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Spectroscopic and Crystallographic Characterization of (σ^2-terpyridyl)Re(CO)$_3$Cl. 2D-NMR Evidence for a Linkage Isomerization Reaction

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Introduction

2,2′:6′,2″-Terpyridine (terpy) is a heterocyclic nitrogen ligand which generally binds metals in a tridentate fashion with *mer* stereochemistry.[1] If a *mer* coordination geometry is not available, the terpy ligand may presumably bind in a bidentate fashion, leaving one of the outer pyridyl rings uncoordinated. Several examples of this mode of coordination have been proposed on the basis of empirical formulas and molecular conductivities[2,3] or substitution kinetics.[4] Other studies have inferred a bidentate binding mode from spectroscopic data, including IR,[5] optical absorbance,[6] fluorescence,[7] or from NMR spectra.[8,9] Only two examples of crystallographically defined complexes of neutral[10] bidentate terpy have been reported.[11,12] It is of interest to spectroscopically characterize an authentic bidentate terpy since such species have been postulated to be important in thermal reaction pathways[6] and as the products of photolysis of tridentate terpy complexes.[8b] We were attracted to (terpy)Re(CO)$_3$Cl since most structurally characterized complexes of the Re^I(CO)$_3$ moiety are facial isomers,[13] and terpy should not bind as a tridentate ligand. (L$_2$)Re(CO)$_3$Cl (L$_2$ is a bidentate ligand) complexes are especially convenient for such studies since they are generally quite thermally stable and contain no other organic ligands. The crystal structure of (σ^2-terpy)Re(CO)$_3$Cl·H$_2$O has recently appeared[12] and confirms the bidentate coordination of terpy. We have been able to obtain crystals of the anhydrous complex and report here the X-ray crystal structure of (σ^2-terpy)Re(CO)$_3$Cl and its characterization by NMR techniques. The complete ^{1}H NMR spectrum has been assigned using a combination of NMR techniques, and the rate of a surprisingly fast ligand-exchange process involving the uncoordinated pyridyl ring has been measured using EXSY spectroscopy.

Experimental Section

Synthesis. (σ^2-terpyridyl)Re(CO)$_3$Cl was synthesized by modification of literature methods.[15,16] Re(CO)$_5$Cl (Pressure Chemical Co.) was heated at reflux with 1 molar equiv of terpyridine (Aldrich) in isooctane for approximately 1 h. The complex was formed in essentially quantitative yield and was filtered from the cooled mixture as a yellow solid. Crystals suitable for X-ray structure determination were obtained by slow evaporation of a 1:1:1 acetonitrile:ether:toluene solution of the complex. Anal. Calcd for C$_{18}$H$_{11}$ClN$_3$O$_3$Re: C, 40.11; H, 2.06; N, 7.80. Found: C, 40.08; H, 2.04; N, 7.81. Other properties (i.e., IR, optical absorbance, and electrochemistry) agree with the values previously reported.[12,16] (bpy)Re(CO)$_3$Cl (bpy is 2,2′-bipyridine) was obtained by an analogous procedure.

[(terpy)$_2$Fe](PF$_6$)$_2$ was synthesized by adding a slight excess of terpyridine to a solution of ferrous chloride in water followed by an excess of aqueous NH$_4$PF$_6$. The crude product was filtered from the mixture and recrystallized by slow addition of an acetonitrile solution of the product to stirred ether.

Spectroscopy. ^{1}H NMR spectra were obtained in CD$_3$CN on a Bruker AM-500 (500 MHz) FT-NMR spectrometer. All spectra were obtained in aerated solutions at room temperature. 1D spectra were obtained with resolutions of no greater than 0.213 Hz/point. Standard pulse sequences[17] were used for COSY and NOESY(EXSY) data collection. The COSY spectrum of (σ^2-terpy)Re(CO)$_3$Cl was acquired in absolute magnitude mode using a 45° pulse after the incremental delay. The data consisted of 128 256W FID's of 32 scans over a sweep width of 850 Hz with a recycle delay of 4.0 s. Data were processed in each dimension with sine-bell apodization, zero-filled to 512W × 512W prior to Fourier transformation, phased by absolute magnitude calculation, and symmetrized. The NOESY(EXSY) spectra were acquired in the phase-sensitive TPPI mode; 128 512W FID's of 48 scans over a sweep width of 850 Hz with a recycle delay of 3.5 s were collected. Data were processed in each dimension with 90°-shifted sine-bell apodization and zero-filled to 512W × 512W prior to Fourier transformation and phase correction. EXSY peak intensities were determined by integration using routines supplied by Bruker. The integrated intensities were used to determine the exchange rate constant and variance as described in the discussion using the program MATW4 which performs mathematical functions on general real and complex matrices.[18]

X-ray Structure Determination. A suitable single crystal of (σ^2-terpy)Re(CO)$_3$Cl was obtained as described above. The space group ($P\bar{1}$) and preliminary cell dimensions were obtained from precession photography. A single crystal was mounted on an Enraf-Nonius CAD-4 diffractometer, and final cell parameters were obtained by least-squares refinement of the angular settings of 24 strong reflections in the 2θ range $23.9^\circ \le 2\theta \le 29.3^\circ$. Applying θ-2θ scan techniques with Mo Kα radiation, 2255 intensity data $(+h, \pm k, \pm l)$ were collected at 25 °C.[19] Cell parameters and other crystallographic data are summarized in Table I. The raw intensity data were converted into structure factor amplitudes and their corresponding estimated structure deviations by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the list of intensity standards showed no significant decomposition during data collection, and hence no decay correction was applied. An

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(10) The structure of a monoprotonated bidentate terpy complex has recently appeared.[3]

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(13) A search of the Cambridge Structural Database[14] for complexes of the {Re(CO)$_3$} moiety yielded 83 matches, only two of which were not facial isomers. (a) *mer*-Re(CO)$_3$Cl(PEt$_3$)$_2$: Bucknor, S.; Cotton, F. A.; Falvello, L. R.; Reid, A. H., Jr.; Schmulbach, C. D. *Inorg. Chem.* **1986**, *25*, 1021. (b) [Re(CO)$_3$(PPh$_3$)]$_2$(μ-I)(μ-GaI$_2$) (formally a Re(0) complex): Haupt, H.-J.; Balsaa, P.; Flörke, U. *Z. Anorg. Allg. Chem.* **1988**, *557*, 69.

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(17) See, for example: Bovey, F. A.; Jelinski, L.; Mirau, P. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic: New York, 1988.

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Table I. Crystal Data and Intensity Collection

empirical formula	$C_{18}H_{11}ClN_3O_3Re$	μ(Mo Kα) (cm^{-1})	72.6
		radiation	Mo Kα (λ = 0.7107 Å)
fw	538.96		
cryst dimens (mm)	0.23 × 0.28 × 0.33	reflns measd	$+h,\pm k,\pm l$
		scan speed (deg/min)	0.74–6.67
cell params			
a (Å)	7.401 (1)	scan method	θ–2θ
b (Å)	8.280 (2)	2θ limits (deg)	3.0–45.0
c (Å)	14.464 (4)	no. of unique data	2255
α (deg)	80.69 (2)	no. of data for $(F_o)^2 > 3\sigma((F_o)^2)$	2204
β (deg)	86.35 (2)		
γ (deg)	84.09 (2)	no. of variables	236
V (Å^3)	869.1 (3)	R	0.018
space group	$P\bar{1}$ (No. 2)	R_w	0.026
Z	2	goodness of fit	1.61
d_{calc} (g/mL)	2.06		
d_{obs} (g/mL)	1.93[a]		

[a] Measured by flotation in bromoform/toluene mixtures.

absorption correction was made using ψ-scan data.[20] The structure was solved by standard heavy-atom procedures and refined by full-matrix least-squares methods. A difference Fourier map calculated after anisotropic refinement of all non-hydrogen atoms revealed the positions of all hydrogen atoms. The terpyridine hydrogens were introduced at fixed positions (C–H distance = 0.95 Å) for inclusion in the structure factor calculation. Analysis of F_o and F_c values indicated that a secondary extinction correction was necessary and that four reflections should be rejected. Full-matrix least-squares refinement with 236 variables, using 2200 reflections, led to convergence with R = 0.018, R_w = 0.026. Supplemental Tables S1 and S2 list complete bond distances and angles for (σ^2-terpy)Re(CO)$_3$Cl.

Results and Discussion

Molecular Structure. The crystallographically determined structure of (σ^2-terpy)Re(CO)$_3$Cl is shown in Figure 1. In each unit cell there are two molecules of the complex which are symmetry-related to each other by an inversion center. The molecule as shown in Figure 1 is chiral, and the other molecule in the unit cell is its enantiomeric isomer. Thus, the crystal is a racemic mixture of the two enantiomers.

The structure of (σ^2-terpy)Re(CO)$_3$Cl is nearly the same as that of the previously reported hydrate.[12] Based on the bond angles, the coordination geometry of the rhenium atom is essentially a distorted octahedron and one pyridyl ring of the terpy ligand is not coordinated to the metal. This arrangement is no doubt due to the fact that terpy can only assume a *mer* stereochemistry if it coordinates as a tridentate ligand. Only one crystallographically defined *mer*-Re^I(CO)$_3$ complex has been reported,[13a] and in general the Re^I(CO)$_3$ unit appears to have a strong preference for a facial geometry. It is also important to note that the uncoordinated pyridyl ring interacts sterically with a carbonyl group and thus cannot assume an orientation coplanar with the other two rings. The N(2)–C(10)–C(11)–N(3) torsional angle is −130.0 (3)°. In the crystal structure of the hydrate of (σ^2-terpy)Re(CO)$_3$Cl,[12] the corresponding torsional angle is only −114.9°. The difference can be ascribed to interaction of the uncoordinated nitrogen atom with water in the hydrated crystal.[12]

The steric interactions in (σ^2-terpy)Re(CO)$_3$Cl lead to significant distortions of the bond lengths and angles relative to those typically found for tridentate terpy complexes. A survey of published structures for σ^3-terpy complexes[21] indicates that the M–N distance for the central pyridyl ring is on average 0.10 Å shorter than the M–N distances to the outer pyridyl rings. In contrast, for (σ^2-terpy)Re(CO)$_3$Cl the steric bulk of the uncoordinated pyridyl (which is effectively a substituent to the central pyridyl) prevents such a close approach and the Re–N(2) distance is 0.077 Å longer than the Re–N(1) distance. The steric bulk of the uncoordinated pyridyl ring is also manifested in the N(2)–Re–C(18) angle (102.6°), which is the largest angle between any two cis ligands in the complex. Very similar distortions are apparent in the crystal structures of (σ^2-terpy)Ru(CO)$_2$Br$_2$[11] and (σ^2-terpy)Re(CO)$_3$Cl·H$_2$O[12] (and in the monoprotonated terpy complex [(σ^2-terpyH)Ru(CO)$_2$(phen)](BF$_4$)$_3$[3]). These distortions thus appear to be an intrinsic structural feature of σ^2-terpy.

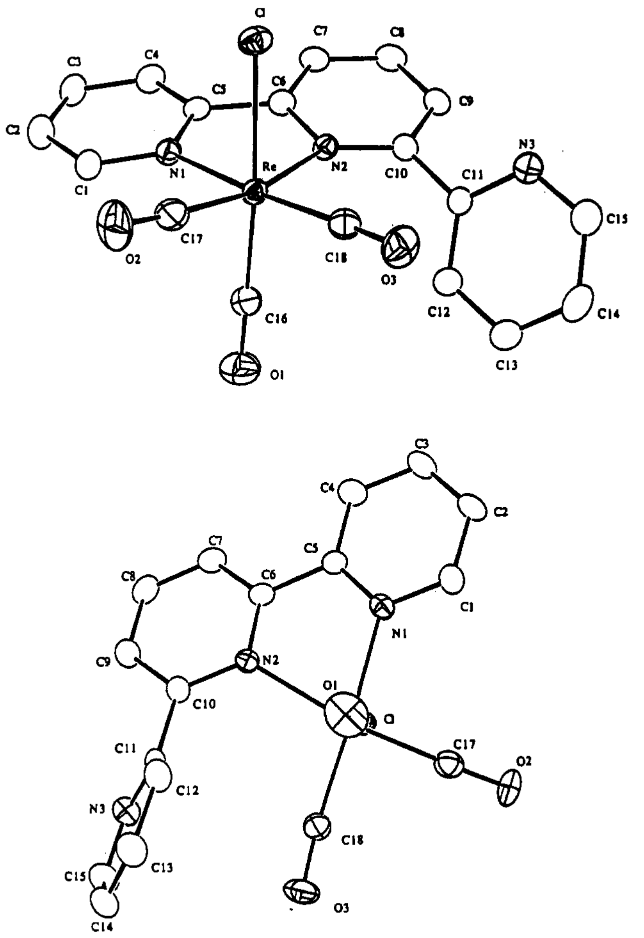

Figure 1. Two views of the molecular structure of (σ^2-terpy)Re(CO)$_3$Cl. The lower view illustrates the non-coplanarity of the coordinated and uncoordinated pyridyl rings. Selected bond distances (Å) and angles (deg): Re–N(1) = 2151 (3), Re–N(2) = 2.228 (3), Re–Cl = 2.493 (1); N(1)–Re–(N2) = 74.3 (1), N(1)–Re–C(17) = 96.8 (1), N(2)–Re–C(18) = 102.6 (1), Cl–Re–N(1) = 82.68 (8), Cl–Re–N(2) = 82.0 (8), Cl–Re–C(16) = 154.7 (1), N(1)–C(5)–C(6)–N(2) = 6.9 (4), N(2)–C(10)–C(11)–N(3) = 130.0 (3).

NMR Spectroscopy. 1D Spectrum. In Figure 2 are compared ^{1}H NMR spectra of (bpy)Re(CO)$_3$Cl, (σ^2-terpy)Re(CO)$_3$Cl, and [Fe(terpy)$_2$]$^{2+}$. In each compound the only protons present are those of the polypyridyl ligand. For both [Fe(terpy)$_2$]$^{2+}$ and (bpy)Re(CO)$_3$Cl, the spectra indicate a 2-fold magnetic symmetry. The [Fe(terpy)$_2$]$^{2+}$ spectrum shows the magnetic equivalence of the two outer pyridyl rings, and the assignment shown in Table II is that given in previous studies.[22] These spectra may be contrasted with that of (σ^2-terpy)Re(CO)$_3$Cl in which the magnetic symmetry has clearly been lowered, as is expected on the basis of the solid-state structure of the complex. In fact, no two protons in the σ^2-terpy ligand need be magnetically equivalent although some near degeneracies are manifested as doublets of doublets. Since all the resonances occur in a narrow range of chemical shifts and since the coupling constants are very similar,

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(20) Reflections used for the azimuthal (ψ) scans were located near χ = 90°, and the intensities were measured at 10° increments of rotation of the crystal about the diffraction vector.

(21) A Cambridge Structural Database[14] search of tridentate terpy complexes gave 102 matches. The reported M–N(outer) distances ranged from 1.917 to 2.321 Å (mean = 2.083 ± 0.082 Å), and M–N(inner) distances ranged from 1.810 to 2.271 Å (mean = 1.976 ± 0.085 Å).

(22) Elsbernd, H.; Beattie, J. K. *J. Inorg. Nucl. Chem.* **1972**, *34*, 771.

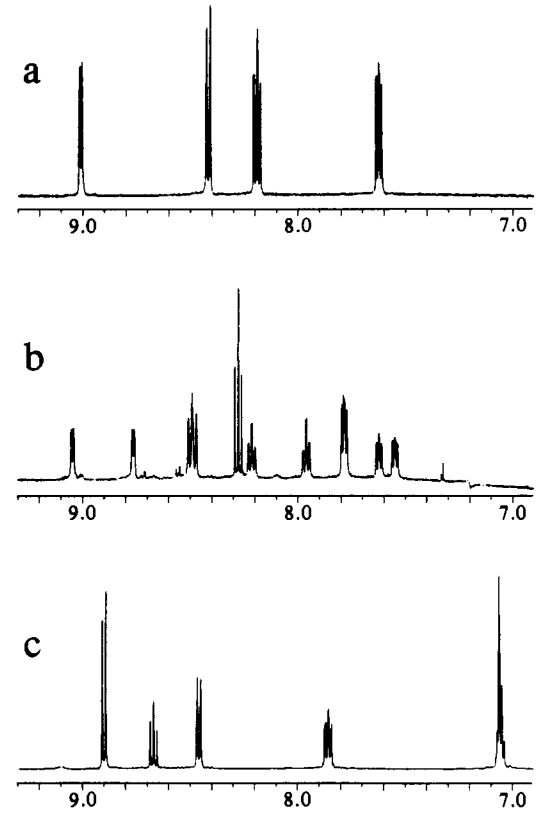


Figure 2. ^{1}H NMR spectra of (a) (bpy)Re(CO)$_3$Cl, (b) (σ^2-terpy)Re(CO)$_3$Cl, and (c) [(terpy)$_2$Fe]PF$_6$. Chemical shifts are in ppm and are referenced to the solvent (CD$_3$CN, δ = 1.93 ppm).

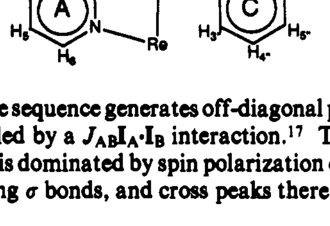
Table II. Proton Chemical Shifts[a]

^{1}H position[b]	$[(terpy)_2Fe]^{2+}$ [c]	(σ^2-terpy)Re(CO)$_3$Cl	(bpy)Re(CO)$_3$Cl
6	7.065	9.045	9.008
5	7.049	7.621	7.622
4	7.856	8.213	8.188
3	8.458	8.479	8.415
3′	8.899	8.500	8.415
4′	8.668	8.276	8.188
5′	8.899	7.788	7.622
6′			9.008
3″	8.458	7.779	
4″	7.856	7.959	
5″	7.049	7.547	
6″	7.065	8.763	

[a] Values are in ppm and are referenced to the solvent (CD$_3$CN, δ = 1.930 ppm). [b] See text for numbering scheme. [c] as PF$_6^-$ salt.

an unambiguous assignment based only on the 1D spectrum in Figure 2 is not possible. It is apparent, however, that one hallmark of bidentate coordination of terpy is the distinct absence of symmetry in the NMR spectrum.

COSY Spectrum. In order to assign the spectrum of (σ^2-terpy)Re(CO)$_3$Cl, 2D-NMR techniques were employed. It will be convenient for the discussion to refer to the ring labeling scheme shown as follows:



The COSY pulse sequence generates off-diagonal peaks for nuclei which are coupled by a $J_{AB}I_A \cdot I_B$ interaction.[17] The mechanism of this coupling is dominated by spin polarization of the electrons in the intervening σ bonds, and cross peaks therefore arise from protons coupled through bonds. In the COSY spectrum of (σ^2-terpy)Re(CO)$_3$Cl (Figure 3), the underlying structure of the 1D spectrum is revealed. The COSY spectrum permits clear identification of the resonances associated with each pyridyl ring, made possible by the presence of strong cross-ring J coupling. Three separate spin systems can be observed in Figure 3. Two contain four spins (rings A and C) and one contains three spins (ring B). The doublets at 9.045 and 8.763 ppm (H$_6$ and H$_{6''}$) are each coupled to three other protons. On the basis of the coupling patterns, the proton at 9.045 ppm and those to which it is coupled in the COSY spectrum (8.479, 8.213, 7.621 ppm) are associated with either ring A or ring C. The peak at 8.763 ppm and its associated protons (7.959, 7.779, 7.547 ppm) belong to the other outer ring, and the peaks at 8.500, 8.276, and 7.788 ppm are associated with the central pyridyl ring (B).

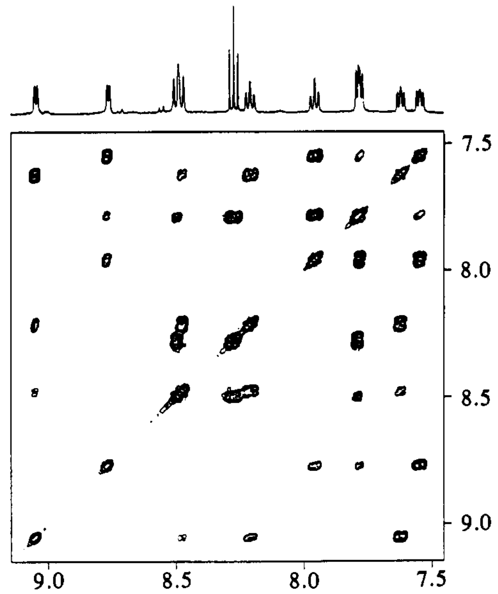


Figure 3. COSY spectrum of (σ^2-terpy)Re(CO)$_3$Cl. Acquisition and data processing parameters are given in the Experimental Section.

Further assignment of the spectrum can be made by comparison of the COSY spectrum with the 1D spectrum of (bpy)Re(CO)$_3$Cl as follows. The peak from ring B at 8.276 ppm appears as a pure triplet with no long-range coupling and is assigned as H$_{4'}$. This assignment is further supported by the similarity in chemical shifts with H$_4$ of (bpy)Re(CO)$_3$Cl and with H$_{4'}$ of $[Fe(terpy)_2]^{2+}$.[22] The peaks at 8.500 and 7.788 ppm must correspond to H$_{3'}$ and H$_{5'}$ protons. In the 1D spectrum they appear as multiplets due to overlap with resonances from other rings, but in the COSY spectrum they are clearly revealed to be doublets. The structure of (σ^2-terpy)Re(CO)$_3$Cl suggests that the magnetic environment of H$_{3'}$ is similar to that of H$_3$ in $[Fe(terpy)_2]^{2+}$, which appears at 8.415 ppm, while H$_{5'}$ should be similar to H$_5$ in the bpy complex (7.622 ppm). Thus the resonances at 8.500 and 7.788 ppm in (σ^2-terpy)Re(CO)$_3$Cl correspond to the H$_{3'}$ and H$_{5'}$ protons, respectively.

The coordinated pyridyl ring (A) of (σ^2-terpy)Re(CO)$_3$Cl should exhibit chemical shifts similar to those in (bpy)Re(CO)$_3$Cl. A comparison shows that the set of resonances at 9.045, 8.479, 8.213, and 7.621 ppm most closely match the chemical shifts in (bpy)Re(CO)$_3$Cl. This set is thus assigned to the coordinated ring (H$_3$–H$_6$), and the various positions are assigned by analogy with (bpy)Re(CO)$_3$Cl as given in Table II. This assignment is further supported by the NOESY spectrum as described below. For the remaining four resonances, direct comparisons with (bpy)Re(CO)$_3$Cl or $[Fe(terpy)_2]^{2+}$ are less revealing. Although these peaks must be assigned to the uncoordinated pyridyl ring, the COSY spectrum does not resolve the ambiguities in the detailed assignment of the resonances.

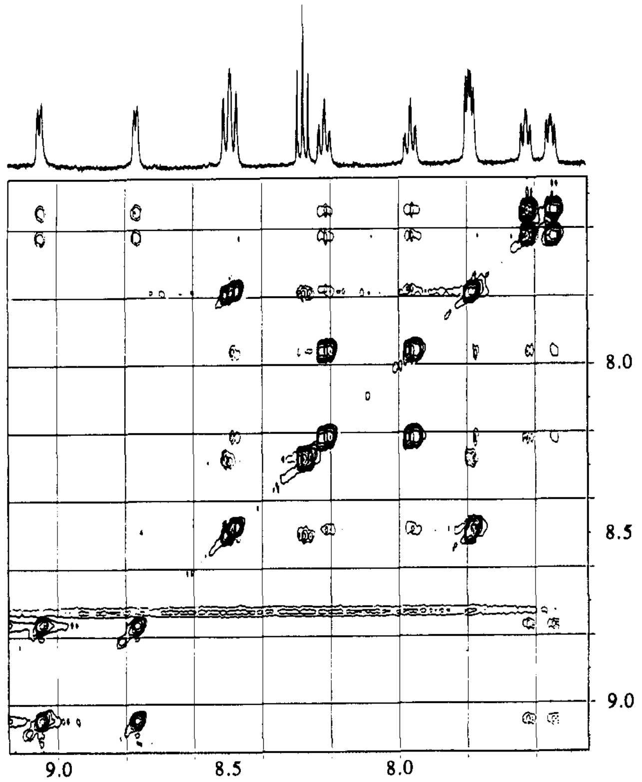


Figure 4. NOESY(EXSY) spectrum of (σ^2-terpy)Re(CO)$_3$Cl with τ_m = 3.0 s. Darker lines indicate peaks of the same phase as the diagonal and represent chemically exchanging resonances, while the lighter lines indicate peaks of the opposite phase and represent NOE interactions.

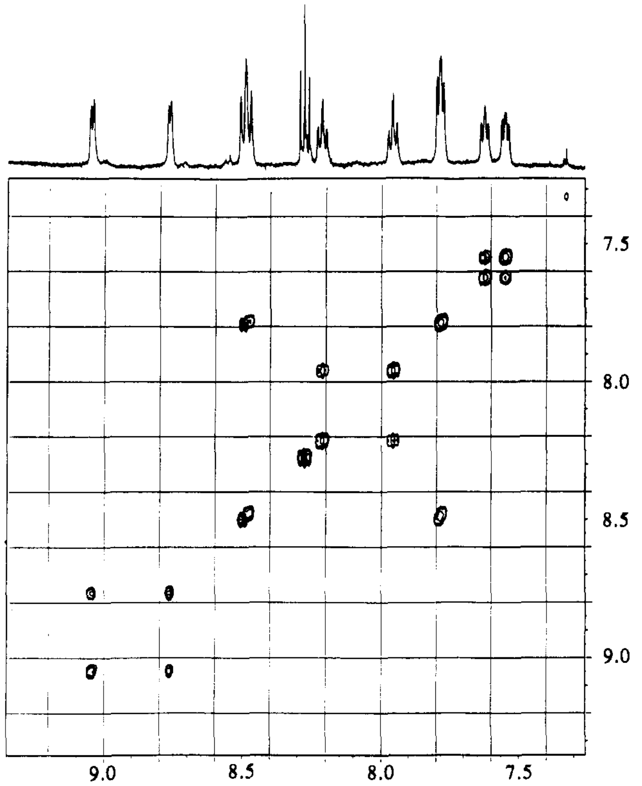
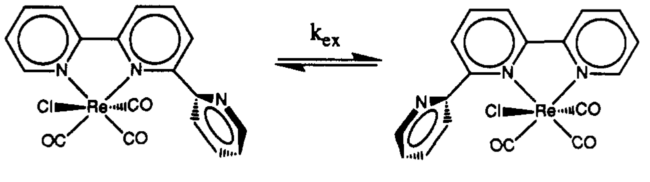


Figure 5. NOESY(EXSY) spectrum of (σ^2-terpy)Re(CO)$_3$Cl with τ_m = 0.4 s. All peaks are of the same phase as the diagonal.

NOESY Spectrum. The NOESY spectrum of (σ^2-terpy)Re(CO)$_3$Cl was obtained in order to assign the resonances of the uncoordinated ring. The phase-sensitive NOESY pulse sequence generates off-diagonal cross peaks between nuclei that are coupled through space by a dipole–dipole (NOE) interaction or by chemical exchange.[17] Since rings A and B are coplanar and rings B and C are not, a dipole–dipole interaction between H_3 and $H_{3'}$ should lead to a cross peak while the H_5–$H_{3''}$ cross peak should be much smaller or absent. It is important to note that, for small- to medium-sized molecules with short correlation times, these NOE cross peaks are of opposite phase to that of the diagonal peaks. The NOESY spectrum obtained using a mixing time of 3.00 s, shown in Figure 4, was quite unexpected. While there is evidence for an NOE interaction between H_3 and $H_{3'}$, there was also unmistakable evidence for chemical exchange between the A and C rings. Cross peaks of the same phase as the diagonal are observed for protons which are chemically exchanging on the time scale of the experiment, defined by the mixing time, τ_m. These exchange interactions constitute the EXSY spectrum.[23] By use of a shorter mixing time, the NOE cross peaks were suppressed and the exchange cross peaks could be observed unobscured as shown in Figure 5. The cross peaks in Figure 5 correlate the spins between the A and C rings (H_6–$H_{6''}$, H_5–$H_{5''}$, etc.). The $H_{3'}$ and $H_{5'}$ spins are clearly chemically exchanging as well. From the pattern of NOE and EXSY peaks, the remaining ambiguities in the assignment of the spectrum can be resolved.

The patterns of cross peaks in Figures 4 and 5 establish the nature of the chemical exchange as the intramolecular isomerization



This assignment is also supported by recently published results on the temperature dependence of the 1D spectrum of the closely related complex (σ^2-terpy)Re(CO)$_3$Br.[9] Thus, H_6 shows an EXSY peak with $H_{6''}$, confirming $H_{6''}$ as the resonance at 8.763 ppm. At the longer mixing time H_6 shows NOE peaks with both H_5 and $H_{5''}$. This last peak is a consequence of the combined effect of chemical exchange of H_6 and $H_{6''}$ and the NOE interaction of $H_{6''}$ with $H_{5''}$. The NOESY(EXSY) spectra also confirm the assignment of H_5 and establish $H_{5''}$ as the peak at 7.547 ppm. It is also clear that H_5 and $H_{5''}$ are exchanging. H_5 gives EXSY peaks with $H_{5''}$ and NOE peaks with H_4, H_6, $H_{4''}$, and $H_{6''}$. Therefore the resonance at 7.959 ppm is assigned as $H_{4''}$. Similar considerations lead to the assignment of $H_{3''}$ (7.779 ppm). Thus, through a combination of COSY, NOESY, and EXSY spectroscopies, the complete assignment of the ^{1}H NMR spectrum of (σ^2-terpy)Re(CO)$_3$Cl is established as given in Table II.

The values of the chemical shifts and coupling constants are fully consistent with the observed solid-state structure. Of particular note is the significant downfield shifting of the resonances of the bound rings relative to the unbound pyridyl ring. This is most reasonably attributed to anisotropic effects associated with both coordination to the metal and to π ring currents in the pyridyl and CO ligands. The downfield shift of H_6 is very likely to be the result of its proximity to the adjacent CO, which has a strong deshielding effect. Similarly, H_3 and $H_{3'}$ are expected to be downfield from the corresponding position in free pyridine because they are forced to reside in the plane of a nearby pyridine ring and are thus subject to deshielding effects.

Exchange Kinetics. The EXSY peaks in Figures 4 and 5 provide clear evidence for the chemical exchange process given in the scheme above. The relative intensities of the cross peaks and the diagonals are related to the rate of exchange and the mixing time

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[23] (a) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546. (b) Macura, S.; Ernst, R. R. *Mol. Phys.* **1980**, *41*, 95. (c) Mendz, G. L.; Robinson, G.; Kuchel, P. W. *J. Am. Chem. Soc.* **1986**, *108*, 169. (d) Abel, E. W.; Coston, T. P. J.; Orrell, K. G.; Sik, V.; Stephenson, D. *J. Magn. Reson.* **1986**, *70*, 34.

as shown in the equation[23]

$$\mathbf{I} = \mathbf{P} \exp(-\mathbf{L}\tau_m)$$

In the equation, **I** is the matrix of EXSY peak intensities, **P** is the population vector for each site, **L** is the kinetic matrix which contains the exchange and relaxation rates, and τ_m is the mixing time. For the specific case of two intramolecularly exchanging sites, A and B (for example, $H_{3'}$ and $H_{5'}$), the equation can be explicitly written as

$$\begin{pmatrix} I_{AA} & I_{AB} \\ I_{BA} & I_{BB} \end{pmatrix} = \begin{pmatrix} n_A \\ n_B \end{pmatrix} \exp\left[\begin{pmatrix} -R_A - k_{AB} & k_{AB} \\ k_{BA} & -R_B - k_{BA} \end{pmatrix} \tau_m\right]$$

where I_{AA} and I_{BB} are the integrated intensities of the diagonal peaks for sites A and B, respectively, I_{AB} and I_{BA} are the integrated intensities of the cross peaks, n_A and n_B are the mole fractions of the sites, R_A and R_B represent rate constants for spin–lattice relaxation ($1/T_1$), and k_{AB} and k_{BA} represent the exchange rate constants in the forward and reverse directions. By performing the EXSY experiment using an appropriate mixing time, it is possible to calculate the elements of the kinetic matrix and, thus, the exchange rate. The results of such a calculation on (σ^2-terpy)Re(CO)$_3$Cl indicate that $k_{ex} = 1.72 \pm 0.06$ s^{-1} at 298 K.[24,25] From the Eyring equation (assuming a transmission coefficient of 1.0), ΔG^* for the exchange reaction is estimated to be 71.6 ± 0.09 kJ mol^{-1}.

This is a rather surprising result. Re(I) is a low-spin d^6 third-row transition metal ion and is expected to be quite substitutionally inert. This lack of reactivity is evident in the substitution chemistry of other (diimine)Re(CO)$_3$Cl complexes in which ligand substitution reactions tend to displace Cl$^-$ rather than the diimine and long reaction times at high temperatures are generally required.[26] Thus, the exchange reaction represents a novel reactivity mode for Re(I). The origin of the significant rate of this reaction at room temperature is not clear, but an associative interchange (I$_a$) mechanism seems reasonable on the basis of the fact that the diimine ligand does not dissociate readily. A recently published study[9] of the temperature dependence of the ^{1}H NMR spectrum of (terpy)Re(CO)$_3$Br revealed line broadening and coalescence with $\Delta G^* = 71.6 \pm 0.3$ kJ mol^{-1} for the analogous exchange reaction. This activation barrier is identical to that determined for (σ^2-terpy)Re(CO)$_3$Cl and indicates that the exchange process is insensitive to moderate variations in the electronic structure of the complex.

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Supplementary Material Available: Tables of bond distances (Table S1), bond angles (Table S2), torsional angles (Table S3), positional parameters and esd's (Table S4), general temperature factor expressions (Table S5), and root-mean-square amplitudes (Table S6) for (σ^2-terpy)Re(CO)$_3$Cl and tables of ^{1}H–^{1}H coupling constants for (σ^2-terpy)Re(CO)$_3$Cl (Table S7), (bpy)Re(CO)$_3$Cl (Table S8), and [(terpy)$_2$Fe]PF$_6$ (Table S9) (7 pages). Ordering information is given on any current masthead page.

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(24) The value of k_{ex} was essentially independent of which exchanging pair was used. The $H_{3'}/H_{5'}$ exchange system was used for the rate determination, since these protons have the shortest relaxation time ($T_1 \approx 2.5$ s) and give the most accurate values. The reported value of k_{ex} is the weighted average of the values determined at three different mixing times, $\tau_m = 0.4$, 0.5, and 0.7 s.

(25) The variance was calculated from the signal-to-noise ratio: Kuchel, P. W.; Bulliman, B. T.; Chapman, B. E.; Mendz, G. L. *J. Magn. Reson.* **1988**, *76*, 136.

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