(2)	94.7 (7)	C(1)–Re–C(2)	81.2 (4)

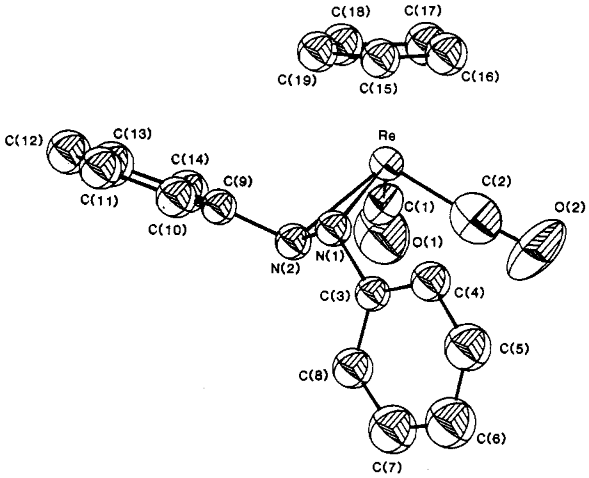

Figure 1. Perspective view of a molecule of $CpRe(CO)_2(\eta^2\text{-}N_2Ph_2)$ (**1a**) with atom labeling.

The Re atom coordinates were obtained from a Patterson map. All remaining non-hydrogen atoms were located in subsequent Fourier syntheses. The phenyl and cyclopentadienyl hydrogen atom positions were calculated [d(C–H) = 0.98 Å], assigned isotropic temperature factors of 0.075 Å^2, and included as fixed contributions in further refinement. These atoms were repositioned periodically during refinement. The Re atom, carbonyl groups, and nitrogen atoms were refined anisotropically. After three cycles of full-matrix least-squares refinement, an analysis of F_o and F_c revealed that a correction for extinction should be included in the refinement. The structure was then further refined until all shift-to-error ratios were less than 0.02. Final residuals were R_F = 0.0244 and R_{wF} = 0.0271, the goodness-of-fit was 1.55, and the extinction correction refined to 0.473×10^{-6}. For the final cycles, the weighting scheme used was $w = [\sigma(F_o)^2 + pF_o{}^2]^{-1}$. The value of parameter p (0.0001) was that for which the variation of the averaged $\sum\{w(|F_o| - |F_c|)\}^2$, with F_o and $(\sin\theta)/\lambda$, was observed to be a minimum. The largest peaks in a final difference map were of height 0.55 (9) e Å^{-3} and were located near the cyclopentadienyl ring. To ascertain that the correct enantiomorph had been chosen, the coordinates of all the atoms were inverted and the model refined to convergence. This gave values of R_F = 0.0257 and R_{wF} = 0.0292 and the goodness-of-fit was 1.68. This demonstrated the correctness of the original model.

Neutral scattering factors with anomalous dispersion corrections for the non-hydrogen atoms were used.[11a] Computer programs[11b] were run on an in-house VAX 11-750. Positional parameters are listed in Table II. Selected bond distances and angles are in Table III. Tables of anisotropic thermal parameters, calculated hydrogen atom coordinates, calculated mean planes and dihedral angles, and calculated and observed structure factors are available as supplementary material (Tables S1–S4, respectively).

Results

(a) Solid-State Structures. Crystals of $CpRe(CO)_2(N_2Ph_2)$ (**1**) obtained from hexane–$CHCl_3$ appear to be uniformly those of a single product, though the ν(CO) IR spectrum (KBr) is more complex than the simple two-band spectrum anticipated (see below). A crystal structure determination of **1** reveals it to consist of discrete mononuclear molecules of isomer **1a** with no short inter- or intramolecular contacts. The *trans*-N_2Ph_2 ligand is bound "side-on", or η^2, to the rhenium, as illustrated in Figure 1. It is presumed that **1–3** all adopt a similar η^2-form of the ligand in the solid state; i.e., they occur as the isomers **1a**, **2a**, and **3a**.

The geometry of the rhenium coordination sphere in **1a** is that of a four-legged "piano stool" with the Cp ring as the seat and C(1), C(2), N(1), and N(2) as the base, much like the structure that we determined earlier for $CpRe(CO)_2(\eta^2\text{-}C_2Ph_2)$.[12] However, in that structure the four carbon atoms located in the base of the

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(11) (a) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1975; Vol IV. (b) Larsen, A. C.; Gabe, E. J. *Computing in Crystallography*; Schenk, H., et al., Eds.; Delft University Press: Delft, Holland, 1978; p 81. Larsen, A. C.; Lee, F. L.; LePage, Y.; Gabe, E. J. *The NRC Vax Crystal Structure System*; Chemistry Division, NRC: Ottawa, Canada, 1983.

(12) Einstein, F. W. B.; Tyers, K. G.; Sutton, D. *Organometallics* **1985**, *4*, 489.

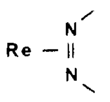
Table IV. Structurally Characterized Azobenzene and Transition-Metal–η^2-Azobenzene Compounds

compd	C—N, Å	N═N, Å	C—N═N, deg	M—N, Å	N—M—N, deg
trans-azobenzene[a]	1.434 (3)	1.243 (3)	113.3 (3)	...	...
cis-azobenzene[b]	1.449 (4)	1.253 (4)	121.9 (3)	...	...
trans-p,p'-azotoluene[c]	1.433 (4)	1.244 (4)	113.8 (3)	...	...
$Cp_2Ti(N_2Ph_2)$[d,h]	1.397 (9) 1.393 (9)	1.339 (8)	122.5 (3) 123.7 (3)	1.965 (6) 1.971 (5)	39.8 (5)
$[P(C_6H_4CH_3)_3]_2Ni(N_2Ph_2)$[e]	1.427 (8) 1.423 (8)	1.371 (6)	111.6 (5) 112.2 (5)	1.932 (5) 1.927 (5)	41.6 (2)
(*t*-BuNC)$_2$Ni(N$_2$Ph$_2$)[f]	1.421 (5) 1.424 (5)	1.385 (5)	111.6 (3) 111.9 (3)	1.897 (4) 1.899 (5)	42.8 (2)
$CpRe(CO)_2(N_2Ph_2)$[g]	1.406 (20) 1.424 (18)	1.415 (17)	113.7 (10) 114.4 (10)	2.048 (12) 2.136 (11)	39.5 (4)

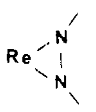
[a] Reference 13. [b] Reference 14. [c] Reference 15. [d] Reference 16. [e] Reference 18. [f] Reference 17. [g] This work. [h] Reference 26.

alkyne complex described[12] a well-defined plane ($\chi^2 = 1.8$); this is not the case in **1a**, where it is observed that C(1), C(2), N(1), and N(2) deviate considerable from coplanarity (for the calculated mean plane, $\chi^2 = 154$).

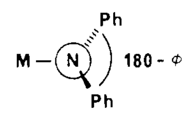
The η^2-N_2Ph_2 ligand in **1a** is not symmetrically bound to Re; the Re–N(1) bond length is 2.048 (12) Å, and the Re–N(2) bond length is 2.136 (11) Å. This contrasts with the symmetrically bound η^2-C_2Ph_2 ligand in $CpRe(CO)_2(\eta^2\text{-}C_2Ph_2)$[12] and undoubtedly reflects the overall asymmetry imposed on **1a** by the trans disposition of the phenyl groups. The N(1)–N(2) distance of 1.415 (17) Å is one of the longest to be found so far in a metal–azobenzene complex (Table IV)[13-17] and approaches that expected for a single N–N bond.[13-15] This also contrasts with the structure of $CpRe(CO)_2(\eta^2\text{-}C_2Ph_2)$ where the alkyne C–C bond was one of the *shortest* to be observed, and the alkyne was viewed as being minimally perturbed as a result of coordination.[12] In **1a**, coordination has had a dramatic effect on the structure of the azobenzene molecule, and the NN bond lengthening may be accounted for by significant Re–N π-back-bonding in the idealized π-complex mode (X) or perhaps may be more realistically represented by a σ-bonded metallocycle (XI).



X



XI



XII

Ibers[17] has suggested that, in η^2-azobenzene complexes, the extent of metal–azo interaction is reflected in the size of the dihedral angle (ϕ in the Newman projection XII) between the NNC and NNC′ planes (C and C′ being the ipso-carbon atoms of the phenyl groups), since these are coplanar in free *trans*-azobenzene (and the angle is zero), but the phenyl groups become "bent back" away from the metal upon coordination. In [(*p*-tol)$_3$P]$_2$Ni(N$_2$Ph$_2$)[18] and (*t*-BuNC)$_2$Ni(N$_2$Ph$_2$)[17] this dihedral angle (ϕ) was observed to be 25.5 (4) and 26.8 (4)°, respectively. In **1a** the angle is much larger, at 43(1)°, and correspondingly, the N–N bond length in **1a** is longer than in the two nickel compounds. All of these observations indicate a high degree of rhenium–azobenzene interaction in **1a**.

(b) Solution Structures. The IR spectra of **1**–**3** in solution exhibit more ν(CO) bands than are to be expected if only a single structure is present in solution. Hexane solution spectra for **1**–**3** are shown in Figure 2. Compound **1** exhibits four sharp bands at 2006, 1947, 1939 and 1890 cm^{-1}, as does compound **3** at 2008, 1950, 1941 and 1893 cm^{-1}. For compound **2**, only three resolved bands are observed, at 2004, 1945 and 1887 cm^{-1}, with the first very much weaker than the latter two. By comparison with the spectra of **1** and **2**, the 1945-cm^{-1} band in **3** most likely is a superposition of two unresolved and near-coincident bands. There is a solvent dependence of the ν(CO) bands for **1**–**3** that favors interpretation of the spectra as consisting of two pairs of ν(CO) absorptions, each pair attributable to an individual isomer. As an example, for **1** in CH_2Cl_2, the bands at 2006 and 1939 cm^{-1} are reduced to about one-third of their intensity in hexane, allowing them to be assigned to one isomer. Removal of CH_2Cl_2 and redissolving in hexane restores the original spectrum. Table V lists the ν(CO) absorptions of **1**–**3** with the proposed assignments and those of $CpRe(CO)_2(C_2Ph_2)$ and *cis*-$CpRe(CO)_2I_2$ for comparison. We think that the higher ν(CO) pair (i.e., 2006 and 1939 cm^{-1} for **1** and related values for **2** and **3** (Table V) correspond to an isomer with an η^2-N_2Ph_2 ligand in each case. This is likely to be the isomer observed in the X-ray structure, having the phenyl groups trans (furthermore, this is consistent with NMR results, see below). The justification for this assignment is as follows.

(i) Such an isomer should have ν(CO) values somewhat greater (and certainly not lower) than those of $CpRe(CO)_2(\eta^2\text{-}C_2Ph_2)$, since N_2Ph_2 is expected to be a better π-acceptor than C_2Ph_2.[19] (ii) The high ν(CO) values also suggest a relatively more oxidized Re (cf., *cis*-$CpRe(CO)_2I_2$), consistent with a significant contri-

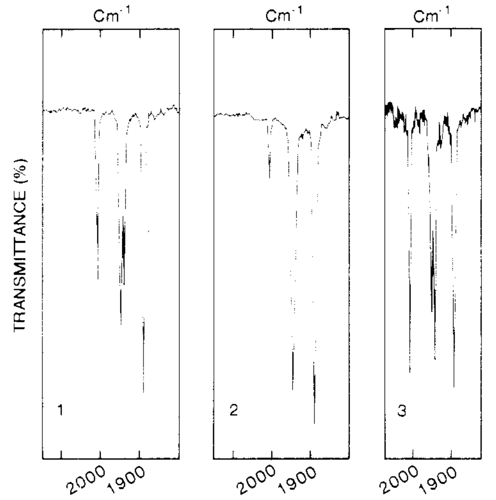


Figure 2. IR spectra (ν(CO) region) for hexane solutions of **1**–**3**.

Table V. ν(CO) Bands for Mononuclear Rhenium Compounds

compd	ν(CO),[a] cm^{-1}
$CpRe(CO)_2(N_2Ph_2)$ (**1a**)	2006, 1939
$CpRe(CO)_2(N_2Ph_2)$ (**1b**)	1947, 1898
$CpRe(CO)_2(N_2(C_6H_4Me\text{-}p)_2)$ (**2a**)	2004, ca. 1945
$CpRe(CO)_2(N_2(C_6H_4Me\text{-}p)_2)$ (**2b**)	ca. 1945, 1887
$CpRe(CO)_2(N_2(C_6H_4F\text{-}p)_2)$ (**3a**)	2008, 1941
$CpRe(CO)_2(N_2(C_6H_4F\text{-}p)_2)$ (**3b**)	1950, 1893
$CpRe(CO)_2(C_2Ph_2)$[b]	1980, 1904
cis-$CpRe(CO)_2I_2$[c]	2040, 1977

[a] In hexanes. [b] Reference 12. [c] Reference 2.

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(13) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146.
(14) Mostad, A.; Romming, C. *Acta Chem. Scand.* **1971**, *25*, 3561.
(15) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 153.
(16) Bart, J. C. J.; Bassi, I. V.; Cerruti, G. F.; Calcaterra, M. *Gazz. Chim. Ital.* **1980**, *110*, 423.
(17) Dickson, R. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2988.
(18) Ittel, S. D.; Ibers, J. A. *J. Organomet. Chem.* **1973**, *57*, 389.
(19) Otsuka, S.; Yoshida, T.; Tatsuno, Y. *J. Am. Chem. Soc.* **1971**, *93*, 6462.

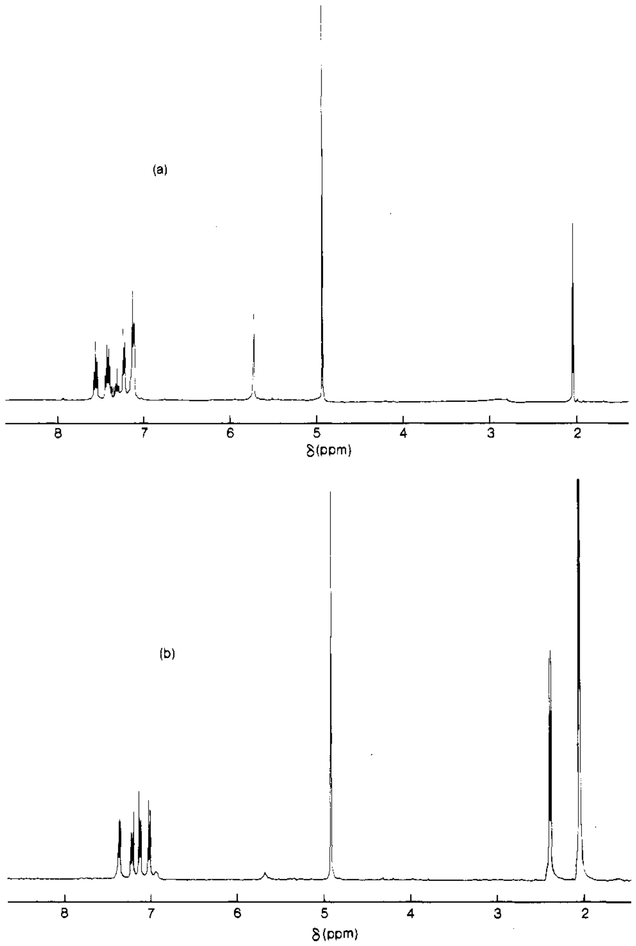
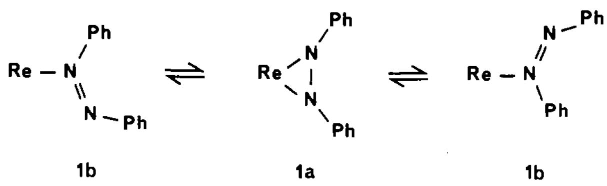


Figure 3. (a) 400-MHz ^{1}H NMR (acetone-d_6) spectrum of CpRe(CO)$_2$(N$_2$Ph$_2$) (**1**) showing Cp resonances of the major (**1b**) and minor (**1a**) isomers at δ 4.95 and 5.72, respectively, and phenyl resonances for two inequivalent phenyls of **1b**. (b) 400-MHz ^{1}H NMR (acetone-d_6) spectrum of CpRe(CO)$_2${N$_2$(C$_6$H$_4$Me-p)$_2$} (**2**). The Cp resonances of the major (**2b**) and minor (**2a**) isomers are δ 4.92 and 5.68, respectively.

bution from the Re(III) metallocyclic structure (XI) as is already evident from the structure parameters discussed earlier. (iii) Although, because of the overlapping central two bands, it is difficult to obtain accurate measured intensities, the intensity patterns nevertheless are consistent with the proposed assignments.[20] The relative intensities of ν(CO)$_{sym}$ and ν(CO)$_{asym}$ (the high and low wavenumber bands, respectively) for the higher ν(CO) pair in **1** and **3** yield[20] an estimated angle for the Re(CO)$_2$ fragment of about 80–85° (the relative intensities are also similar to those for CpRe(CO)$_2$(η^2-C$_2$Ph$_2$) for which the observed angle[12] is 83°). The observed angle in the η^2-N$_2$Ph$_2$ structure **1a** is 81°.

Ideally, the solid–state IR spectrum of the crystalline sample should easily confirm this assignment. However, the KBr spectrum obtained by using a small number of crystals from the same sample that furnished the X-ray crystal does not do so because not two, but three ν(CO) bands at 2001, 1928, and 1900 cm^{-1} are present. The identical spectrum is also observed by using the bulk solid product from which crystals were grown. This may be the authentic solid-state spectrum of the η^2-isomer above, with the increased complexity and positional shifts arising from solid-state effects. Alternatively, it may once again reflect the superposition of the spectrum from two isomers similar to those in solution; perhaps isomerization is induced by the pressure (and localized heating) incurred in preparing the KBr disk. Either way, it has not been possible to obtain a satisfactory correlation between the solid-state IR and X-ray structures to use in further support of the IR assignments of the isomers in solution. Common mulling agents, such as Nujol, as normally used to prepare solid dispersions for IR sampling, all significantly dissolved the sample, and therefore, also produced IR spectra having three or four ν(CO) bands (like the solution spectra), which indicate the presence of both isomers under these conditions also.

Scheme I



Proton NMR spectra were obtained for solutions of **1** in acetone-d_6 or CDCl$_3$, solvents for which IR data had already shown isomer b with low ν(CO) absorptions (ca. 1947 and 1898 cm^{-1}) to be predominant. Two Cp resonances were observed, the major one at δ 4.95 for isomer b and the minor one at δ 5.72 for isomer a in a ratio near 4:1 in acetone-d_6 (Figure 3a). The resonance for **1b** was sharp, but that for **1a** was noticeably broader. The phenyl region exhibited sharp resonances for the ortho, meta, and para protons of two *inequivalent* phenyl groups in approximately equal concentration. These are clearly seen to result from inequivalent phenyls in the major isomer **1b**, as was confirmed by using the azotoluene complex **2**. The ^{1}H NMR of **2** in acetone-d_6 (Figure 3b) is dominated by isomer **2b** (consistent with the IR spectrum in Figure 2); the phenyl region again exhibits resonances from two nonidentical phenyl groups, and in agreement, there are also two equal intensity methyl resonances. In the ^{1}H NMR of both **1** and **2** the phenyl (and, for **2**, the methyl) resonances of the minor isomers **1a** and **2a** were not readily apparent. We conclude that these resonances are broadened virtually into the baseline by some kind of phenyl group exchange mechanism operating in isomer a (see below).

The observation that the isomer b has inequivalent phenyl groups is consistent with the earlier proposal, based on the IR frequencies, that this is the η^1-isomer. If correct, this still leaves either the cis (*cis*-**1b**) or trans (*trans*-**1b**) structures to be considered as possibilities. On the other hand, if the major isomer were instead to be the η^2-isomer, then immediately both of the cis forms of this isomer can be ruled out since these must have equivalent phenyls. This leaves only the trans-η^2 structure as a possibility (ie., the structure observed in the crystal). As mentioned earlier, we do not think that the IR evidence favors this interpretation for isomer b.

Isomers a and b are undergoing slow interconversion in solution as demonstrated in two ways. First, both Cp resonances broaden, collapse and recombine into a single broadened signal with an increase in temperature. For **1** the coalescence temperature was 332 K. Second, irradiation of one Cp resonance results in saturation transfer to the other Cp resonance, plus an NOE enhancement of *all* the phenyl resonances of isomer b by comparable amounts. The latter further suggests, then, that the two phenyls in isomer b attain *equivalent* positions relative to the Cp group (so as to experience a similar NOE) during the time for NOE buildup (10 s). In other words, the phenyls in isomer b must be undergoing a slow exchange of position. It was thus not practicable to use NOE to establish which of the inequivalent phenyl resonances arose specifically from the α-phenyl group, bound to the coordinated nitrogen in **1b** (the one that would be expected to experience the greatest NOE from the Cp protons), because even with NOE buildup times shortened to 5, 3, 1, 0.3, and 0.1 s, NOE enhancements of both sets of phenyl resonances were always observed.

These results we take as evidence first of slow site exchange of the α- and β- phenyl groups in the η^1-isomer b resulting from an η^1-η^1 coordination shift (otherwise the β phenyl group is always too remote from the Cp ring to experience an observable NOE), and second of the exchange occurring via the intermediacy of the side-on or η^2-form (isomer a) (Scheme I).

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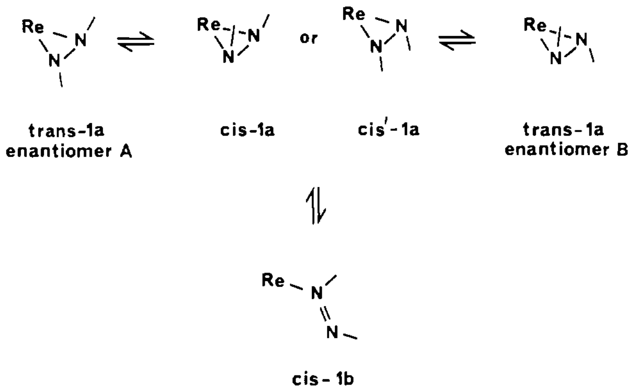
[20] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980; p 1074.

Scheme II



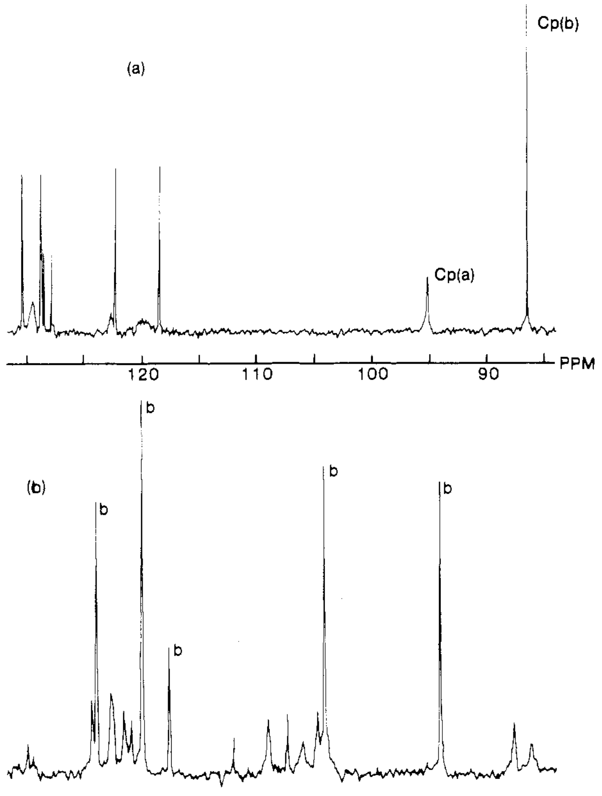
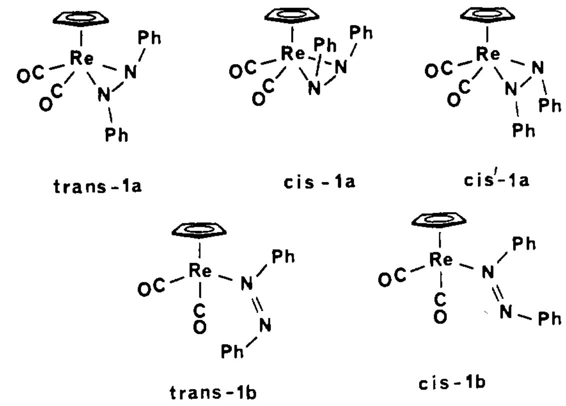


Figure 4. 100-MHz $^{13}C\{^1H\}$ NMR spectra of $CpRe(CO)_2(N_2Ph_2)$ (**1**) in acetone-d_6 at (a) 297 K, showing sharp Cp and phenyl resonances for isomer **1b** and broad resonances for **1a**, and at (b) 189 K (phenyl region; resonances for **1b** are identifed). (Spectra at 221 and 200 K are available as supplementary material.)

Considering now the ^1H NMR resonances for the minor isomer **1a**, the somewhat broad δ 5.72 Cp resonance and the inability to discern any phenyl resonances suggest that this isomer is undergoing further fluxional processes at a rate faster than the interconversion with **1b**, but not fast enough to produce a sharp averaged spectrum. The spectrum of **2** is similar; the minor Cp resonance is broad and very weak in acetone-d_6 (Figure 3b), and in $CDCl_3$ it is hardly observable above the baseline. We think that this fluxional process is probably inversion at the nitrogen atoms in the η^2-form (Scheme II).

Similar features are observed in the ^{13}C and $^{13}C\{^1H\}$ NMR spectra of **1**. At 297 K, the Cp resonance of the minor isomer **1a** occurs at δ 93.4 and is broader and weaker than the Cp resonance of **1b** at δ 85.8 (Figure 4a). The phenyl resonances for **1b** occur as three pairs of sharp lines assigned to the ortho, meta, and para carbons of the two inequivalent phenyls.[21] The phenyl carbon resonances of the minor isomer **1a** are very broad and centered at about δ 120, 123, and 129. Lowering the temperature results in dramatic changes in the phenyl resonances of this isomer resulting ultimately, at 189 K, in a total of 11 or 12 lines being discernible that belong to it (Figure 4b); Parts c (221 K) and d (200 K) of Figure 4 for intermediate temperatures are included as supplementary material. The resonances of **1b** remain invariant. At the present time we cannot offer a clear interpretation of the low-temperature spectrum (some of the resonances are still broad), but the observed number of phenyl resonances for isomer **1a** suggests the presence of a minimum of two species. Curiously, however, a detailed examination of the Cp resonance of **1a** at 189 K shows that it is still broader than the **1b** Cp resonance and has not yet become separated into the expected individual Cp resonances for two or more species. In the CO region only one resonance could be located, and this remained as a single line down to 189 K. This is the CO resonance of the major isomer **1b**, and it implies equivalent CO groups. In agreement, the two CO groups are expected to be equivalent in this isomer on account of the anticipated free rotation of the N_2Ph_2 ligand around the Re–N σ bond. Resonances from CO groups of the minor isomer(s) could not be located. The ipso-carbon region shows two sharp peaks due to the major isomer **1b** at δ 159.2 and 167.2 and a small broad resonance at δ 163 that may be an ipso-carbon resonance from the minor isomer(s).

Chart I



Although it has not been possible to locate all the resonances for isomer **1a** and its low-temperature forms with certainty and completeness, we think that the results consistently point to the correctness of Scheme II. The major isomer **1b** has the N_2Ph_2 ligand coordinated in an η^1-fashion with the N_2Ph_2 ligand in its cis geometry. This interconverts with the η^2-form **1a** that is observed in the crystal (with the N_2Ph_2 ligand now exhibiting trans geometry) by the intermediacy of the two possible cis cyclic structures that would be formed immediately on ring closure, *cis*-**1a** and *cis′*-**1a** (Chart I). We think that the approximately 12 protonated carbon phenyl resonances that appear in the low-temperature $^{13}C\{^1H\}$ spectrum of the minor isomer result from the four distinguishable phenyl rings of the frozen out isomers trans-**1a** (two phenyls), cis-**1a** (one), and cis′-**1a** (one). In Scheme II we assume that interconversion between η^2-stereoisomers can only occur by consecutive nitrogen inversion and not by two coincident, synchronous inversions at the different nitrogen atoms. This is in keeping with the calculations of Mannschreck, which indicate that a "monoplanar" transition state for inversion at one N atom is much lower in energy than the "biplanar" transition state for two synchronous inversions.[22] The latter transition state will suffer from the high strain energy incurred in the two planar, and ideally sp^2-hybridized, nitrogen atoms.

It was of interest to see whether any further isomer of different behavior might be furnished if *cis*-azobenzene were used instead

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[21] Here we are describing only the protonated carbon atoms of the phenyl groups.

[22] Mannschreck, A.; Seitz, W. *Angew. Chem.* **1968**, *81*, 224. Mannschreck, A.; Radeglia, R.; Grundemann, E.; Ohme, R. *Chem. Ber.* **1967**, *100*, 1778. Hakli, H.; Mintas, M.; Mannschreck, A. *Chem. Ber.* **1979**, *112*, 2028.

of the trans isomer in the synthesis. No such change was observed, the product being identical in all respects with **1**. This is to be expected, since we doubt that uncomplexed molecules of *cis*- and *trans*-azobenzene undergo interconversion during the synthesis but as a result of the interconversions between the *cis*-η^2, *cis′*-η^2, and *trans*-η^2 structures of the *complexes* they must lead to the same isolated product and solution equilibrium.

Discussion

The few diazene or organodiazene transition-metal compounds that have been structurally characterized by X-rays can be grouped in the following way. In the case of N_2H_2, only bridging arrangements have been authenticated. A trans-μ-η^1,η^1 arrangement occurs in $[\{Cr(CO)_5\}_2(N_2H_2)]$[23] and in $[\{(C_5Me_4\text{-}t\text{-}Bu)(t\text{-}BuC)(I)W\}_2(N_2H_2)]$,[24] but a cis-$\mu$-$\eta^2$,$\eta^2$ "butterfly" arrangement occurs in $[\{(PhN)Me_3W\}_2(N_2H_4)(N_2H_2)]$.[25] In the last two, the N–N bond lengths and other features suggest that the compounds are derivatives of the hydrazide ion, $N_2H_2^{2-}$, rather than diazene, N_2H_2. In contrast with this, only mononuclear compounds have been authenticated for monosubstituted diazenes, and the only two X-ray structures to date both show that the aryldiazene ligand is cis and is bound η^1 by the NH group only. The examples are *trans*-$[Pt(p\text{-}HNNC_6H_4F)(PEt_3)_2Cl][ClO_4]$ and $[RuCl(CO)_2(HNNPh)(PPh_3)_2][ClO_4]\cdot CH_2Cl_2$.[9] Where disubstituted diazenes are concerned, this type of bonding has also been observed in a few cases by X-rays, but many of the known mononuclear structures have the ligand bound side-on in an η^2-fashion. The examples are the azobenzene complexes $Cp_2Ti($*cis*-$N_2Ph_2)$,[16,26] $\{(p\text{-}tol)_3P\}_2Ni($*trans*-$N_2Ph_2)$,[18] and $(t\text{-}BuNC)_2Ni($*trans*-$N_2Ph_2)$[17] and the structure of $CpRe(CO)_2($*trans*-$N_2Ph_2)$ described here. Binuclear μ-η^2,η^2 structures such as that of $Fe_2(CO)_6\ (N_2Me_2)$[27,28] are also exhibited. The azobenzene ligand is also clearly side-on (η^2) coordinated in $Cp_2Mo(N_2Ph_2)$, as evidenced by NMR.[29]

Azobenzene is coordinated η^1 in the X-ray structure of $(Ph_2N_2)_2PdCl_2$,[30] as is azotoluene (azotol) in (4,4′-azotol)$AuCl_3$[31] and Me_2N_2 in $(\mu\text{-}Me_2N_2)Cu_2Cl_2$.[32] There is also spectroscopic evidence for end-on (η^1) coordination of disubstituted diazenes in other cases[33-35] since, for example, the nonequivalence in the metal complexes of protons that are symmetry related in the free ligand signifies η^1-coordination of the diazene ligand in $M(CO)_5L$ (M = Cr, Mo, W; L = benzo[*c*]cinnoline,[33] *cis*- or *trans*-diisopropyldiazene,[34b] *cis*- or *trans*-dimethyldiazene[34a]) and $ACr(CO)_2L$ (L = 2,3-diazabicyclo[2.2.1]hept-2-ene, A = substituted benzene).[35] In several of these η^1-disubstituted diazene complexes the NMR spectra are temperature dependent and indicate that the metal is undergoing nondissociative η^1–η^1 coordination site exchange or "shuttling"[33] between the nitrogen atoms.[33-35] In the case of the cyclic azo compounds benzo[*c*]cinnoline[33] and 2,3-diazabicyclo[2.2.1]hept-2-ene[35] the ring fusion fixes the geometry as cis. Interestingly, in the acyclic cases Ackermann[34] notes also that the *cis*-diisopropyldiazene complexes $M(CO)_5L$ (M = Cr, Mo, W) and the *cis*-dimethyldiazene complex $W(CO)_5(N_2Me_2)$ undergo site exchange, but the corresponding *trans*-dialkyldiazene complexes do not. Unfortunately, the corresponding azobenzene compounds $M(CO)_5(N_2Ph_2)$ appear not to have been examined. Nevertheless, this difference in properties for disubstituted *cis*- and *trans*-diazenes prompted Ackermann to propose that, in $M(CO)_5L$, the shuttling probably occurs by a movement of the $M(CO)_5$ group from one nitrogen lone pair to the other through an in-plane transition state where the metal orbital partly overlaps with both lone pairs, rather than through a π-complex. This is because such a transition state should be accessible (in the absence of ligand isomerism) only for a disubstituted *cis*-diazene complex, whereas a π-complex was considered to involve a geometry with the $M(CO)_5$ moiety out of the skeletal plane of the *cis*-diazene ligand, and as such might be expected to be equally accessible to both *cis*- and *trans*-diazene complexes.

The present study appears to be the first to demonstrate η^2-coordination of a disubstituted diazene in the solid state *together* with fluxional processes for the disubstituted diazene ligand in solution. There are several differences from the $M(CO)_5L$ system which lead us to believe that the mechanisms in the two cases may not be similar. First, we obtain the same product whether *cis*- or *trans*-azobenzene is used in the synthesis. Second, if our assignments are correct, we observe interconversion of η^1- and η^2-forms of the complex as well as coordination site exchange in the η^1-isomer.[36] A plausible deduction is that the site exchange takes place through the intermediacy of the η^2-structure, and that this structure in solution does not differ significantly from the one that we observe in the crystal structure. It is reasonably described as a π-complex, although, in our view, the twisting of the ends of the diazene about the NN bond that is evident from the large deviation of the dihedral angles in this and the other known η^2-complexes[16-18] from the value of 0 or 180° for rigorously planar trans or cis free azo ligands obscures the distinction between a σ,η^2-complex and a π,η^2-complex; the lone-pair orbitals are no longer coplanar, nor are the nitrogen p_π orbitals, with the result that the ReNN framework orbitals have contributions from both. Thirdly, the η^2-structure undergoes rapid inversion at each nitrogen. Therefore, it is understandable that the same equilibrium mixture is obtained whether *cis*- or *trans*-azobenzene is used in the synthesis since these isomers will rapidly interchange in the η^2-structure.[37] However, the scission of the metallocycle to give the η^1-form occurs only to yield a single ligand geometry which we assign to be η^1-*cis*-azobenzene on the basis of the X-ray structure of monosubstituted η^1-*cis*-diazenes[9] and the known preference for *cis*- rather than *trans*-dialkyldiazenes in the $M(CO)_5L$ complexes.[34] Note, however, that η^1-*trans*-diaryldiazenes were found in the structures of the two (uncrowded) square-planar complexes with $PdCl_2$ and $AuCl_3$.[30,31]

The η^2-bonded diazene structure has been shown by Albini and Kisch[38] to be a better π-acceptor than the η^1-form. So, an electron-withdrawing substituent on the phenyl ring in N_2Ph_2 that increases the π-acidity should, on this basis, increase the proportion of the η^2-isomer in the mixture of isomers for $CpRe(CO)_2(N_2R_2)$, and the converse should be true for an electron-donating group. The IR and NMR spectra of the complexes $CpRe(CO)_2\{N_2(C_6H_4F\text{-}p)_2\}$ (**2**) and $CpRe(CO)_2\{N_2(C_6H_4Me\text{-}p)_2\}$ (**3**) are entirely in accord with this idea, and fit exactly with our already proposed assignments of the bands in the spectra to the η^1- and η^2-isomers for $CpRe(CO)_2(N_2Ph_2)$ (**1**). For example, as Figure 2 shows, the IR spectrum of **2** exhibits a relative increase in the higher

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(37) Otsuka et al. report[19] that *cis*-azobenzene is catalytically isomerized to the trans form in the presence of Cp_2MoH_2. From the reaction $Cp_2Mo(\eta^2\text{-}N_2Ph_2)$ can be isolated, so this isomerization may also proceed by rapid inversion in the η^2-complex.

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wavenumber pair of ν(CO) absorptions, whereas in the IR spectrum of **3** the intensity of this pair has been reduced almost to zero. This lends further support to the notion that this upper pair of ν(CO) absorptions belongs to the η^2-isomer. The correctness of this assignment is, of course, crucial to the arguments presented in this paper. There is no evidence that it should be otherwise and considerable evidence in its favor.

Conclusions

It has been demonstrated that the azobenzene ligand is bound in the η^2-form (**1a**) in the crystal structure of $CpRe(CO)_2(N_2Ph_2)$ (**1**). In solution, IR and NMR spectroscopic data have been interpreted as evidence for both η^2- (**1a**) and η^1-coordinated (**1b**) azobenzene complexes in equilibrium, with the η^1-form undergoing coordination site shift, probably via the same η^2-form that is observed in the crystal structure, and with the η^2-form undergoing further fluxional behavior, which is likely to be inversion at each nitrogen atom. This appears to be the first demonstration of a η^1–η^2 coordination shift in diazene chemistry.

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Supplementary Material Available: Anisotropic thermal parameters (Table S1), calculated hydrogen atom coordinates (Table S2), calculated mean planes and dihedral angles (Table S3), and $^{13}C\{^1H\}$NMR spectra of **1** at 221 K (Figure 4c) and 200 K (Figure 4d) (6 pages); calculated and observed structure factors (Table S4) (8 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Materials Science Center,
Cornell University, Ithaca, New York 14853

Tin Sulfide, $(Te_2)_2I_2$, and Related Compounds: Symmetry-Controlled Deformations in Solid-State Materials

Wolfgang Tremel[1] and Roald Hoffmann*

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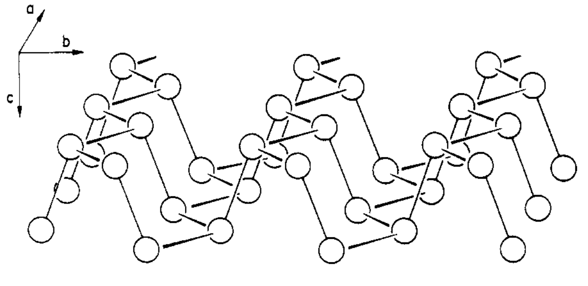
The layered compound SnS normally adopts the GeS structure but is also observed to undergo a second-order phase transition to the more symmetric TlI structure close to the melting point. GeS and TlI, however, prefer the distorted low-temperature or the undistorted high-temperature structure, respectively, at ambient pressure. The band structures for both SnS modifications are constructed, and in a 2-dimensional picture the distortion can be traced to a mixing of the conduction band into the valence band, similar to a second-order Jahn–Teller distortion. The band gap (or the relative electronegativities) determines whether the distortion occurs. The derived picture can be used to analyze the electronic structure of related compounds, such as $(Te_2)_2I_2$, InS, or HgCl.

The solid-state structures of 10-electron (per two atoms) compounds can be related to the rock salt structure by a successive bond-breaking process. Burdett and McLarnan[2] have given an enumeration of the resulting structures. While the As[3] or GeTe[4] structure types arise from a rhombohedral distortion, a quasi-tetragonal distortion leads to the structure of black P[5] or GeS[6] (**1**). This deformation transforms six "bonds" in the NaCl structure into three bonds in the GeS structure. Both Ge and S atoms have three neighbors at somewhat shorter (2.7 Å) and longer (3.3 Å) distances, so that GeS could be viewed as a distorted rock salt structure. Actually phosphorus is known to transform under high pressure to a rock salt modification.[7]



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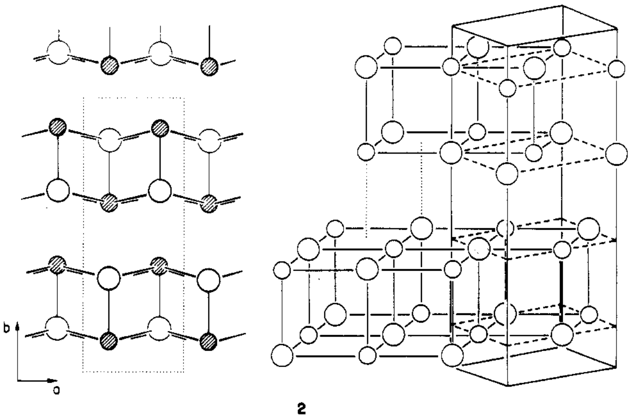
In and Tl halides are isoelectronic with group IV (group 14[40]) chalcogenides, although their structure looks different.[8] It can be built up, however, by stacking double layers from the NaCl structure, where consecutive layers are shifted due to the stereochemically active electron lone pairs. This is depicted schematically in **2**. Every atom has 1 + 4 neighbors making up a distorted octahedron with one unoccupied position. There is a little buckling of alternate pairs of atoms in one direction, so that the cations project out of the layer. Interestingly enough SnS and SnSe were found to undergo a structural transformation from the GeS to the TlI type, as shown in **3**. The phase transition takes place just below the melting point, and it is a second-order transition.[9]



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[1] DAAD/NATO Postdoctoral Fellow 1984–1985, DFG Fellow 1985–1986. Present address: Anorganisch-Chemisches Institut der Universität Münster, D4400 Münster, Federal Republic of Germany.

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