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Several Novel N-Donor Tridentate Ligands Formed in Chemical Studies of New *fac*-$Re(CO)_3$ Complexes Relevant to *fac*-$^{99m}Tc(CO)_3$ Radiopharmaceuticals: Attack of a Terminal Amine on Coordinated Acetonitrile

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To evaluate syntheses of *fac*-$[Re(CO)_3L]^+$ complexes in organic solvents, we treated *fac*-$[Re(CO)_3(CH_3CN)_3]PF_6$/BF_4 in acetonitrile with triamine ligands (L). When L had two primary or two tertiary terminal amine groups, the expected *fac*-$[Re(CO)_3L]^+$ complexes formed. In contrast, *N,N*-dimethyldiethylenetriamine (*N,N*-Me_2dien) formed an unusual compound, *fac*-$[Re(CO)_3(DAE)]BF_4$ {DAE = (*Z*)-*N*′-(2-(2-(dimethylamino)ethylamino)ethyl)acetimidamide = $(Me_2NCH_2CH_2)NH(CH_2CH_2N{=}C(NH_2)Me)$}. DAE is formed by addition of acetonitrile to the *N,N*-Me_2dien terminal primary amine, converting this sp^3 nitrogen to an sp^2 nitrogen with a double bond to the original acetonitrile sp carbon. The three Ns bound to Re derive from *N,N*-Me_2dien. The pathway to *fac*-$[Re(CO)_3(DAE)]BF_4$ is suggested by a second unusual compound, *fac*-$[Re(CO)_3(MAE)]PF_6$ {MAE = *N*-methyl-*N*-(2-(methyl-(2-(methylamino)ethyl)-amino)ethyl)acetimidamide = MeN(H)—CH_2CH_2—N(Me)—CH_2CH_2—N(Me)—C(Me)=NH}, isolated after treating *fac*-$[Re(CO)_3(CH_3CN)_3]PF_6$ with *N,N*′*,N*″-trimethyldiethylenetriamine (*N,N*′*,N*″-Me_3dien). MAE chelates via a terminal and a central sp^3 N from *N,N*′*,N*″-Me_3dien and via one sp^2 NH in a C(Me)=NH group. This group is derived from acetonitrile by addition of the other *N,N*′*,N*″-Me_3dien terminal amine to the nitrile carbon. This addition creates an endocyclic NMe group within a seven-membered chelate ring. The structure and other properties of *fac*-$[Re(CO)_3(MAE)]PF_6$ allow us to propose a reaction scheme for the formation of the unprecedented DAE ligand. The new compounds advance our understanding of the spectral and structural properties of Re analogues of ^{99m}Tc radiopharmaceuticals.

Introduction

Radiopharmaceuticals containing the *fac*-$\{^{99m}Tc^I(CO)_3\}^+$ core hold promise for the development of new clinically useful imaging agents, *fac*-$[^{99m}Tc^I(CO)_3L]^n$ (L is a facially coordinated tridentate ligand).[1,2] The development of ^{99m}Tc radiopharmaceutical agents benefits from an understanding of the features of *fac*-$[Re^I(CO)_3L]^n$ analogues. Also, ^{186}Re and ^{188}Re are among the most promising radionuclides for therapeutic applications.[3] Many ligands having the ability to chelate facially with three donors such as N or a combination of N and O donors form stable and kinetically inert complexes with the *fac*-$\{M^I(CO)_3\}^+$ core (M = ^{99m}Tc, Re).[3−5] Although N donor groups are superior to the carboxylate O donor group in enhancing the ability of L to form *fac*-$[^{99m}Tc^I(CO)_3L]^n$ complexes,[6] carboxylate groups generally have superior biological properties as radiopharmaceutical renal imaging agents.[1,7] *fac*-$[^{99m}Tc^I(CO)_3(NTA)]^{2-}$ ($NTAH_3$ = nitrilotriacetic acid) was recently reported to have pharmacodynamic renal clearance properties in rats good enough to merit testing in humans.[8] This radiopharmaceutical is based on an aminopolycarboxylate ligand that can realistically form only one isomer. However, renal imaging agents with other target ligands, which usually have more N donors (such as polyamino-polycarboxylic acid ligands), form isomers under the normal aqueous conditions in which they are made.[7,9] The presence of isomers complicates biomedical imaging.

While much of our work has centered on examining preparations of *fac*-$[M(CO)_3L]^n$ (M = Re or ^{99m}Tc)

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complexes in water,[1,7,8,10−14] for a number of reasons we wished to explore preparative chemistry in nonaqueous solvents. First, understanding the nonaqueous chemistry might allow us to prepare renal agents with only one or mainly one isomer. Second, isostructural technetium (radioactive imaging) and rhenium (fluorescence microscopic imaging) compounds allow correlation of images from in vivo and in vitro studies, respectively.[4,15,16] However, the ligands needed to prepare fluorescent compounds are often only sparingly soluble in aqueous media. Third, for some L, the preparation of *fac*-$[M(CO)_3L]^n$ (M = Re or ^{99m}Tc) complexes in water was not successful. Reasoning that reactions in organic solvents might be followed more easily in real time by NMR spectroscopy, we decided to evaluate *fac*-$[Re(CO)_3(CH_3CN)_3]^+$ as a soluble precursor for synthesizing *fac*-$[Re(CO)_3L]^n$ compounds in organic solvents. We began our work with relatively simple tridentate amine ligands because complexes of several of these ligands had already been prepared in water.

Treatment of *fac*-$[Re(CO)_3(CH_3CN)_3]^+$ with various tridentate amine ligands has produced several novel compounds, which most likely arise from reaction of the coordinated nitrile with ligand terminal amines. The reactivity of coordinated nitriles is an important, well-studied topic, and the reader is referred to several excellent recent reviews and articles for background information.[17−20]

An important goal is to interpret how structure affects the NMR spectra of the *fac*-$[Re^I(CO)_3L]^n$ complexes. Previous work having this goal benefited from the study of the interaction of the chloride anion with the protons of the Re−NH groups of *fac*-$[Re(CO)_3L]^n$ complexes.[10] The topic of metal complexes as anion receptors is currently under intense study.[21−23] Thus, we utilize here the same approach to evaluate the interaction of Cl^- with some of the new *fac*-$[Re(CO)_3L]^n$ complexes because these complexes have unusual NH groups. When discussing specific compounds, we generally do not use the *fac*- designation because all the new compounds have this geometry.

Experimental Section

Materials. $Re_2(CO)_{10}$, diethylenetriamine (dien), *N,N′,N″*-trimethyldiethylenetriamine (*N,N′,N″*-Me_3dien), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (*N,N,N′,N″,N″*-Me_5dien), tetraethylammonium chloride, $AgPF_6$, and $AgBF_4$ from Aldrich, *N,N*-dimethyldiethylenetriamine (*N,N*-Me_2dien) from Ames Laboratories, *N,N′,N″*-triethyldiethylenetriamine (*N,N′,N″*-Et_3dien) from City Chemical LLC, and *N′*-methyldiethylenetriamine (*N′*-Medien) from TCI America were used as received. $Re(CO)_5Br$, and $[Re(CO)_3(CH_3CN)_3]^+$ salts were synthesized by using slight modifications of known methods.[24−26] $[Re(CO)_3(dien)]PF_6$ was prepared as previously reported.[10]

NMR Measurements. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Peak positions are relative to TMS or solvent residual peak, with TMS as reference. All NMR data were processed with TopSpin and Mestre-C software.

X-ray Data Collection and Structure Determination. Colorless single crystals were placed in a cooled nitrogen gas stream at 90 K on a Nonius Kappa CCD diffractometer fitted with an Oxford Cryostream cooler with graphite-monochromated Mo Kα (0.71073 Å) radiation. Data reduction included absorption corrections by the multiscan method, with HKL SCALEPACK.[27] All X-ray structures were determined by direct methods and difference Fourier techniques and were refined by full-matrix least-squares by using SHELXL97.[28] All non-hydrogen atoms were refined anisotropically. All H atoms were visible in difference maps, but were placed in idealized positions, except for some on N, which were refined when their positions were not unambiguously predictable. A torsional parameter was refined for each methyl group. The anion in $[Re(CO)_3(EAE)]BF_4$ also exhibits both orientational and substitutional disorder. The F atoms of the BF_4^- occupy two sets of sites, and a site of apparent ~5% occupancy by Br^- lies near the B position. Crystal data and refinement details are presented in Table 1.

$[Re(CO)_3(DAE)]BF_4$ (DAE = (*Z*)-*N′*-(2-(2-(dimethylamino)ethylamino)ethyl)acetimidamide). *N,N*-Me_2dien (15 μL, 0.10 mmol) was added to a solution of $[Re(CO)_3(CH_3CN)_3]BF_4$ (48 mg, 0.10 mmol) in 6 mL of acetonitrile, and the reaction mixture was heated at reflux for 24 h. The volume was reduced to ~2 mL, and diethyl ether was added until a fine precipitate was just visible. The reaction mixture was allowed to stand at room temperature; colorless crystals were observed in 2−3 days (15 mg, 28% yield). ^{1}H NMR signals (ppm) in DMSO-d_6: 7.99 (s, 1H, NH), 7.28 (s, 1H, NH), 7.10 (s, 1H, NH), 3.19 (m, 4H, CH_2), 3.03 (s, 3H, CH_3), 2.97 (m, 2H, CH_2), 2.63 (m, 2H, CH_2), 2.44 (s, 3H, CH_3), 2.31 (s, 3H, CH_3). The product was characterized by single-crystal X-ray diffraction.

$[Re(CO)_3(MAE)]PF_6$ (MAE = *N*-methyl-*N*-(2-(methyl-(2-(methylamino)ethyl)amino)ethyl)acetimidamide). A 10% excess of *N,N′,N″*-Me_3dien (16 μL, 0.11 mmol) was added to a solution of $[Re(CO)_3(CH_3CN)_3]PF_6$ (54 mg, 0.10 mmol) in 10 mL of acetonitrile. The reaction mixture was heated at reflux for 24 h. A white powder was collected, which later gave X-ray quality crystals upon slow evaporation of a methanol solution (29 mg, 48% yield). ^{1}H NMR signals (ppm) in DMSO-d_6: 7.17 (s, 1H, NH), 4.50 (s, 1H, NH), 4.22 (m, 1H, CH_2), 3.20 (m, 1H, CH_2), 3.10 (s, 3H, CH_3), 3.03 (m, 2H, CH_2), 2.98 (s, 3H, CH_3), 2.91 (d, 3H, N1CH_3), 2.80 (m, 2H, CH_2), 2.60 (m, 2H, CH_2), 2.14 (s, 3H, CH_3). The above complex can be prepared more readily and

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Table 1. Crystal Data and Structure Refinement for $[Re(CO)_3(DAE)]BF_4$ (**1**), $[Re(CO)_3(MAE)]PF_6$ (**2**), $[Re(CO)_3(MAEH)F]PF_6$ (**3**), and $[Re(CO)_3(EAE)]BF_4$ (**4**)

	1	2	3	4
empirical formula	$C_{11}H_{20}N_4O_3Re\cdot BF_4$	$C_{12}H_{22}N_4O_3Re\cdot PF_6$	$C_{12}H_{23}FN_4O_3Re\cdot PF_6$	$C_{15}H_{28}N_4O_3Re\cdot(BF_4)_{0.95}\cdot Br_{0.05}$
fw	529.32	601.51	621.51	586.98
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	*Cc*	*C*2/*c*	*P*2$_1$/*n*	$P\bar{1}$
unit cell dimensions				
a (Å)	12.521(2)	30.442(4)	7.4371(10)	8.4928(15)
b (Å)	9.4781(15)	10.7593(14)	18.446(3)	10.491(2)
c (Å)	14.730(2)	11.8166(12)	14.738(3)	12.073(3)
α (deg)	90	90	90	76.289(8)
β (deg)	106.172(8)	97.335(7)	96.900(12)	79.818(10)
γ (deg)	90	90	90	87.570(11)
V (Å^3)	1678.9(4)	3838.7(8)	2007.2(6)	1028.6(4)
T (K)	90.0(5)	90.0(5)	90.0(5)	90.0(5)
Z	4	8	4	2
ρ_{calc} (g/m^3)	2.094	2.082	2.057	1.895
abs coeff (mm^{-1})	7.30	6.49	6.22	6.06
$2\theta_{max}$ (°)	67.4	69.8	60.0	63.8
R indices[a]	0.026	0.026	0.047	0.033
wR2 = $[I > 2\sigma(I)]$[b]	0.069	0.054	0.079	0.072
data/param	5921/222	7926/257	5840/258	7050/257

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, in which $w = 1/[\sigma^2(F_o^2) + (dP)^2 + (eP)]$ and $P = (F_o^2 + 2F_c^2)/3$; d = 0.0368, 0.0192, 0.0151, and 0.0305 and e = 5, 5.2495, 4.1664, and 1.826 for $[Re(CO)_3(DAE)]BF_4$, $[Re(CO)_3(MAE)]PF_6$, $[Re(CO)_3(MAEH)F]PF_6$, and $[Re(CO)_3(EAE)]BF_4$, respectively.

reliably by the following procedure: *N,N′,N″*-Me$_3$dien (14 μL, 0.10 mmol) was added to a solution of $[Re(CO)_3(CH_3CN)_3]PF_6$ (54 mg, 0.10 mmol) in 8 mL of acetonitrile, and the reaction mixture was heated at reflux for 16 h, whereupon a very small amount of a fine precipitate was visible. The reaction mixture was transferred to a vial and allowed to evaporate to dryness at room temperature. The residue was dissolved in methanol, an excess of diethyl ether was added, and the mixture was left at room temperature. The white precipitate that had aggregated into clumps after 2 days was scraped from the walls of the vial, placed on a filter, and washed with diethyl ether. The NMR spectrum of this precipitate was identical to that of the crystals described above. The BF_4^- salt could also be obtained by using a similar procedure, which yielded a white precipitate having an NMR spectrum identical to that of the PF_6^- crystals; however, the precipitate could not be crystallized.

$[Re(CO)_3(MAEH)F]PF_6$. Crystallization of the precipitate obtained during one of the syntheses of $[Re(CO)_3(MAE)]PF_6$ produced two types of crystals. One type, which was more abundant, was that just described for $[Re(CO)_3(MAE)]PF_6$, as confirmed by measurement of the unit cell dimensions. The less abundant type of crystals (needle-like), characterized by single-crystal X-ray diffraction, contained $[Re(CO)_3(MAEH)F]PF_6$. ^{1}H NMR signals (ppm) of the mixture in DMSO-d_6 attributable to $[Re(CO)_3(MAEH)F]PF_6$: 6.93 (s, N4H), 6.19 (s, N1H), 3.03 (s, CH_3), 2.99 (s, CH_3), 2.56 (d, N1CH_3), 2.23 (s, C12H_3).

$[Re(CO)_3(EAE)]BF_4$ (EAE = *N*-ethyl-*N*-(2-(ethyl-(2-(ethylamino)ethyl)amino)ethyl)acetimidamide). A 10% excess of *N,N′,N″*-Et$_3$dien (20 μL, 0.11 mmol) was added to a solution of $[Re(CO)_3(CH_3CN)_3]BF_4$ (48 mg, 0.10 mmol) in 6 mL of acetonitrile, and the reaction mixture was heated at reflux for 16 h. The volume was reduced to ~2 mL, and diethyl ether (10−15 mL) was added, whereupon a fine precipitate formed. After about 30 min the precipitate was collected on a filter and washed with diethyl ether (24 mg, 40% yield). (When the precipitate was too fine to filter, crystals could be obtained by letting the mixture stand covered and undisturbed for 1 day.) Crystals suitable for single-crystal X-ray diffraction grew upon slow evaporation of a solution of the compound in methanol. ^{1}H NMR signals (ppm) in DMSO-d_6: 7.03 (s, 1H, NH), 4.40 (s, 1H, NH), 4.15 (m, 1H, CH_2), 3.42 (m, 2H, CH_2), 3.20 (m, 2H, CH_2), 3.08 (m, 5H, CH_2), 2.80 (m, 2H, CH_2), 2.62 (m, 2H, CH_2), 2.18 (s, 3H, CH_3). 1.23 (t, 3H, CH_3), 1.14 (overlapping triplets, 6H, CH_3). The PF_6^- salt could also be obtained by using a similar procedure, which yielded a white precipitate having an NMR spectrum identical to that of $[Re(CO)_3(EAE)]BF_4$.

Cl^- Titrations. Aliquots of a NEt_4Cl stock solution containing 5 mM of the desired *fac*-$[Re(CO)_3(L)]^+$ complex in DMSO-d_6 or acetonitrile-d_3 were added to 600 μL of a 5 mM solution of the complex, giving 1 to 140−150 mM Cl^-. The solution was monitored by ^{1}H NMR spectroscopy upon each addition.

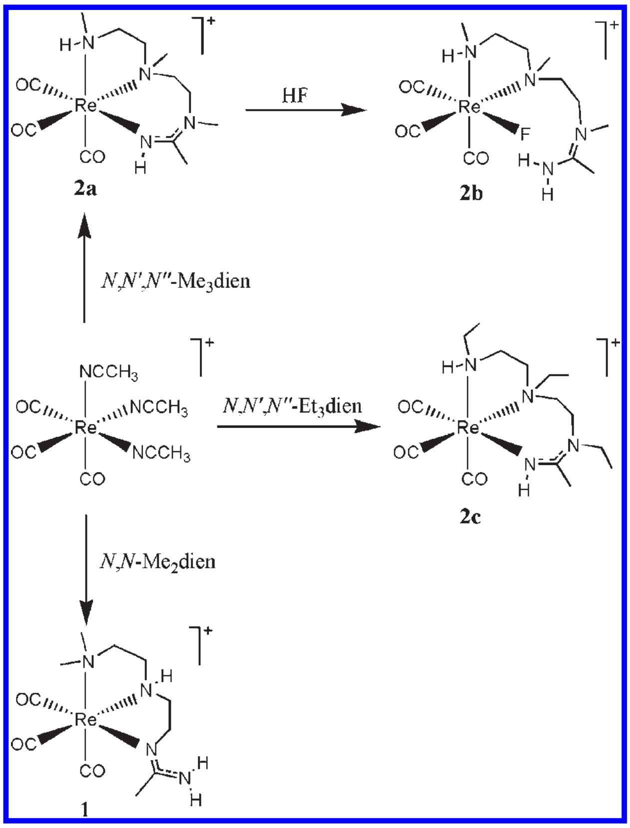
Addition of Base to $[Re(CO)_3(MAE)]PF_6$ and $[Re(CO)_3(EAE)]BF_4$. A 5 mM solution of $[Re(CO)_3(MAE)]PF_6$ crystals in DMSO-d_6 (600 μL) was treated with aqueous sodium hydroxide (0.1 M, 10 μL), and the solution was monitored by ^{1}H NMR spectroscopy. Similar experiments were conducted with a dilute NaOH solution (0.033 M, 10 μL) and with $[Re(CO)_3(EAE)]BF_4$ (0.1 M, 10 μL).

Results and Discussion

Synthetic Results. New $[Re(CO)_3L]^n$ products prepared from $[Re(CO)_3(CH_3CN)_3]PF_6/BF_4$ in acetonitrile are shown in Scheme 1. In water starting with $[Re(CO)_3(H_2O)_3]^+$, the ligands in Scheme 1 coordinate unchanged in a tridentate fashion to form normal $[Re(CO)_3L]^n$ products.[10] Because dien and *N,N,N′,N″,N″*-Me$_5$dien gave the same normal $[Re(CO)_3L]^n$ products in acetonitrile starting with $[Re(CO)_3(CH_3CN)_3]PF_6/BF_4$ (details not given) or in water starting with $[Re(CO)_3(H_2O)_3]^+$,[10] the formation of different products in acetonitrile than in water for *N,N*-Me$_2$dien, *N,N′,N″*-Me$_3$dien, and *N,N′,N″*-Et$_3$dien is attributable to the presence in these ligands of both steric bulk and NH groups. The reaction pathways in acetonitrile leading to the compounds in Scheme 1 are best discussed after we describe the structures of the new $[Re(CO)_3L]^n$ complexes.

Structural Results. All complexes reported here exhibit a pseudo octahedral structure, with the three carbonyl ligands occupying one face and having typical Re−CO bond distances.[10] The remaining three coordination sites are occupied by three nitrogen atoms of novel ligands in $[Re(CO)_3(DAE)]BF_4$ (Figure 1), $[Re(CO)_3(MAE)]PF_6$ (Figure 2a), and $[Re(CO)_3(EAE)]BF_4$ (Figure 2c).

Scheme 1. Products obtained in the syntheses using acetonitrile as a solvent. The compound numbers correspond to the structures in Figures 1 and 2. Adventitious HF from the decomposition of PF_6^- transformed some of **2a** to **2b**.



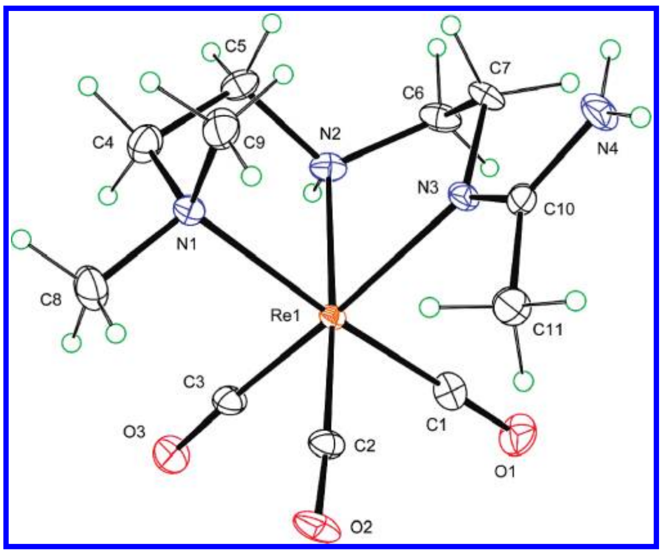


Figure 1. ORTEP plot of the cation in $[Re(CO)_3(DAE)]BF_4$. Thermal ellipsoids are drawn with 50% probability.

However, in $[Re(CO)_3(MAEH)F]PF_6$, two coordination sites are occupied by nitrogens and the third by fluoride (Figure 2b). Crystal data and details of the structural refinement for all these complexes are summarized in Table 1. The atom numbering systems in the ORTEP figures are used to describe the solid-state data. All complexes in Table 2 have a five-membered chelate ring with comparable N1−Re−N2 angles.

The molecular structure of $[Re(CO)_3(DAE)]BF_4$ (Figure 1) reveals that the bound tridentate DAE ligand is an addition product between *N*,*N*-Me_2dien and acetonitrile. None of the Re-bound Ns are derived from acetonitrile. One of the two five-membered chelate rings anchored by the central N (N2) is terminated by N3, the original *N*,*N*-Me_2dien primary amine N. The relatively short N3−C10 bond (1.293(6) Å; C10 is the original nitrile C) indicates double-bond character and an sp^2 N. The other chelate ring is terminated by N1, the original *N*,*N*-Me_2dien tertiary amine N.

In $[Re(CO)_3(MAE)]PF_6$ (Figure 2a), one terminal amine N of the *N*,*N*′,*N*″-Me_3dien ligand has now become an endocyclic nitrogen (N3) having three bonds to C and no NH bonds. This N has characteristics of an sp^2 N and is part of a seven-membered chelate ring terminated by N4 (the original nitrile N) and anchored by N2, the original *N*,*N*′,*N*″-Me_3dien central N. N2 anchors the other chelate ring, and thus an uncommon five-membered/seven-membered chelate ring combination is created.

The bond lengths and angles centered on N3, N4, and C11 show that these are sp^2 hybridized (relatively planar, bond angles near 120°) and that the N4−C11−N3 grouping exhibits electron delocalization. The N4−C11 (1.318(3) Å) and N3−C11 (1.344(3) Å) bonds show double-bond character. $[Re(CO)_3(EAE)]BF_4$ (Figure 2c) has a structure very similar to that of $[Re(CO)_3(MAE)]PF_6$, differing only in having ethyl groups instead of methyl groups at N1, N2, and N3.

Compared to $[Re(CO)_3(MAE)]PF_6$, the molecular structure of $[Re(CO)_3(MAEH)F]PF_6$ (Figure 2b) has the striking feature that N4 (derived from acetonitrile) is no longer part of an NH group bound to Re; the N4H has been protonated to become a dangling NH_2 group, as found in $[Re(CO)_3(DAE)]BF_4$. This NH_2 group forms a hydrogen bond to F, which is directly bound to Re.

Other complexes are known to have a seven-membered chelate ring similar to the type found in the MAE and EAE complexes.[29−32] One example is *cis*-[Pt(NH═CPh-$NBu^tCH_2CH_2NHBu^t)Cl_2$]; Natile and co-workers[30] described this pseudo square planar Pt^{II} compound as the final product of the addition of *N*,*N*′-Bu^t_2ethylenediamine to coordinated benzonitrile. The obvious difference in geometry between six-coordinate Re^I tricarbonyl complexes versus four-coordinate Pt^{II} complexes might suggest that useful comparisons are not possible because octahedral complexes are usually subject to greater interligand steric interactions. However, Re^I tricarbonyl complexes are sterically undemanding because of the small size of the CO ligands and the relatively long bonds made by Re^I. Bond distances involving Re^I are longer than those involving Pt^{II}.[11,25,33,34] N−M−N bite angles for

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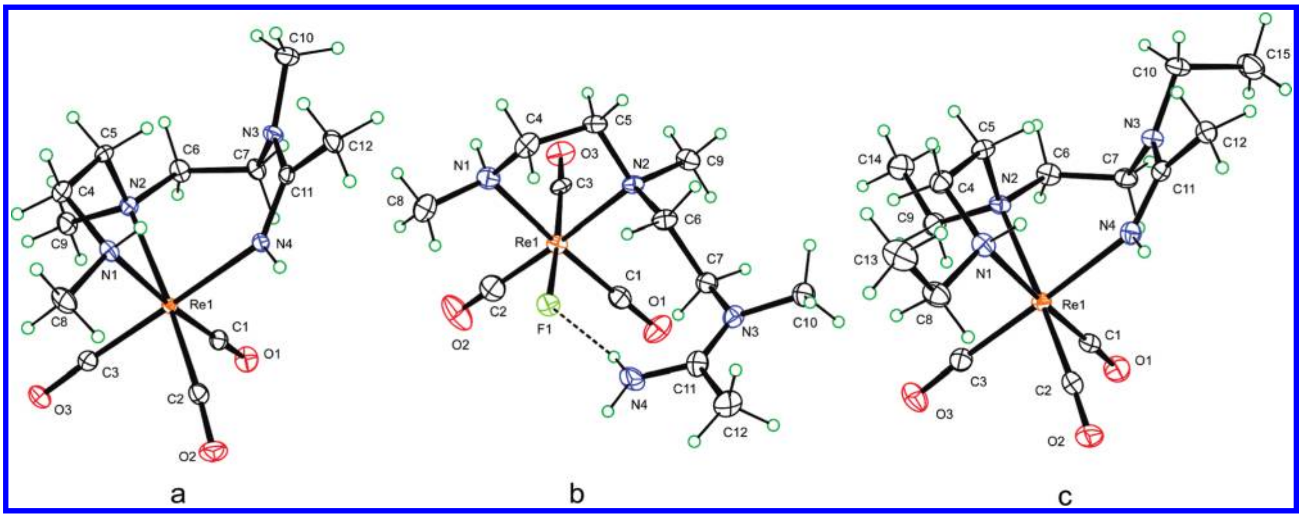


Figure 2. ORTEP plots of the cations in (a) [Re(CO)$_3$(MAE)]PF$_6$, (b) [Re(CO)$_3$(MAEH)F]PF$_6$, and (c) [Re(CO)$_3$(EAE)]BF$_4$. Thermal ellipsoids are drawn with 50% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Re(CO)$_3$(DAE)]BF$_4$ (**1**),[a] [Re(CO)$_3$(MAE)]PF$_6$ (**2**), [Re(CO)$_3$(MAEH)F]PF$_6$ (**3**), and [Re(CO)$_3$(EAE)]BF$_4$ (**4**)

	1	**2**	**3**	**4**
bond distances				
Re−N1	2.272(4)	2.235(2)	2.228(5)	2.241(3)
Re−N2	2.216(4)	2.2695(19)	2.274(4)	2.273(3)
Re−N*x*	2.242(4)[b]	2.206(2)[c]		2.201(3)[c]
N3−C10	1.293(6)	1.463(3)	1.465(7)	1.473(5)
N4−C10	1.350(6)			
N4−C11		1.318(3)	1.321(7)	1.304(5)
N3−C11		1.344(3)	1.305(7)	1.346(5)
bond angles				
N1−Re−N2	78.33(14)	79.30(7)	79.56(17)	79.59(12)
N1−Re−N*x*	88.96(13)[b]	80.10(7)[c]		80.13(13)[c]
N2−Re−N*x*	75.97(14)[b]	90.47(7)[c]		87.56(12)[c]
Re−N4−C11		138.74(16)		141.2(3)
N3−C*x*−N4	123.8(4)[d]	120.6(2)[e]	121.5(5)[e]	122.1(4)[e]
C3−Re−C1	88.5(2)	89.4(10)	88.4(2)	87.89(17)
C3−Re−N1	92.33(16)	92.86(9)	94.3(2)	93.98(15)
C1−Re−N*x*	89.41(18)[b]	98.05(8)[c]		98.12(15)[c]
N4−C11−N3−C7		23.4(4)	4.1(8)	15.9(6)

[a] The N3−C10 bond distance of **1** should be compared with the N3−C11 bond distance of complexes **2**-**4**. [b] N*x* = N3. [c] N*x* = N4. [d] C*x* = C10. [e] C*x* = C11.

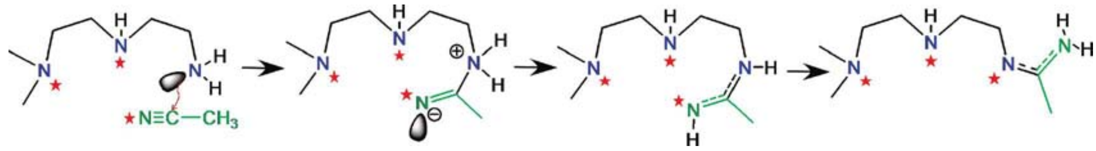
chelate rings in related Pt^{II} and Re^{I} compounds are more acute in Re^{I} compounds.[11,35] We believe this is true because the chelate rings normally adopt a preferred conformation or pucker; this conformation fixes the N-to-N nonbonded distance. However, the angles in the Pt^{II} and the Re^{I} seven-membered chelate rings being compared here have similar values, 89.0(7) and 90.47(7)°, in contrast to the normal situation. Also in contrast to the normal situation, the nonbonded distance between these N atoms is much smaller in the Pt complex (2.79(2) Å) than in the Re complex (3.178(3) Å). The seven-membered chelate ring may be inherently strained and, unlike in other cases, the longer Re−N bond distances seem to allow the ring to reduce strain, explaining the unusually long N-to-N nonbonded distance, the large N−Re^{I}−N bite angle, and the low chelate ring pucker in Re^{I} vs Pt^{II} (Figure S1, Supporting Information). This strain aids in the transformation of the seven-membered chelate ring to a five-membered chelate ring as discussed next.

Implications for the Reaction Pathway Forming [Re(CO)$_3$(DAE)]BF$_4$ from the Structures of [Re(CO)$_3$(MAE)]PF$_6$ and [Re(CO)$_3$(MAEH)F]PF$_6$. We believe that a complex of the [Re(CO)$_3$(MAE)]$^+$ type initially formed as an intermediate, which then rearranged to give [Re(CO)$_3$(DAE)]$^+$ (Scheme 2). We propose that the early phase of the reaction between *N,N*-Me$_2$dien and [Re(CO)$_3$(CH$_3$CN)$_3$]BF$_4$ includes an attack of a terminal amine on the sp carbon of a coordinated acetonitrile. This attack leads to formation of a seven-membered ring (as found in [Re(CO)$_3$(MAE)]PF$_6$); this ring then rearranges to give the [Re(CO)$_3$(DAE)]BF$_4$ product. The key reason that the rearrangement is possible relates to the fact that the putative [Re(CO)$_3$(MAE)]$^+$ type intermediate on the pathway to the [Re(CO)$_3$(DAE)]BF$_4$ product would have an endocyclic NH (N3H) rather than an N3Me group in the seven-membered ring of [Re(CO)$_3$(MAE)]PF$_6$ (Scheme 3). The stable [Re(CO)$_3$(MAE)]$^+$ and [Re(CO)$_3$(EAE)]$^+$ compounds share with the stable Pt complex, *cis*-[Pt(NH=CPhNBu^{t}CH$_2$CH$_2$NHBu^t)Cl$_2$],[30] the feature that the endocyclic noncoordinated nitrogen does not have a bound proton. All bonds to N3 in [Re(CO)$_3$(MAE)]PF$_6$ are to carbon. The N3 atom in this ring has no lone pair available to coordinate to Re. However, the similarly situated N3 of the postulated seven-membered ring of the intermediate on the pathway to [Re(CO)$_3$(DAE)]BF$_4$ has one bound proton; this N3H could release its proton as it generates the lone pair needed to form the Re−N3 bond. This proton can serve as the proton needed to convert the dissociating N4H to a NH$_2$ group (Scheme 2); this process could be stepwise or concerted. In the Supporting Information, we illustrate some of these points using a scheme based on the X-ray structures.

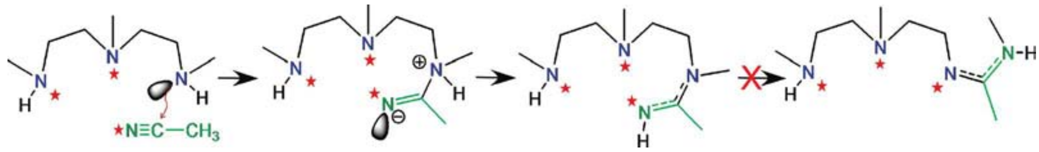
The large angle within the chelate ring involving N4 (Re−N4−C11∼139°) of [Re(CO)$_3$(MAE)]PF$_6$ provides evidence that strain may predispose N4 to dissociate.

(35) Perera, T.; Marzilli, P. A.; Fronczek, F. R.; Marzilli, L. G. Manuscript in Preparation.

Scheme 2. Likely pathway for DAE ligand formation from *N*,*N*-Me_2dien and acetonitrile (green). Stars indicate the location of the lone pair on the nitrogens known to be used or likely to be used in Re coordination at each stage of the process. The *fac*-$\{Re(CO)_3\}^+$ fragment is not shown.



Scheme 3. The likely pathway for MAE ligand formation from *N*,*N'*,*N''*-Me_3dien and acetonitrile (green). Stars indicate the location of the lone pair on the nitrogens known to be used or likely to be used in Re coordination at each stage of the process. The *fac*-$\{Re(CO)_3\}^+$ fragment is not shown. Only one proton can be transferred (in the second step). The hypothetical step which would be needed to form the DAE analogue does not occur because the methyl group can not transfer.



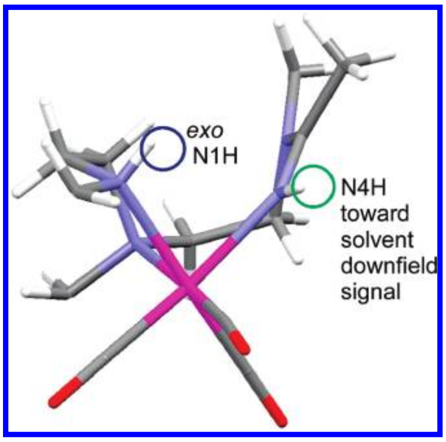


Figure 3. Designation of the *exo*-NH proton (pointing away from the carbonyl groups and toward the hydrophobic pocket of the ligand) of $[Re(CO)_3(MAE)]PF_6$ and $[Re(CO)_3(EAE)]BF_4$. N4H is not classified as either *endo* or *exo*.

The molecular structure of $[Re(CO)_3(MAEH)F]PF_6$ (Figure 2b) may provide some evidence as to the tendency of N4H to dissociate and be protonated to form an NH_2 group. Although the process involves a proton from the HF formed in situ from the PF_6^- anion or present as an impurity in the $AgPF_6$ reagent, $[Re(CO)_3(MAEH)F]PF_6$ may be considered to resemble a species that could be present in the rearrangement pathway discussed in the preceding paragraph if the process is not concerted.

NMR Spectroscopy. All complexes reported were characterized by NMR spectroscopy in DMSO-d_6 and acetonitrile-d_3. On the basis of the molecular structure of $[Re(CO)_3(MAE)]PF_6$, two different types of NH groups are present, as illustrated in Figure 3. For *fac*-$[Re(CO)_3L]^n$ complexes,[7,10] N1H is referred to as an *exo*-NH proton, as it points away from the carbonyl groups (versus an *endo*-NH proton pointing toward the carbonyl groups). The N4H is not classified in this way because N4 is sp^2 hybridized. Two ^1H NMR peaks of $[Re(CO)_3(MAE)]PF_6$ in DMSO-d_6 decreased in size when D_2O was added, indicating that these are NH signals. The broad NH signal at 4.50 ppm (Table 3), assigned to the *exo*-N1H from the COSY cross-peak to the $N1CH_3$ doublet at 2.91 ppm (Figure S2, Supporting Information), falls within the range observed for *exo*-NH's.[10] Of the four methyl peaks for $[Re(CO)_3(MAE)]PF_6$, only $N1CH_3$ could be a doublet. The sharp NH peak at 7.17 ppm, which must be from N4H, has a COSY cross-peak to a singlet at 2.14 ppm; this must be the $C12H_3$ signal.

Table 3. ^1H NMR Chemical Shifts (ppm) of $[Re(CO)_3(DAE)]BF_4$ (**1**), $[Re(CO)_3(MAE)]PF_6$ (**2**), and $[Re(CO)_3(EAE)]BF_4$ (**4**) in DMSO-d_6 at 25 °C and Selected NH Shifts in Acetonitrile-d_3[a]

	1	2	4
exo-N1H		4.50 (3.39)	4.40 (3.22)
N2H	7.10 (5.53)		
N4H/N4Ha	7.28 (6.02)	7.17 (6.41)	7.03 (6.28)
N4Hb	7.99 (6.48)		
CH_3CN-derived CH_3	2.31	2.14	2.18
$C7H_2$	3.19	4.22, 3.20	4.15, 3.42

[a] Assignments of the NH signals were verified by COSY spectra in DMSO-d_6. NH shifts in acetonitrile-d_3 are enclosed in parentheses.

Additional confirmation for the $C12H_3$ signal assignment comes from the presence of a similar methyl singlet at 2.18 ppm in the spectrum of $[Re(CO)_3(EAE)]BF_4$, which can have only the $C12H_3$ signal as a singlet because the other three methyl groups are in the ethyl groups. Many signals such as a multiplet at ~4.2 ppm (assigned by COSY to one of the protons of the $C7H_2$ methylene group bonded to the delocalized N3−C11−N4 amidine group) and the NH signals have similar shifts for both $[Re(CO)_3(MAE)]PF_6$ and $[Re(CO)_3(EAE)]BF_4$ (Table 3). For both, the NH signals are more upfield in acetonitrile versus DMSO, a finding attributable to the weaker interaction of acetonitrile with the NH groups.

For $[Re(CO)_3(DAE)]BF_4$ (Figure 1), 2D NMR experiments were used to assign the signals in DMSO-d_6 (Figures S3 and S4, Supporting Information), and NH signals were identified by addition of D_2O (Table 3). The $N1CH_3$ signals were assigned from an NOE cross-peak at 3.03 and 2.44 ppm. The peak of the central NH (N2H, 7.10 ppm) was identified by COSY and NOE correlations with two multiplets, at 3.19 and 2.97 ppm, from the N2-CH_2 groups. The COSY cross-peak between the relatively sharp NH peak at 7.28 ppm (Figure 4) and the CCH_3 signal at 2.31 ppm (Figure S4, Supporting Information) assigns these to N4Ha and the methyl group derived from

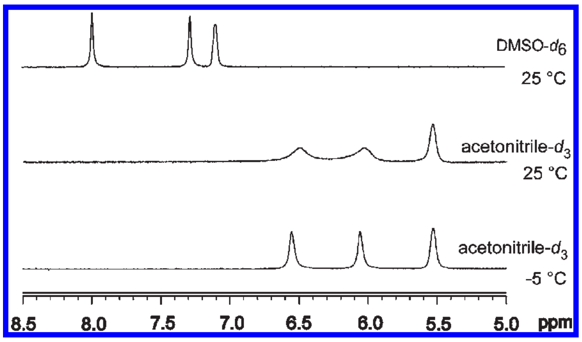


Figure 4. ^{1}H NMR spectrum showing NH signals of $[Re(CO)_3(DAE)]BF_4$ in DMSO-d_6 at 25 °C (top), in acetonitrile-d_3 at 25 °C (middle), and in acetonitrile-d_3 at −5 °C (bottom).

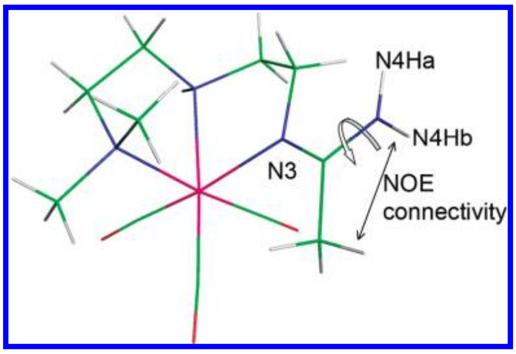


Figure 5. Designation of the N4Ha and N4Hb protons of $[Re(CO)_3(DAE)]BF_4$, indicating the proximity of N4Hb to the methyl group and the rotation of the NH_2 group.

acetonitrile. (See Figure 5 for the designations of the N4Ha and N4Hb protons.) This assignment was confirmed by the relatively stronger NOE cross-peak from the CCH_3 peak to the N4Hb signal (7.99 ppm) than to the N4Ha signal.

In general, the NH signals of the new compounds were sharp at 25 °C. In contrast, for $[Re(CO)_3(DAE)]BF_4$ the NH_2 peaks were sharp in DMSO-d_6 but broad in acetonitrile-d_3 (Figure 4), a solvent that interacts weakly with NH groups. We reasoned that the NH_2 group may rotate at room temperature, but that DMSO may restrict this rotation by H-bonding to the NH_2 protons. Indeed, all three NH signals were sharp in acetonitrile-d_3 at −5 °C. Increasing the temperature resulted in considerable broadening of the NH_2 signals (Figure S5, Supporting Information). The peak width of the central NH (N2H) was hardly affected. The behavior of the NH_2 signals above 25 °C was complicated, suggesting that a dynamic process in addition to rotation about the C−N bond occurs at elevated temperatures. Therefore, we performed a ROESY experiment at −5 °C in acetonitrile-d_3. The spectrum contained a negative cross-peak between NH signals at 6.58 and 6.02 ppm (Figure S6, Supporting Information). The magnitude was larger than a negative N4Ha-N4Hb exchange cross-peak in a ROESY spectrum recorded in DMSO-d_6 at room temperature (Figure S3, Supporting Information). Thus, the rate of rotation of the $N4H_2$ group is faster in acetonitrile-d_3 at −5 °C than in DMSO-d_6 at 25 °C.

NH to ND Exchange. After addition of D_2O (100 μL) to DMSO-d_6 solutions (5 mM, 600 μL), the two NH_2

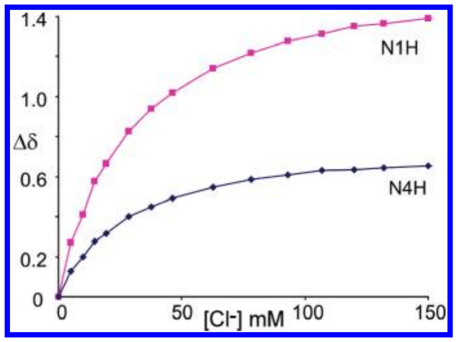


Figure 6. Change in chemical shift (Δδ, ppm) of the NH signals of $[Re(CO)_3(MAE)]PF_6$ (5 mM) caused by added Cl^- in DMSO-d_6 at 25 °C.

protons of $[Re(CO)_3(DAE)]BF_4$ underwent immediate H to D exchange, whereas the central N2H had an exchange half-life of ∼5 min. A similar experiment for $[Re(CO)_3(MAE)]PF_6$ showed that the *exo*-NH in the terminal $NH(CH_3)$ group had a half-life of ∼30 min, and N4H had a half-life of 24 h. The N4H exchange half-life of $[Re(CO)_3(EAE)]BF_4$ (24 h) was the same as that of $[Re(CO)_3(MAE)]PF_6$. However, the half-life of the exchange of the *exo*-N1H of $[Re(CO)_3(EAE)]BF_4$ was longer (∼1 h) than that of $[Re(CO)_3(MAE)]PF_6$, undoubtedly because of the better electron donation of Et vs Me. These results indicate that the Re-bound sp^2 N of the seven-membered ring is relatively electron rich and therefore could protonate and dissociate.

Under similar experimental conditions, the exchange half-lives of the $[Re(CO)_3(dien)]PF_6$ complex were found to be ∼1, 2, and 12 h for the central, *exo*-NH, and *endo*-NH protons, respectively.

Interaction of NH Protons with the Cl^- Anion. When Cl^- was added to 5 mM solutions of *fac*-$[Re(CO)_3L]^+$ complexes, downfield shift changes, Δδ, were observed.[10] The Δδ of the relatively upfield $[Re(CO)_3(MAE)]PF_6$ *exo*-N1H signal reached a plateau of ∼1.3 ppm at 100 mM Cl^- in DMSO-d_6 (Figure 6). This behavior is in agreement with the finding that the *exo*-NH group typically shifts downfield by ∼1 ppm in DMSO-d_6 on addition of Cl^- to *fac*-$[Re(CO)_3L]^+$ complexes having L = dien or simple dien-related derivatives.[10] Because H-bonding to solvent causes downfield shifts, the relatively upfield shift of *exo*-NH signals was attributed to steric hindrance to solvation of the *exo*-NH groups of $[Re(CO)_3(dien)]PF_6$ by virtue of their being located in the pocket (as illustrated for $[Re(CO)_3(MAE)]PF_6$ in Figure 3 above). This Δδ behavior was explained by suggesting that the Cl^- anion, owing to its small size, can enter the sterically hindered pocket and form H-bonds to the two *exo*-NHs. These *exo*-NHs are close enough (∼2.5 Å) to interact simultaneously with the chloride ion; this two-proton interaction was more favorable than when only one *exo*-NH was present in the complex.[10] A similar explanation accounts for the Δδ of the *exo*-NH signal of $[Re(CO)_3(MAE)]PF_6$. The plot in Figure 6 is very close to that for the *exo*-NH of $[Re(CO)_3(dien)]PF_6$.[10] The Δδ of the N4H signal of $[Re(CO)_3(MAE)]PF_6$ exactly paralleled that of the *exo*-NH, but Δδ was only ∼0.6 ppm. These results are consistent with synergistic interaction with chloride of both NH protons, which are separated by ∼2.5 Å (Figure 3).

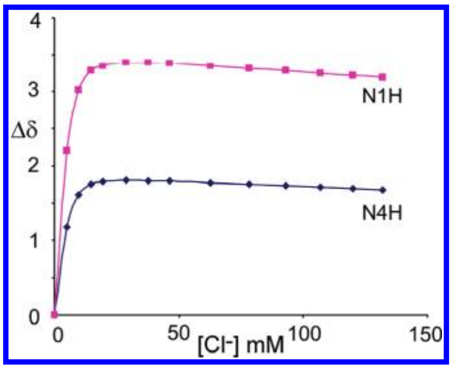


Figure 7. Change in chemical shift (Δδ, ppm) of the NH signals of $[Re(CO)_3(MAE)]PF_6$ (5 mM) caused by added Cl^- in acetonitrile-d_3 at 25 °C.

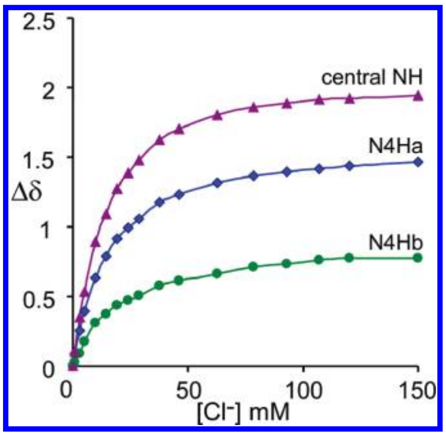


Figure 8. Change in chemical shift (Δδ, ppm) of the NH signals of $[Re(CO)_3(DAE)]BF_4$ (5 mM) caused by added Cl^- in acetonitrile-d_3 at 25 °C.

In acetonitrile-d_3, on addition of Cl^- the relatively upfield $[Re(CO)_3(MAE)]PF_6$ *exo*-N1H signal (at 3.39 ppm, Table 3) shifted downfield (Δδ ~ 3.3 ppm). The N4H signal (at 6.41 ppm) shifted downfield only ~1.8 ppm. The maximum shift change was observed at a much lower concentration of Cl^- in acetonitrile-d_3 (20 mM, Figure 7) than in DMSO-d_6 (~100 mM), consistent with the weaker H-bonding of the acetonitrile solvent. The plots for Δδ for both signals are parallel for the reason given in the preceding paragraph, namely both protons interact with chloride ion.

When Cl^- was added to a solution of $[Re(CO)_3(DAE)]BF_4$ in acetonitrile-d_3, the three NH signals shifted downfield in parallel (Δδ plateau values at ~110 mM Cl^- = ~1.5, ~0.8, and ~2 ppm for N4Ha, N4Hb, and the central NH, respectively, Figure 8). A Δδ of 2 ppm is large for a central NH signal, as the maximum change in shift for the central NH of related N donor Ls in *fac*-$[Re(CO)_3L]^n$ complexes is ≤1 ppm and occurs at higher Cl^- concentration (unpublished results).[10] The NH_2 group of $[Re(CO)_3(DAE)]BF_4$ is not close enough to the central NH to interact synergistically with Cl^-. In other cases in which the central NH group was present, the complex had *exo*-NH groups that could cooperatively bind the Cl^- anion.[10] Thus, Cl^- interacted preferentially at this site. The resulting H-bonded ion pair would have zero overall charge, decreasing the interaction of a second Cl^- with the central NH of the complex, which is now a neutral ion pair.

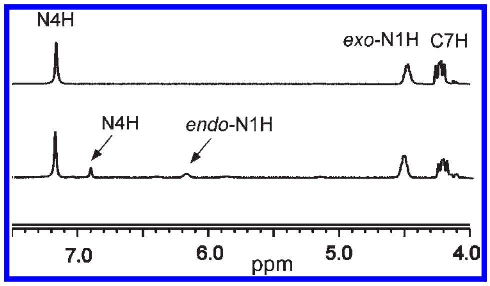


Figure 9. ^1H NMR spectra of $[Re(CO)_3(MAE)]PF_6$ (5 mM) in DMSO-d_6 at 25 °C before (top) and 20 min after (bottom) addition of OH^- (1.7 mM). The multiplet at ~4.2 ppm arises from one of the $C7H_2$ protons.

However, the competing NH_2 site of $[Re(CO)_3(DAE)]BF_4$ is far from the positive metal center (Figure 5), and this group interacts relatively weakly with Cl^-. Thus, the interaction of Cl^- with the central NH may be more favorable than in previous cases.[10] Nevertheless, this interaction is relatively weak because a fairly high Cl^- concentration is needed for Δδ of the central NH signal of $[Re(CO)_3(DAE)]BF_4$ to plateau (Figure 8).

Isomerization of $[Re(CO)_3(MAE)]PF_6$. One important issue relevant to radiopharmaceuticals is the stereochemistry of coordinated secondary amines, which have two configurations that can interconvert via base catalysis.[7,10] We assessed isomerization at N1 of $[Re(CO)_3(MAE)]PF_6$, resulting from addition of aqueous NaOH to a DMSO-d_6 solution. An initial NMR spectrum (Figure 9, top) recorded before addition of OH^- confirmed that the complex was isomerically pure. After addition of OH^- (1.7 mM), a new set of signals observable in the first recorded spectrum (5 min) grew within 20 min to its final intensity (13% new signals vs 87% initial signals). The new product has a sharp and a broad NH signal (Figure 9, bottom) and a methyl doublet (not shown). The broad signal and an associated methyl doublet allow us to establish that the new signals come from the isomer of $[Re(CO)_3(MAE)]PF_6$ having the inverted N1 configuration (*endo* NH, the H points toward the carbonyls). Upon addition of D_2O to this base-isomerized sample, the $N1CH_3$ doublet for both isomers immediately became singlets. The new *endo*-NH signal is more downfield (6.19 ppm) than the *exo*-NH signal (4.50 ppm), and the new *exo*-$N1CH_3$ signal (2.56 ppm) is more upfield than the *endo*-$N1CH_3$ signal (2.91 ppm). The more downfield NH signal correlates with the more upfield CH_3 signal. These shift values and correlations agree well with data for *chiral* $[Re(CO)_3(N,N',N''\text{-}Me_3\text{-}dien)]PF_6$ (ppm: *endo*-N1H, 6.39, *exo*-$N1CH_3$ doublet 2.66; and *exo*-N1H 5.15, *endo*-$N1CH_3$ doublet 2.94).[10] The sharp signal (6.90 ppm, Figure 9) upfield of the initial N4H signal (7.18 ppm) was assigned to the N4H of this new *endo*-N1H/*exo*-$N1CH_3$ isomer.

To confirm that OH^- is acting as a catalyst and does not coordinate directly to Re, a 1.7 mM NaOH and a 0.54 mM NaOH solution were prepared from the same stock solution of $[Re(CO)_3(MAE)]PF_6$. If hydroxide adds to Re and is not acting as a catalyst, decreasing the hydroxide concentration to 0.54 mM would not only decrease the rate of reaction but would also decrease the percentage of the new product. When the solutions were monitored by NMR spectroscopy, the 1.7 mM NaOH sample reached equilibrium in 20 min as before, whereas the 0.54 mM NaOH sample required more time (1−2 h) to reach equilibrium, as expected. In both solutions, the new product abundance was the same (13%). Thus, hydroxide is not coordinating but is acting as a catalyst.

In the identical 1.7 mM NaOH study, but with $[Re(CO)_3(EAE)]BF_4$, the new minor set of signals appeared and reached its maximum intensity in 40 min (12% minor isomer, 88% major isomer). The new *endo*-NH signal appears more downfield (5.78 ppm) than the *exo*-NH signal (4.40 ppm) of the original isomer. The new N4H signal appeared upfield (6.77 ppm) of the initial N4H signal (7.03 ppm). The faster rate of isomerization of $[Re(CO)_3(MAE)]PF_6$ versus $[Re(CO)_3(EAE)]BF_4$ is attributable to the slightly greater N1H acidity of $[Re(CO)_3(MAE)]PF_6$, as suggested by its shorter NH to ND exchange half-life than that of $[Re(CO)_3(EAE)]BF_4$.

When Cl^- was added to a base-isomerized sample of $[Re(CO)_3(MAE)]PF_6$, the N1H signal of the minor *endo*-N1H/*exo*-$N1CH_3$ isomer shifted only minimally downfield ($\Delta\delta \sim 0.28$ ppm at 150 mM Cl^-), while the N4H signal was not shifted. The NH signals of the starting major *exo*-N1H/*endo*-$N1CH_3$ isomer shifted as described previously. This observation highlights a new application of Cl^- addition as an aid in identifying which isomer of a *fac*-$[Re(CO)_3L]^n$ complex has an *endo*-NH/*exo*-alkyl and which has an *exo*-NH/*endo*-alkyl terminal amine. The small $\Delta\delta$ for the N4H signal further indicates that this proton is not very acidic. The isomerization at N1 should have no effect on the electronic character of N4. This result and the relatively long half-life for H to D exchange indicate a lower acidity for the N4H. This lower acidity in turn means that N4 is relatively electron rich, and thus N4 is poised to accept a proton during the reaction pathway to $[Re(CO)_3(DAE)]BF_4$ (Scheme 2).

Conclusions

As shown by Natile et al.[30] for a stable Pt^{II} compound with a closely related seven-membered ring, we conclude that the Re^I seven-membered chelate rings in $[Re(CO)_3(MAE)]PF_6$ and $[Re(CO)_3(EAE)]BF_4$ products shown in Scheme 1 arise from intramolecular attack by a terminal amine on a coordinated acetonitrile. The novel DAE ligand in $[Re(CO)_3(DAE)]BF_4$ provides an interesting and highly unusual variation having an sp^2 N donor derived from an sp^3 primary amine. Complexed DAE has a five-membered chelate ring and a dangling NH_2 group. DAE is formed via a series of steps, and the likely pathway has two proton transfer steps and a Re−N bond disruption step, Scheme 2. The stable Pt^{II} and Re^I complexes with seven-membered chelate rings cannot convert to a complex with the DAE-type ligand (Scheme 3), because the endocyclic nitrogen bears an alkyl or aryl group rather than the proton needed for the second proton transfer step forming the dangling NH_2 group in DAE, as shown in Scheme 2. Thus, the seven-membered chelate ring of the MAE-type ligand serves as a model for one likely intermediate in the formation of the DAE ligand. Two types of evidence suggest that the sp^2 NH donor bound to Re in this MAE-type ring is poised to undergo dissociation and protonation. First, $[Re(CO)_3(MAE)]PF_6$ has a large Re−N4−C11 angle, indicating strain and favoring Re−N bond breaking. Second, N4H is relatively nonacidic (revealed by slow H to D exchange and by weak interaction with chloride ion of the N4H of the minor *endo*-N1H/*exo*-$N1CH_3$ isomer of $[Re(CO)_3(MAE)]PF_6$), indicating an electron-rich N ready to accept a second proton.

Our studies on chloride interaction complement reports of the use in anion receptors[36] of transition-metal fragments to serve as scaffolds onto which H-bonding donor groups can be connected.[23] Chloride and other anions interact with the pyrazole NH's of *fac*-$[Re^I(CO)_3(\text{generic pyrazole})_3]^+$ cations.[22] This work is related to our present findings on chloride interactions with six-coordinate Re^I tricarbonyl complexes. However, we expand the field of the interaction of anions with NH groups in metal complexes by showing that such interactions provide a useful approach for both interpreting NMR data and for elucidating the structure of isomers; such information is useful for probing properties of Re analogues of ^{99m}Tc radiopharmaceuticals.

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Supporting Information Available: Crystallographic data for $[Re(CO)_3(MAE)]PF_6$, $[Re(CO)_3(MAEH)F]PF_6$, $[Re(CO)_3(EAE)]BF_4$, and $[Re(CO)_3(DAE)]BF_4$ in CIF format, a scheme based on X-ray structures for formation of $[Re(CO)_3(DAE)]^+$, a figure with seven-membered chelate ring pucker, $^1H-^1H$ COSY NMR spectra of $[Re(CO)_3(MAE)]PF_6$ and $[Re(CO)_3(DAE)]BF_4$ in DMSO-d_6, ROESY NMR spectra of $[Re(CO)_3(DAE)]BF_4$ in DMSO-d_6 and in acetonitrile-d_3, and ^1H NMR spectra of $[Re(CO)_3(DAE)]BF_4$ in acetonitrile-d_3 at different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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