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Superbasic Amidine Monodentate Ligands in *fac*-[Re(CO)$_3$(5,5′-Me$_2$bipy)(Amidine)]BF$_4$ Complexes: Dependence of Amidine Configuration on the Remote Nitrogen Substituents

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Addition of various RNH$_2$ to *fac*-[Re(CO)$_3$(5,5′-Me$_2$bipy)(CH$_3$CN)]BF$_4$ (**1**) converts the acetonitrile ligand to the amidine ligand (a superbase) in *fac*-[Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NHR)]BF$_4$ products. Each complex has four conceivable isomers (*E*, *E*′, *Z*, and *Z*′) because the amidine CN bonds have double-bond character, and the two remote NHR group substituents are different. The reaction of **1** in acetonitrile is complete in 6 to 96 h (25 °C) and forms *fac*-[Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NHR)]BF$_4$ *E*′ and *Z* isomers. Only the *E*′ isomer formed crystals (R = methyl, isopropyl, isobutyl, *tert*-butyl, and benzyl). Upon dissolution of such crystals in acetonitrile-d_3, NMR spectra with highly dominant *E*′ signals gradually changed (∼15 min at room temperature) to spectra with signals for an equilibrium mixture of *E*′ and *Z* isomers. Such slow *E*′-to-*Z* isomer interchange is also indicated by 2D ROESY NMR data used primarily to assign solution structure. Equilibrium ratios (*E*′:*Z*) of ∼65:35 for R = methyl, isopropyl, and isobutyl and 83:17 for R = *tert*-butyl demonstrate that increasing the remote NHR group steric bulk above a threshold size favors the *E*′ isomer. Consistent with this trend, *fac*-[Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NH$_2$)]BF$_4$, with a remote NH$_2$ (low bulk) group, favors the *Z* isomer. In contrast, although the remote NH(benzyl) group in *fac*-[Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NH(CH$_2$C$_6$H$_5$)]BF$_4$ has only moderate bulk, the *E*′ isomer has high abundance as a result of favorable 5,5′-Me$_2$bipy/benzyl stacking, evidence for which is present in both solid and solution states. The *fac*-[Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NHR)]BF$_4$ *E* isomer can be detected in solvents of low polarity. However, the *Z*′ isomer was not observed, undoubtedly because unfavorable remote-group clashes with the equatorial ligands destabilize this isomer. Challenge studies with a 5-fold excess of 4-dimethylaminopyridine in acetonitrile-d_3 establish that *fac*-[Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NHCH(CH$_3$)$_2$)]BF$_4$ is robust because the isopropylamidine ligand was not displaced, consistent with the superbase character of amidine ligands.

Introduction

The chemistry of amidine complexes of several metals (including platinum, iridium, cobalt, and manganese) has been described in several reviews.[1−3] Because the *fac*-{M^{I}(CO)$_3$} (M = Tc or Re) core is important in radiopharmaceuticals,[4−6] the acetonitrile reaction chemistry of Re^{I} complexes has recently become a subject of scrutiny.[7−9]

Both of the amidine carbon-to-nitrogen bonds have double-bond character. The bond between the amidine carbon and the superbasic coordinated nitrogen[10−12] leads to two configurations dictating the description of amidine stereochemistry as *E* or *Z* (Figure 1). When the remote nitrogen has two different substituents, the two resulting configurations about the bond to the amidine carbon lead to a total of four conceivable configurations depicted in Figure 1 (*E*, *E*′, *Z*, and *Z*′ labels follow previous usage).[13,14] Whereas detection of isomers involving the two configurations about the bond

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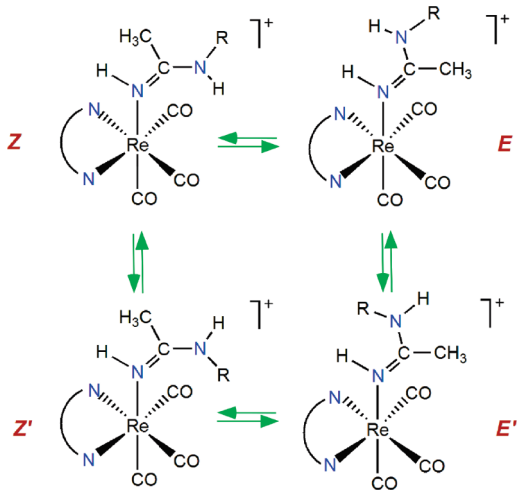

Figure 1. Conceivable *fac*-$[Re(CO)_3(L)(HNC(CH_3)NHR)]^+$ isomers, in which L is a bidentate ligand denoted by N−N donor atoms.

between the amidine carbon and the metal-bound nitrogen is a common occurrence for amidine ligands as well as iminoether ligands,[15] there have been few reports of isomers resulting from restricted rotation about the other amidine carbon-to-nitrogen bond, in part because amidine ligands often have a symmetrical remote NH_2 or NR_2 grouping, thus precluding such isomers. Also, in previously studied Re^I carbonyl compounds, ring formation restricted the amidine stereochemistry.[7,8]

Most reports on monodentate amidine ligands of interest to the current study on complexes with the *fac*-$\{Re^I(CO)_3\}$ core involve pseudo square planar Pt^{II} complexes, about which many studies have been performed in view of the demonstrated cytotoxicity of many iminoether and amidine Pt complexes.[13,16−18] Iminoether and amidine ligands are related. Natile and co-workers have contributed substantially to this field because the first Pt^{II} compound with a trans configuration shown to have anticancer activity was an iminoether complex;[19] these and other investigators later extended such studies to the evaluation of ketimine[20] and amidine[13,21,22] Pt complexes.

In reports on Pt complexes, the dependence of the amidine ligand configuration on the steric bulk and the presence of NH groups of the remote amidine NR_2, NHR, or NH_2 group in the ligand have been assessed.[14,22,23] Both amidine ligands in *trans*-$[Pt(HNC(CH_3)NHCH_3)_2Cl_2]$ have the *Z* configuration,[22]

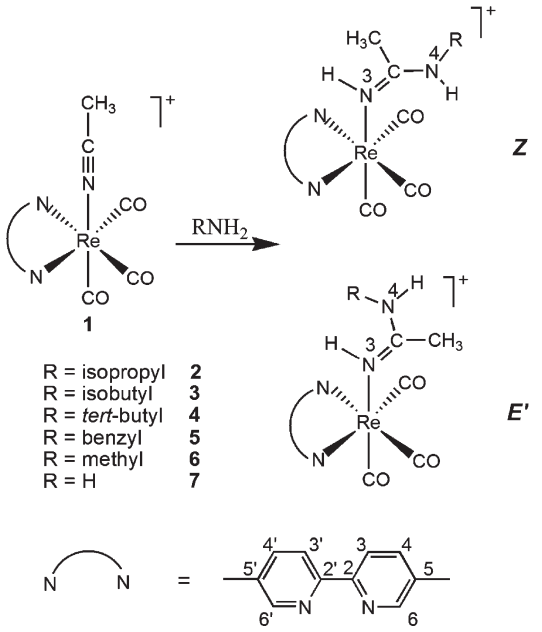

Figure 2. $[Re(CO)_3(L)(HNC(CH_3)NHR)]^+$ isomers observed upon treatment of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(CH_3CN)]^+$ with RNH_2 in acetonitrile at 25 °C.

thought to be stabilized by strong intramolecular H-bonds between chloride and the remote NH group.[22] The amidine ligands in *cis*-$[Pt(HNC(CH_3)N(CH_3)_2)_2Cl_2]$ lack a remote NH group, however, and adopt the *E* configuration.[23] Belluco et al. reported that, on the basis of ^1H NMR data, the addition reactions of primary amines and secondary amines to *cis*- and *trans*-$[PtCl_2(PhCN)_2]$ afforded a complicated mixture of amidine complexes, with the amidine having a mixture of *E*, *E*′, *Z*, and *Z*′ configurations in CD_2Cl_2.[14] In a more recent study, Marzano et al. conducted additional chemical studies of some of these amidine complexes because they have promising antitumor activity.[13] These investigators noted that the reaction forming *cis*-$[PtCl_2(HNC(Ph)NHCH_3)_2]$ afforded a mixture of *E*, *E*′, *Z*, and *Z*′ isomers, unlike such reactions with acetonitrile derivatives; heating converted the product to the *Z* isomer stabilized by intramolecular H-bonding to chloride ligands.[13] Both steric effects and H-bonding play a role in dictating stereochemistry in these Pt amidine complexes.[22,23]

Nucleophilic attack of pyrazole on a coordinated, metal-activated nitrile resulted in the formation of a pyrazolylamidino chelate ring in Re^I carbonyl compounds.[7] We recently reported some unusual Re^I amidine complexes formed by attack of primary or secondary amine terminal groups of polyamines on coordinated acetonitrile, in one case giving a seven-membered chelate ring.[8] The starting complex in that study[8] had three coordinated acetonitrile ligands, and the attacking amines were complicated.

To assess Re^I amidine chemistry, we have now investigated amidine products formed by treating *fac*-$[Re(CO)_3(5,5'\text{-}Me_2bipy)(CH_3CN)]BF_4$ (a complex with only one coordinated acetonitrile) with ammonia and amines (Figure 2). In the resulting complexes, such as *fac*-$[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$, the monodentate amidine ligand can conceivably have any of the four possible configurations. Unlike in the cases of many other Re and Pt complexes, these configurations will not be confounded by H-bonding interactions or controlled by ring formation. Only steric and solvent

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Table 1. Crystal Data and Structural Refinement for $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ Complexes

	R = isopropyl	R = isobutyl	R = *tert*-butyl	R = benzyl	R = H
	2	**3**	**4**	**5**	**7**
empirical formula	$C_{20}H_{24}N_4O_3Re\cdot BF_4$	$C_{21}H_{26}N_4O_3Re\cdot 0.96(BF_4)\cdot 0.04(Br)\cdot 0.33(C_2H_3N)$	$C_{21}H_{26}N_4O_3Re\cdot 0.974(BF_4)\cdot 0.026(Br)$	$C_{24}H_{24}N_4O_3Re\cdot BF_4$	$C_{17}H_{18}N_4O_3Re\cdot BF_4$
fw	641.44	669.73	655.30	689.48	599.36
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	8.4609(5)	8.5566(5)	8.4318(10)	10.4196(10)	13.040(3)
b (Å)	14.4443(10)	17.5817(14)	20.314(3)	22.3643(15)	12.143(3)
c (Å)	19.4276(12)	18.8096(3)	14.2875(15)	11.2768(10)	13.423(4)
α (deg)	90	106.934(3)	90	90	90
β (deg)	102.446(4)	91.331(4)	102.370(7)	104.117(3)	103.453(12)
γ (deg)	90	103.427(5)	90	90	90
V (Å^3)	2318.5(3)	2620.4(3)	2390.4(5)	2548.4(4)	2067.1(9)
T (K)	90	100	90	90	180
Z	4	4	4	4	4
ρ_{calc} (mg/m^3)	1.838	1.698	1.821	1.797	1.926
abs coeff (mm^{-1})	5.30	4.76	5.19	4.83	5.94
$2\theta_{max}$ (deg)	66.2	64.0	65.2	72.0	50.1
R indices[a]	0.024	0.034	0.032	0.030	0.048
wR2 = $[I > 2\sigma(I)]$[b]	0.053	0.078	0.067	0.067	0.091
data/param	8796/310	18182/663	8717/321	11976/344	3649/274

[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 $P = (F_o^2 + 2F_c^2)/3$, $d = 0.0218$, 0.0341, 0.0284, 0.0275, and 0.0331, and $e = 1.2987$, 0.9602, 0, 1.9993, and 2.9329 for complexes **2**−**5** and **7**, respectively.

effects and intrinsic electronic structures of the amidine ligands will influence geometry and stability. Two-dimensional NMR spectroscopy, in conjunction with structural characterization of several complexes by single-crystal X-ray crystallography, has been utilized to evaluate which monodentate amidine ligand configurations (Figure 1) are favored in solution.

Note: We omit the *fac*-designation when discussing specific complexes. Also, to simplify the text, we shall use the terms, *E, E′, Z,* or *Z′* isomer, to designate the isomers of the entire complex with the amidine ligand in the respective configurations.

Experimental Section

Starting Materials. $Re(CO)_5Br$ was synthesized as described in the literature.[24] $Re_2(CO)_{10}$, 5,5′-dimethyl-2,2′-bipyridine (5,5′-Me_2bipy), isopropylamine, isobutylamine, *tert*-butylamine, benzylamine, anhydrous methylamine and ammonia in steel cylinders, and $AgBF_4$ were obtained from Aldrich. $[Re(CO)_3(CH_3CN)_3]BF_4$ was synthesized by a slight modification of a known procedure.[25] The synthesis of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(CH_3CN)]BF_4$ (**1**) from $[Re(CO)_3(CH_3CN)_3]BF_4$ is described elsewhere.[26] Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

NMR Measurements. ^{1}H NMR spectra were recorded on a 400 MHz Bruker 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. For specific assignments of signals listed in the synthetic section below, please see tables in the text and the Supporting Information.

X-ray Data Collection and Structure Determination. Intensity data were collected at low temperature on a Nonius Kappa CCD diffractometer fitted with an Oxford Cryostream cooler with graphite-monochromated Mo Kα ($\lambda = 0.71073$ 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 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 N−H hydrogen atoms, which were refined individually where possible. A torsional parameter was refined for each methyl group. For compound **3**, the contribution to the structure factors from disordered solvent was removed by using SQUEEZE,[29] amounting to 4/3 molecules of acetonitrile per unit cell. For compounds **3** and **4**, BF_4^- sites were shared by a small amount of bromide, and the occupancies of BF_4^- and Br^- were constrained to sum to unity. The occupancies were fixed in final refinements for **3**. The structure of compound **6** was determined from a crystal having more substantial substitutional disorder for the anion, apparently about 52% BF_4^- and 48% ReO_4^-. In compound **3**, the isobutyl group of one of the two independent cations is disordered into two orientations with 0.725(7)/0.275(7) occupancy. Crystal data and details of refinements are listed in Table 1, except for compound **6**, for which the cation is illustrated in the Supporting Information.

Synthesis of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (2). Isopropylamine (52 μL, 0.60 mmol) was added to an acetonitrile solution (6 mL) of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(CH_3CN)]BF_4$ (**1**, 0.04 g, 0.06 mmol), and the reaction mixture was stirred at room temperature for 24 h. The volume was reduced to ∼1 mL by rotary evaporation, and addition of diethyl ether (∼10 mL) produced a yellow crystalline material, which was collected on a filter and washed with diethyl ether and dried; yield, 40 mg (63%). An NMR spectrum recorded immediately upon dissolution of this material showed mostly one set of signals. ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.84 (s, 2H, H6/6′), 8.28 (d, 2H, H3/3′), 8.04 (d, 2H, H4/4′), 6.10 (b, 1H, NH), 4.51(1H, NH), 3.14 (m, 1H, CH), 2.47 (s, 6H, 5/5′-CH_3), 2.07 (s, 3H, CCH_3), 0.74 (d, 6H, $2CH_3$). However, an NMR spectrum recorded after 15 min shows an equilibrium mixture of *E′* and *Z* isomer signals, as observed in the reactions monitored by NMR spectroscopy and described below.

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Amine reactions of **1** (10 mM in acetonitrile-d_3, 600 μL) were monitored by NMR spectroscopy; we refer to this as the 10 mM solution. The first spectrum recorded at 5 min showed only reactants. On addition of a 10% excess of isopropylamine (5 μL) to the 10 mM solution, NMR signals indicative of a mixture of E' and Z isomers of **2** were observed within 30 min (at 6 h, E':Z = 64:36), and these signals continued to grow (while maintaining the same ratio of isomers) until no starting complex remained the next day. ^{1}H NMR signals (ppm) in acetonitrile-d_3 (see Figure 2 for atom numbering): 8.84 (s, H6/6′), 8.74 (s, H6/6′), 8.28 (overlapping d, H3/3′), 8.04 (d, H4/4′), 6.10 (b, NH), 5.57 (b, NH), 5.33(NH), 4.51(NH), 3.69 (m, CH), 3.14 (m, CH), 2.47 (s, 5/5′-CH_3), 2.07 (s, CCH_3), 1.89 (s, CCH_3), 1.21 (d, $2CH_3$), 0.74 (d, $2CH_3$). Slow evaporation of this acetonitrile solution yielded X-ray quality crystals of the E' isomer. ^{1}H NMR spectrum in acetonitrile-d_3: identical to that of the bulk precipitate.

[Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NHCH$_2$CH(CH$_3$)$_2$)]BF$_4$ (3). The method described above but with isobutylamine (60 μL, 0.60 mmol) produced a yellow crystalline material; yield, 35 mg (54%). ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.84 (s, 2H, H6/6′), 8.29 (d, 2H, H3/3′), 8.04 (d, 2H, H4/4′), 6.29 (b, 1H, NH), 4.52 (1H, NH), 2.49 (m, 2H, CH_2), 2.47 (s, 6H, 5/5′-CH_3), 2.08 (s, 3H, CCH_3), 1.82 (m, 1H, CH), 0.56 (d, 6H, CH_3).

On addition of a 10% excess of isobutylamine (6 μL) to the 10 mM solution, NMR signals of a mixture of E' and Z isomers of **3** were observed within 10 min, and the reaction was complete the next day. ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.84 (s, H6/6′), 8.73 (s, H6/6′), 8.29 (overlapping d, H3/3′), 8.05 (d, H4/4′), 6.29 (b, NH), 5.85 (b, NH), 5.34 (NH), 4.52 (NH), 3.06 (m, CH_2), 2.49 (m, CH_2), 2.47 (s, 5/5′-CH_3), 2.08 (s, CCH_3), 1.87 (s, CCH_3), 1.82 (m, CH), 1.22 (m, CH), 0.95 (d, CH_3), 0.56 (d, CH_3).

X-ray quality crystals of the E' isomer of **3** were produced upon slow evaporation of the solution of the crystalline material (10 mg) in a 1:5 (v/v) mixture of acetonitrile/diethyl ether.

[Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NHC(CH$_3$)$_3$)]BF$_4$ (4). The method described above but with *tert*-butylamine (65 μL, 0.60 mmol) produced a yellow crystalline precipitate (yield, 32 mg, 49%), but the reaction time was longer (4 days). ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.85 (s, 2H, H6/6′), 8.30 (d, 2H, H3/3′), 8.06 (d, 2H, H4/4′), 6.11 (b, 1H, NH), 4.30 (1H, NH), 2.47 (s, 6H, 5/5′-CH_3), 2.01 (s, 3H, CCH_3), 0.80 (s, 9H, CH_3).

On addition of a 10% excess of *tert*-butyl amine (6.5 μL) to the 10 mM solution, NMR signals of a mixture of E' and Z isomers of **4** were observed only after 1 h (reaction time, ~4 days). ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.85 (s, H6/6′), 8.73 (s, H6/6′), 8.30 (overlapping d, H3/3′), 8.06 (d, H4/4′), 6.11 (b, NH), 5.97 (b, NH), 5.38 (NH), 4.30 (NH), 2.47 (s, 5/5′-CH_3), 2.01 (s, CCH_3), 1.95 (s), 1.38 (s, CH_3), 0.80 (s, CH_3). The resulting solution yielded X-ray quality crystals upon slow evaporation.

[Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NHCH$_2$C$_6$H$_5$)]BF$_4$ (5). The method described above but with benzylamine (66 μL, 0.60 mmol) produced a yellow crystalline precipitate; yield, 38 mg (55%). ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.64 (s, 2H, H6/6′), 7.96 (d, 2H, H3/3′), 8.05 (d, 2H, H4/4′), 7.15 (t, 1H), 7.06 (t, 2H), 6.91 (b, 1H, NH), 6.09 (d, 2H), 4.38 (1H, NH), 3.94 (d, 2H, CH_2), 2.47 (s, 6H, 5/5′-CH_3), 2.18 (s, 3H, CCH_3).

On addition of a 10% excess of benzylamine (7 μL) to the 10 mM solution, NMR signals of a mixture of E' and Z isomers of **5** were observed within 15 min, and the reaction was complete the next day. ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.76 (s, H6/6′), 8.64 (s, H6/6′), 8.27 (d, H4/4′), 8.05 (overlapping d, H3/3′ Z and H4/4′ E'), 7.96 (d, H4/4′), 7.38 (t, benzyl), 7.31 (t, benzyl), 7.22 (d, benzyl), 7.15 (t, benzyl), 7.06 (t, benzyl), 6.91 (b, NH), 6.32 (b, NH), 6.09 (d, benzyl), 5.54 (NH), 4.45 (d, CH_2), 4.30 (NH), 3.94 (d, CH_2), 2.44 (s, 5/5′-CH_3), 2.18 (s, CCH_3), 1.84 (s, CH_3). The resulting solution yielded X-ray quality crystals upon slow evaporation.

Synthesis of [Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NHCH$_3$)]BF$_4$ (6). The method described above but with methylamine (~30 μL, volume approximate because the volatile methylamine was added from an inverted container) produced a yellow precipitate; yield, 32 mg (52%). ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.83 (s, 2H, H6/6′), 8.28 (d, 2H, H3/3′), 8.05 (d, 2H, H4/4′), 6.80 (b, 1H, NH), 4.50 (1H, NH), 2.25 (d, 3H, NCH_3), 2.47 (s, 6H, 5/5′-CH_3), 2.07 (s, 3H, CCH_3). Anal. Calcd for $C_{18}H_{20}BF_4N_4O_3Re$: C, 35.25; H, 3.29; N, 9.13. Found: C, 35.36; H, 3.26; N, 9.02.

On addition of a 10% excess of methylamine (~5 μL) to the 10 mM solution, NMR signals indicative of a mixture of E' and Z isomers of **6** were observed within 20 min (E':Z = 66:34) and continued to grow, maintaining the same ratio of isomers until no starting complex signal remained (~6 h). ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.83 (s, H6/6′), 8.73 (s, H6/6′), 8.28 (overlapping d, H3/3′), 8.05 (d, H4/4′), 6.80 (b, NH), 5.90 (b, NH), 5.29 (NH), 4.50 (NH), 2.87 (d, NCH_3), 2.25 (d, NCH_3), 2.47 (s, 5/5′-CH_3), 2.07 (s, CCH_3), 1.86 (s, CCH_3). Upon slow evaporation, the resulting solution yielded X-ray quality crystals of the E' isomer.

Synthesis of [Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NH$_2$)]BF$_4$ (7). The method described above but with ammonia bubbling through for ~5 min (medium flow rate) produced a yellow crystalline precipitate; yield, 25 mg (41%). ^{1}H NMR spectrum in acetonitrile-d_3: identical to that given below. Ammonia gas was bubbled through a 10 mM solution of [Re(CO)$_3$(5,5′-Me$_2$bipy)-(CH$_3$CN)]BF$_4$ in acetonitrile-d_3 (600 μL), and the solution was monitored by NMR spectroscopy. NMR signals of a mixture of E' and Z isomers of **7** were observed. ^{1}H NMR signals (ppm) in acetonitrile-d_3: 8.79 (s, H6/6′), 8.75 (s, H6/6′), 8.29 (overlapping d, H3/3′), 8.04 (d, H4/4′), 6.30 (b, NH), 5.93 (b, NH), 5.45 (NH), 5.33 (NH), 2.48 (s, 5/5′-CH_3), 2.12 (s, CCH_3), 1.83 (s, CCH_3). When the experiment was repeated in $CDCl_3$, a mixture of isomers formed. ^{1}H NMR signals (ppm) in $CDCl_3$: 8.75 (s, H6/6′), 8.60 (s, H6/6′), 8.27 (overlapping d, H3/3′), 7.92 (d, H4/4′), 6.15 (b, NH), 5.86 (b, NH), 5.58 (NH), 2.50 (s, 5/5′-CH_3), 2.21 (s, CCH_3), 2.17 (s, CCH_3). Slow evaporation of this chloroform solution yielded X-ray quality crystals.

Challenge Reactions. A 5 mM solution of [Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC(CH$_3$)NHCH(CH$_3$)$_2$)]BF$_4$ (**2**) in acetonitrile-d_3 (600 μL) was treated with a 5-fold excess of 4-dimethylaminopyridine (2.0 mg, 25 mM), and the solution was monitored by ^{1}H NMR spectroscopy. A similar experiment was conducted in $CDCl_3$.

Results and Discussion

Synthesis. Syntheses of [Re(CO)$_3$(5,5′-Me$_2$bipy)(HNC-(CH$_3$)NHR)]BF$_4$ complexes were carried out in acetonitrile (R = isopropyl (**2**), isobutyl (**3**), *tert*-butyl (**4**), benzyl (**5**), and methyl (**6**)) at room temperature (Figure 2). For R = H (**7**), acetonitrile or chloroform was used. Reactions were monitored at intervals of 10 min, 1 h, and 1 to 4 days (sometimes also 5 min, 30 min, or 6 h) by NMR spectroscopy. Times required for completion of reaction varied (~6 h for **6**; ~1 day for **2**, **3**, **5**, **6**, and **7**; and ~4 days for **4**). For compounds **2** to **6**, the ratio of E' to Z isomers remained the same throughout the course of the reaction. For **7**, which has a symmetrical remote nitrogen group, the isomer designation is restricted to E and Z; experimentally, a trace amount of the E isomer was observed in addition to the major isomer, Z.

Structural Results. Complexes structurally characterized here, having the general formula, [Re(CO)$_3$(5,5′-Me$_2$bipy)-(HNC(CH$_3$)NHR)]BF$_4$ (R = alkyl, benzyl or H, Figures 3 and 4, and Supporting Information, Figure S1), exhibit a distorted octahedral structure, with the three carbonyl ligands occupying one face. The remaining three coordination sites are occupied by the two nitrogen atoms of the

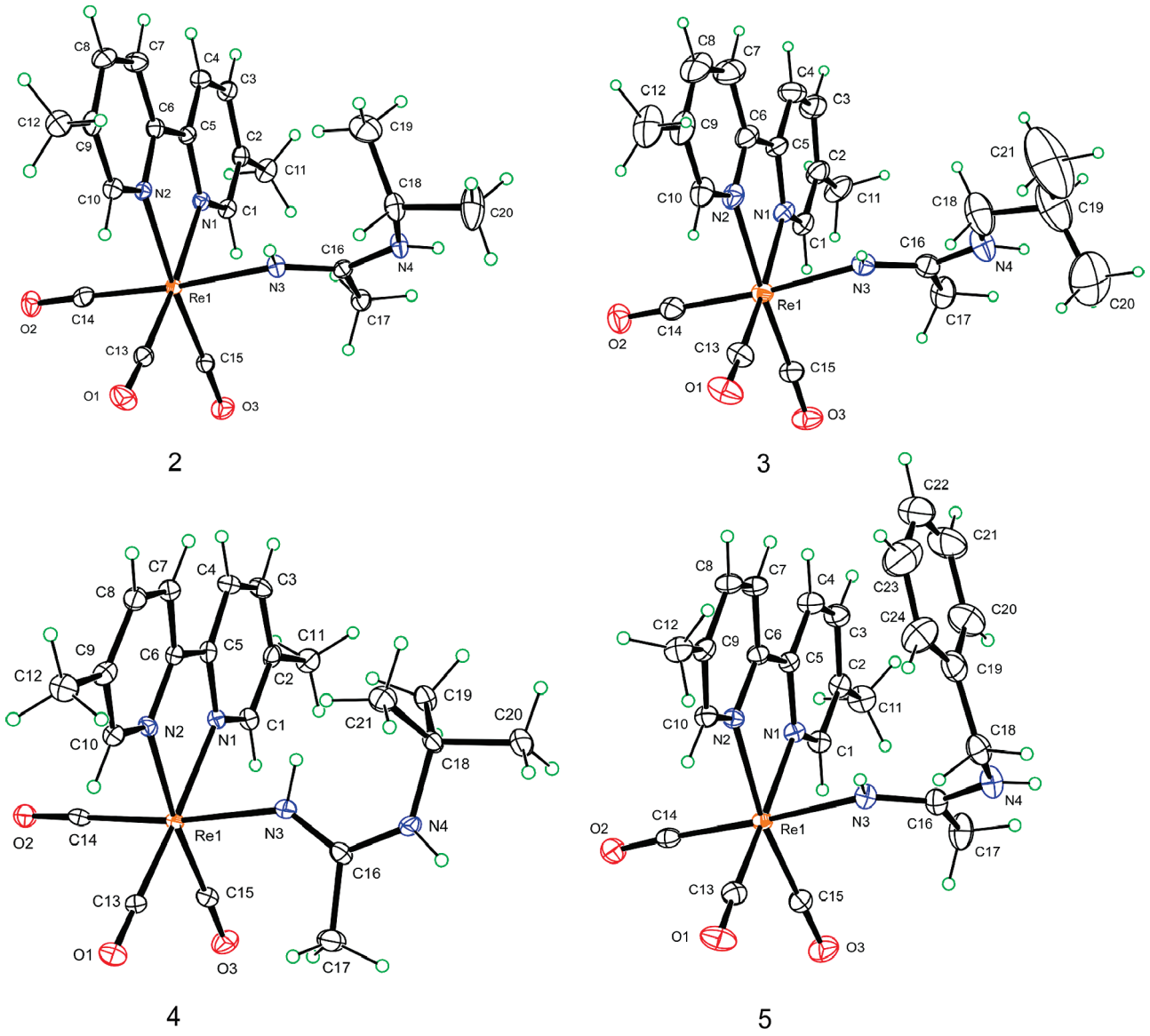

Figure 3. ORTEP plots of the cations in $[Re(CO)_3(5,5'\text{-}Me_2bipy)(E'\text{-}HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**), $[Re(CO)_3(5,5'\text{-}Me_2bipy)(E'\text{-}HNC(CH_3)NHCH_2CH(CH_3)_2)]BF_4$ (**3**), $[Re(CO)_3(5,5'\text{-}Me_2bipy)(E'\text{-}HNC(CH_3)NHC(CH_3)_3)]BF_4$ (**4**), and $[Re(CO)_3(5,5'\text{-}Me_2bipy)(E'\text{-}HNC(CH_3)NHCH_2C_6H_5)]BF_4$ (**5**). Thermal ellipsoids are drawn with 50% probability.

5,5′-Me_2bipy ligand and a nitrogen atom of the neutral monodentate amidine ligand. Crystal data and details of the structural refinement for these complexes are summarized in Table 1. The atom numbering systems in the ORTEP figures are used to describe the solid-state data. The Re−C bond distances (not shown) involving the CO group trans to the amidine group are not significantly different from those of the other Re−C bonds.

These $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ complexes (R = isopropyl (**2**), isobutyl (**3**), *tert*-butyl (**4**), benzyl (**5**), and methyl (**6**)) have an amidine ligand in the E' configuration in the solid state (Figure 3 and Supporting Information, Figure S1), even though NMR data show that both E' and Z isomers exist in acetonitrile (discussed below). The molecular structure of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NH_2)]BF_4$ (**7**) reveals that this non sterically bulky amidine ligand has the Z configuration (Figure 4), in contrast to the structures found here for all other crystals.

The Re−N bond lengths of the amidine complexes (Table 2) are comparable to those found for typical Re sp^2 nitrogen bond lengths, which range from 2.14 to 2.18 Å.[30] Likewise, in all cases the bond distances from the amidine carbon (C16) to the two nitrogen atoms, N3 and N4 (see Figure 2), are closer to the average sp^2 C double-bond length to N (C═N, ∼1.28 Å) than to the average sp^3 C single-bond length to N (C−N, 1.47 Å).[31] For example, in $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**) (Figure 3), the bond distances are 1.308(3) Å (N3−C16) and 1.339(3) Å (N4−C16). The N3−C16 (1.266(12) Å) and N4−C16 (1.359(12) Å) bond distances of **7** (Figure 4) are generally similar to the relevant distances (Table 2) of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ complexes **2** to **5**.

(30) He, H.; Lipowska, M.; Xu, X.; Taylor, A. T.; Carlone, M.; Marzilli, L. G. *Inorg. Chem.* **2005**, *44*, 5437–5446.
(31) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc. Perkin Trans. 2* **1987**, S1–S19.

The relevant angles of the amidine moiety are all ~120° (Table 2), and these facts all indicate electron delocalization along the N−C−N bonds. Furthermore, in all cases as exemplified by **2**, the N4−C16 bond is slightly but significantly longer than the N3−C16 bond (Table 2), suggesting slightly less double-bond character. These slight differences are reflected in the ease of rotation about the N−C bonds.

The orientation of the amidine ligand of **4** is different from that of compounds **2**, **3**, and **7**. (Supporting Information, Figure S2 shows different orientations of the amidine ligands when the Me_2bipy plane is oriented in a similar manner). These differences in orientation are present in the solid state; there are no indications to imply their presence in solution.

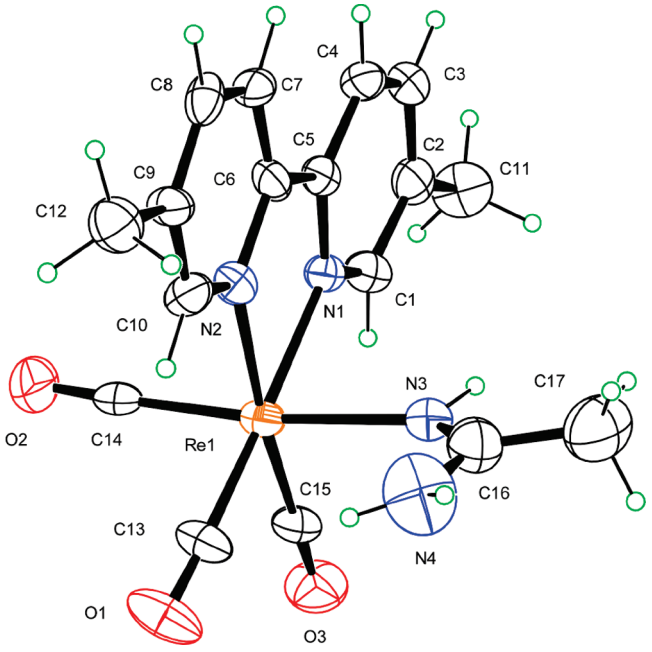

Figure 4. ORTEP plot of the cation in $[Re(CO)_3(5,5'\text{-}Me_2bipy)(Z\text{-}HNC(CH_3)NH_2)]BF_4$ (**7**). Thermal ellipsoids are drawn with 50% probability.

The molecular structure of the benzylamidine complex, $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH_2C_6H_5)]BF_4$ (**5**, Figure 3), shows that the phenyl ring of the amidine moiety is stacked above the bipyridine ligand. The closest C-to-C non-bonded distances are 3.584, 3.586, and 3.953 Å. Stacking is depicted in side and top-down views of the stacked rings in the Supporting Information, Figure S3. Effects of this stacking on NMR shifts of the bipyridine signals are discussed later.

NMR Spectroscopy. General Considerations. All complexes reported in this study were characterized by NMR spectroscopy in acetonitrile-d_3, and selected complexes were studied in other solvents. COSY and ROESY experiments aided in the assignment of the signals of complexes **2**, **3**, and **4** in acetonitrile-d_3 and of **2** in $CDCl_3$ and CD_2Cl_2. (For the NMR discussion, the atom numbering in Figure 2 is used.) NMR spectra recorded immediately after dissolving crystals of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ (R = isopropyl (**2**), isobutyl (**3**), *tert*-butyl (**4**), benzyl (**5**) and methyl (**6**)) complexes in several solvents showed two to three sets of signals, which changed in intensity until equilibrium was reached. In general, one set of signals grew slowly, and all other sets (one or two sets, depending on solvent) decreased with time.

Because rotation about the bond between the amidine carbon and the Re-bound N is expected to be slow compared to the rotation about the bond between the amidine carbon and the remote N, this behavior indicates that the first signals observed are from the E' or E isomer (the solid has the E' isomer). This reasoning allowed us to assign unambiguously the initial set(s) of peaks to an isomer with the amidine ligand in the E' or E configuration and the second set to the isomer with the amidine ligand in the Z' or Z configuration. However, 2D NMR data in combination with studies in several solvents and in mixtures of solvents allowed us to conclude that in every case the E' and Z isomers of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)\text{-}NHR)]BF_4$ complexes coexisted in polar solvents such as acetonitrile-d_3. Only in solvents of low polarity do we observe signals for the E isomer. The Z' isomer was not

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ Complexes

	R = isopropyl	R = isobutyl	R = *tert*-butyl	R = benzyl	R = H
	2	**3**	**4**	**5**	**7**
			Bond Distances		
Re−N1	2.1829(19)	2.167(3)	2.183(2)	2.1746(19)	2.169(6)
Re−N2	2.1819(18)	2.178(3)	2.178(3)	2.1874(18)	2.180(6)
Re−N3	2.1810(18)	2.174(3)	2.158(2)	2.181(2)	2.156(7)
N3−C16	1.308(3)	1.307(4)	1.302(4)	1.298(3)	1.266(12)
N4−C16	1.339(3)	1.331(4)	1.340(4)	1.341(3)	1.359(12)
			Bond Angles		
N1−Re−N2	75.14(7)	74.89(10)	74.88(9)	75.24(7)	75.3(3)
N1−Re−N3	85.31(7)	83.92(10)	79.73(9)	85.78(7)	80.4(3)
N2−Re−N3	81.33(7)	80.76(10)	79.89(9)	77.56(7)	84.6(3)
Re−N3−H3N	109.5(18)	111(3)	111(2)	115(2)	112.5
Re−N3−C16	135.43(16)	135.4(2)	138.7(2)	135.59(16)	135.1(7)
C16−N3−H3N	114.9(18)	113(3)	110(2)	110(2)	112.5
N3−C16−N4	122.9(2)	123.1(3)	123.6(3)	123.4(2)	123.2(10)
N3−C16−C17	121.45(19)	121.4(3)	120.2(3)	120.8(2)	121.6(10)
N4−C16−C17	115.64(18)	115.4(3)	116.2(3)	115.8(2)	115.1(11)
C16−N4−C18	125.25(18)	124.9(3)	126.8(2)	123.9(2)	[a]

[a] Not applicable.

found in any solvent. As an illustration of our solution studies and 2D NMR analysis of amidine complexes in polar solvents, we first discuss **2** (Figure 3) in acetonitrile-d_3; we then extend the discussion to other compounds in this solvent and eventually to other solvents.

The coupling constants (J) are uninformative and do not change appreciably from isomer to isomer or solvent to solvent. For example in acetonitrile-d_3, $CDCl_3$, CD_2Cl_2, and DMSO-d_6, the N4H and CH coupling values to the CH_2 signal of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)\text{-}NHCH_2CH(CH_3)_2)]BF_4$ (**3**) fall within the range of 6.0−6.6 Hz for all isomers (E', E, or Z). The J values of the isobutyl methyl signal coupling to the CH signal are ~6.6−6.7 Hz in all solvents. The 5,5′-Me_2bipy H3/3′-to-H4/4′ coupling constants have nearly invariant values of 8.3−8.4 Hz in all solvents for all isomers of all compounds.

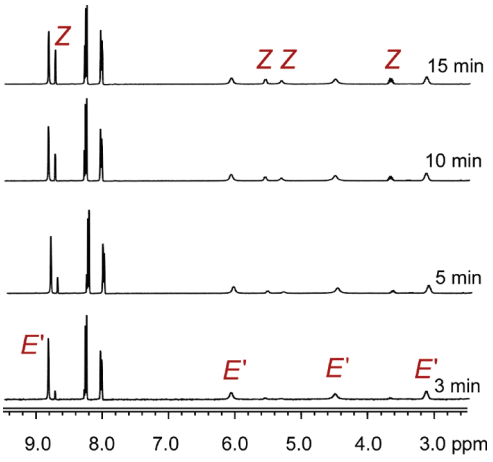

Figure 5. ^1H NMR spectra as a function of time after crystals of the E' isomer of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**) were dissolved in acetonitrile-d_3 at 25 °C.

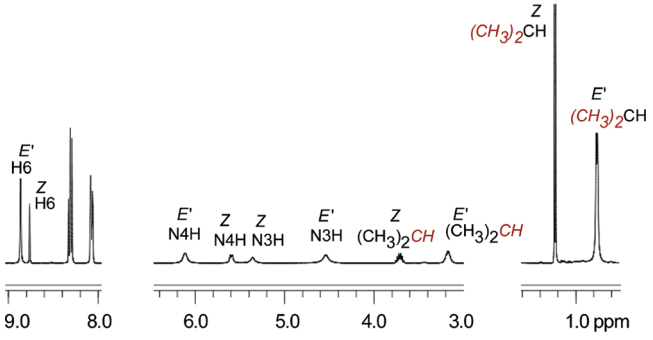

Figure 6. ^1H NMR spectrum of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)\text{-}NHCH(CH_3)_2)]BF_4$ (**2**) in acetonitrile-d_3 at 25 °C.

NMR Studies of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)\text{-}NHCH(CH_3)_2)]BF_4$ (2) in Acetonitrile-d_3. Upon dissolution of **2** (Figure 3) in acetonitrile-d_3, the NMR spectrum showed two sets of signals (Figure 5). The less intense set of signals grew in intensity until equilibrium was reached (~15 min, Figure 5). Integration as well as the slow isomerization of the complex on dissolution allowed us to identify all signals attributable to each of the two sets. Two singlets for the CCH_3 groups derived from acetonitrile occur at 1.89 (Z' or Z) and 2.07 (E' or E) ppm. The four broad peaks between 4.5 and 6.1 ppm (Figure 6) were identified as NH signals by addition of K_2CO_3/D_2O. A CH multiplet at 3.15 ppm (integrating to one proton) for the E' or E isomer has a COSY cross-peak with the CH_3 doublet (0.74 ppm) from the isopropyl group (Figure 7). This CH multiplet correlated in turn with an NH signal at 6.10 ppm, assigning this signal to N4H (Table 3). (See Figure 2 for designations of the N3H and N4H protons.) Likewise, a similar correlation was observed for peaks of the Z' or Z isomer of **2**; the CH_3 doublet (ppm) correlated with the CH multiplet (3.69 ppm), which correlated with the N4H signal at 5.57 ppm (Figure 7).

A strong NOE cross-peak seen in the ROESY spectrum (Supporting Information, Figure S4) between the N3H signal (5.33 ppm) and the CCH_3 singlet (1.89 ppm) for the Z' or Z isomer, together with a strong NOE peak between this CCH_3 singlet and the CH multiplet (3.69 ppm), establishes that this is the Z isomer. The absence of a N4H−CCH_3 NOE cross-peak excludes the presence of the Z' isomer. There is no NOE peak between the N3H signal (4.51 ppm) and the CCH_3 signal (2.07 ppm) attributable to the E' or E isomer, a result consistent with the assignment of these signals to the E' isomer. The presence

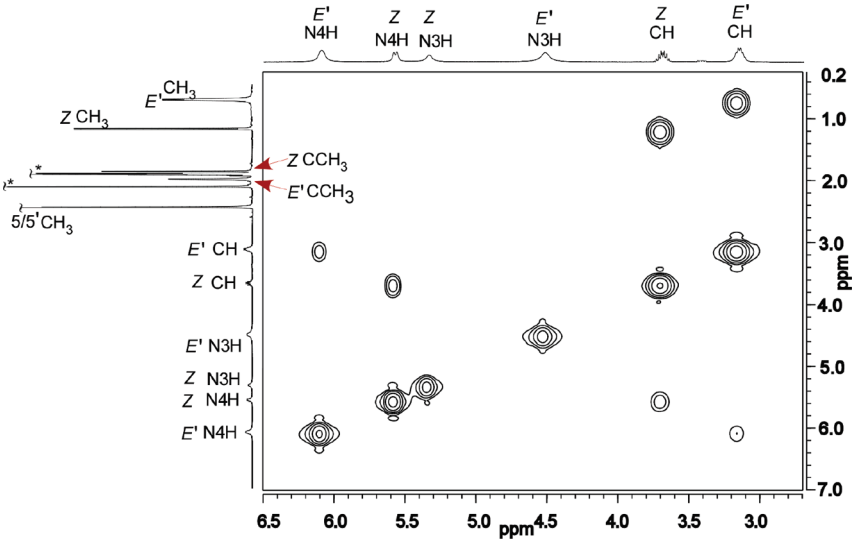

Figure 7. $^1H-^1H$ COSY NMR spectrum of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**) in acetonitrile-d_3 at 25 °C.

Table 3. Selected ^{1}H NMR Shifts (ppm) for $Re(CO)_3[(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ in Acetonitrile-d_3 at 25 °C

R	isomer	N3H	N4H	CH_3 (formerly CH_3CN)	$N4CH_n$[a]	H6/6′
methyl (**6**)	*E*′	4.50	6.80	2.07	2.25(d)[b]	8.83
	Z	5.29	5.90	1.86	2.87(d)[b]	8.73
isopropyl (**2**)	*E*′	4.51	6.10	2.07	3.14(m)[c]	8.84
	Z	5.33	5.57	1.89	3.69(m)[c]	8.74
isobutyl (**3**)	*E*′	4.52	6.29	2.08	2.49(m)[d]	8.84
	Z	5.34	5.85	1.87	3.06(m)[d]	8.73
tert-butyl (**4**)	*E*′	4.30	6.11	2.01	*e*	8.85
	Z	5.38	5.97	1.95	*e*	8.73
benzyl (**5**)	*E*′	4.30	6.91	2.18	3.94(d)[d]	8.64
	Z	5.54	6.32	1.84	4.45(d)[d]	8.76
H (**7**)	*E*′	*f*	*f*	2.12		8.79
	Z	5.45	6.30, 5.93(b)	1.83		8.75

[a] The $N4CH_n$ signals vary in multiplicity according to the R group. [b] $n = 3$. [c] $n = 1$. [d] $n = 2$. [e] $n = 0$. [f] Not observed.

of a very strong NOE peak between the N3H signal (4.51 ppm) and the CH multiplet (3.15 ppm) confirms beyond doubt that this isomer indeed has the *E*′ configuration because the distance between the N3H and CH protons is short for the *E*′ isomer (2.18 Å) but is too long (3.51 to 4.39 Å, Supporting Information) to give a strong NOE peak for all of the other isomers. Thus, we conclude that the two sets of signals observed for **2** in acetonitrile-d_3 arise from the *E*′ and *Z* isomers. The alternative conclusion that the signals arise from a mixture of rapidly interconverting (*E*′/*E* and *Z*′/*Z*) isomers is not supported by the solvent and temperature dependence studies described below.

The 5,5′-Me_2bipy signals of **2** were completely assigned by using NOE and COSY cross-peaks between the 5/5′ CH_3 signals and the H6/6′ and H4/4′ signals for **2** (Supporting Information, Figure S5). The occurrence of only one set of 5,5′-Me_2bipy signals for each isomer indicates rapid rotation about the Re−N3 bond.

NMR Studies of Other $[Re(CO)_3(5,5'\text{-}Me_2bipy)(amidine)]BF_4$ Complexes in Acetonitrile-d_3. The same methods described above revealed that two isomers formed upon dissolution of crystals for compounds **3** to **6**. For all except **5** (see below), the clear chemical shift patterns for the H6/6′ signals in acetonitrile-d_3 (Table 3) indicate that these are *E*′ and *Z* isomers. For **3** and **4**, these conclusions were supported by 2D NMR spectra. For both isomers of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ (R = isopropyl (**2**), isobutyl (**3**), *tert*-butyl (**4**), and methyl (**6**)) complexes, the N3H signals (N bound to Re) are more upfield (4.30−5.34 ppm) than the N4H signals (5.57−6.80 ppm) in acetonitrile-d_3. The signals of the methyl group derived from acetonitrile range from 2.01 to 2.08 ppm for the *E*′ isomers and from 1.86 to 1.95 ppm for the *Z* isomers. Thus, for the typical R group, the isomers are easily identified.

Upfield 5,5′-Me_2bipy Signals of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH_2C_6H_5)]BF_4$ (5) Arising from Stacking. For complexes **2**, **3**, **4**, and **6**, with non-anisotropic R groups, the average shifts in acetonitrile-d_3 are 8.84 (H6/6′), 8.04 (H4/4′), and 8.27 (H3/3′) ppm for *E*′ isomer signals and 8.73 (H6/6′), 8.04 (H4/4′), and 8.29 (H3/3′) ppm for *Z* isomer signals. (The H4/4′ and H3/3′ signals of the *E*′ isomer overlap with the H4/4′ and H3/3′ signals of the *Z* isomer, in some cases.) For $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH_2C_6H_5)]BF_4$ (**5**, Figure 3), the *Z* isomer H6/6′, H4/4′ and H3/3′ signals (8.76, 8.05, and 8.27 ppm, respectively) have the typical values; however, the signals for the *E*′ isomer all appear upfield (8.64, 7.96, and 8.05 ppm, respectively) to typical values of the *E*′ isomer of compounds **2**, **3**, **4**, and **6** (see Experimental Section). (For **5**, the upfield-shifted H3/3′ doublet of the *E*′ isomer overlaps with the H4/4′ doublet of the *Z* isomer.)

Table 4. Distribution (%) of *E*′ and *Z* Isomers of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ in Acetonitrile-d_3 at 25 °C

R	*E*′	*Z*
methyl (**6**)	66	34
isopropyl (**2**)	64	36
isobutyl (**3**)	65	35
tert-butyl (**4**)	82	18
benzyl (**5**)	83	17
H (**7**)	12	88

The upfield shifts of the 5,5′-Me_2bipy signals of the *E*′ isomer of **5** can be reasonably explained only by the stacking of the phenyl moiety over the 5,5′-Me_2bipy ligand in solution. This explanation was apparent when the complex was first prepared, and it derived support when the solid-state structure showed a stacking interaction (Supporting Information, Figure S3). As we noted above and for reasons expanded upon below, the major form that can be present upon dissolution has to be either the *E*′ or the *E* isomer. The *E* isomer (Figure 1) cannot stack and can be excluded because the upfield shifts cannot be explained without phenyl/5,5′-Me_2bipy stacking. Free rotation around the Re−N3 bond, which must occur in solution, explains both the presence of one signal for each type of 5,5′-Me_2bipy proton and the upfield shifts of the H6/6′ and H4/4′ signals.

Influence of Isomerization Rate on NMR Spectra of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH_2CH(CH_3)_2)]BF_4$ (3). ^{1}H NMR spectra of **3** (5 mM) recorded from −15 to 55 °C in acetonitrile-d_3, showed no change in the equilibrium ratios of the H6/6′ and the NH NMR signals and no major shift in these signals. Thus, the *E*′-to-*Z* interchange is too slow on the NMR time scale to influence spectra. The presence of only small EXSY cross-peaks at 65 °C in a ROESY spectrum in acetonitrile-d_3 (not shown) further confirms that the interchange between the *E*′ and *Z* isomers of **3** is slow on the NMR time scale. In addition, at −15 °C no additional signals, which would indicate the presence of the *E* or *Z*′ isomers, were observed.

Dependence of the *E*′:*Z* Equilibrium Ratio on the Nature of R in Acetonitrile. NMR data for a series of amidine complexes in acetonitrile-d_3 at room temperature allowed us to determine the *E*′:*Z* equilibrium ratio (Table 4). The similarity of these *E*′:*Z* ratios for **2** (R = isopropyl), **3** (R = isobutyl), and **6** (R = methyl) indicates that a ratio of ∼65:35 may be the "normal" ratio of *E*′ to *Z* isomers in acetonitrile. Put differently, the ratio is dictated by the relative steric bulk of the N4H and the CCH_3, which project toward the equatorial plane, and by the natural relative energy of the molecular orbitals. The higher equilibrium ratio (*E*′:*Z* = 82:18) for **4** (R = *tert*-butyl) than the baseline value establishes that as the bulk of the amidine ligand R substituent rises above a threshold size, such as for R = *tert*-butyl, the high bulk favors the *E*′ isomer. Likewise, although the benzyl group in **5** has only moderate bulk,

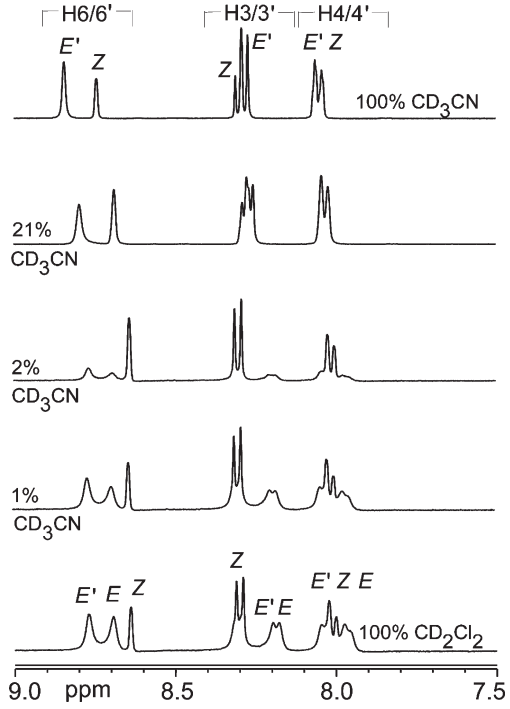

Figure 8. ^{1}H NMR spectra illustrating the distribution of E', E, and Z isomers of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**) in CD_2Cl_2 (with percent acetonitrile-d_3 noted on trace) and acetonitrile-d_3 at 25 °C. *Note*: the bottom two spectra were recorded before equilibrium was reached.

phenyl/5,5′-Me_2bipy stacking favors the E' isomer in acetonitrile (Table 4).

Isomers of 2 Present in Less Polar Solvents, CD_2Cl_2 and $CDCl_3$. When crystals of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**) were dissolved in CD_2Cl_2 and $CDCl_3$, signals for *three* isomers were observed (Figure 8 and Supporting Information, Figure S6). Two sets of signals maintained the same ratio and decreased with time. The third set grew in intensity and has all the characteristics expected for the Z isomer.

In $CDCl_3$, of the two sets of signals that decreased with time, one set had medium intensity (designated as m), and the other had weak intensity (designated as w). In a ROESY spectrum of **2** (Supporting Information, Figure S6) in $CDCl_3$ at 25 °C, EXSY peaks between the respective signals of the m and w sets are present as follows (ppm): CH multiplets, 3.50 (m) and 3.13 (w); N3H, 5.22 (m) and 4.30 (w); N4H, 6.07(m) and 5.77(w); and CH_3 doublets, 1.07(m) and 0.80 (w). The m signals were assigned to the E isomer by an N4H−N3H NOE peak. Also, an NOE cross-peak between the CCH_3 (2.23 ppm) signal and the CH multiplet (3.50 ppm) establishes without doubt that the m set belongs to the E isomer. The w signals belong to the E' isomer, as confirmed above by EXSY peaks. The most intense set of signals was assigned to the Z isomer by NOE cross-peaks relating the CCH_3 signal (2.03 ppm) to the N3H signal (5.75 ppm) and to the CH multiplet of the isopropyl group (3.67 ppm). A CCH_3−N3H NOE peak together with a CCH_3−CH NOE peak is uniquely expected for the Z isomer (Figure 1). Thus, the three sets of ^{1}H NMR signals observed for **2** in $CDCl_3$ belong to the E', E, and Z isomers present in the equilibrium ratio of 5:32:63, respectively.

In CD_2Cl_2, as found in the less polar $CDCl_3$ solvent, **2** exhibits three sets of ^{1}H NMR signals. Two sets of these signals have essentially equal intensity and are connected by E-E' EXSY peaks (ROESY spectrum at 0 °C, not shown) as follows (ppm): CH multiplets, 3.51 and 2.95; N3H, 5.11 and 4.06; N4H, 5.96 and 5.85; and CH_3 doublets, 1.03 and 0.80. The third set of signals is established as belonging to the Z isomer by NOE peaks relating the CCH_3 signal (1.97 ppm) to the N3H signal (5.16 ppm) and to the CH multiplet of the isopropyl group (3.67 ppm). Equilibrium for **2** in CD_2Cl_2 (E':E:Z = 19:19:62) is reached in 3 h.

Mixed-Solvent Studies Exploring the E' Isomer Signals of 2. As mentioned above, in the polar solvent acetonitrile-d_3, the signals for the E' isomer could alternatively represent a rapidly interconverting mixture of E and E' isomers. In solvents such as CD_2Cl_2, the separate signals for these isomers can be observed. Thus, in solvents of low polarity, it is clear that both isomers are present and that interchange is slow on the NMR time scale. We designed an experiment to assess whether in acetonitrile-d_3 a significant amount of an E isomer in rapid exchange with the major E' isomer might be present but undetectable in acetonitrile-d_3.

We initiated our study with a freshly prepared CD_2Cl_2 solution because equilibrium was not reached for ∼3 h after crystals of **2** were dissolved in CD_2Cl_2. The E isomer was initially abundant (E':E:Z = 37:37:28; Figure 8, bottom). Addition of 1% and then 2% of acetonitrile-d_3 into the CD_2Cl_2 solution of **2** (these first two additions were recorded prior to equilibrium to observe abundant E' and E isomers) showed an increase in the relative abundance of the E' isomer, as reflected in the intensities of the H6/6′ signals (Figure 8). At 21% acetonitrile-d_3, the E' isomer H6/6′ signal was observed but not the E isomer signal (Figure 8). Thus, the one set of signals observed in 100% acetonitrile-d_3 is that of the E' isomer, with a negligible (if any) contribution of an E isomer.

NMR Studies of Other $[Re(CO)_3(5,5'\text{-}Me_2bipy)(amidine)]BF_4$ Complexes in CD_2Cl_2 and $CDCl_3$. ^{1}H NMR data for complexes **2**, **3**, and **4** in CD_2Cl_2 and $CDCl_3$ (Supporting Information, Table S1) indicate that complexes **3** and **4** have E', E (in most cases), and Z isomers, as found above for **2**. In $CDCl_3$ and CD_2Cl_2 (as in acetonitrile-d_3), the signals of the methyl group derived from acetonitrile have a more downfield shift (∼2.2 ppm) characteristic for the E and E' isomers and a more upfield shift (∼2.0 ppm) characteristic for the Z isomer. An N3H signal having a shift upfield of 4.60 ppm (Table 3 and Supporting Information, Table S1) in acetonitrile-d_3, CD_2Cl_2, or $CDCl_3$ was another indication allowing the assignment of signals to the E' isomer. As found in the case of every solvent for compounds with non-anisotropic R groups, the H6/6′ signal of the E' isomer in CD_2Cl_2 or $CDCl_3$ is more downfield than that of the E isomer, which in turn is more downfield than this signal for the Z isomer (Supporting Information, Table S1). This relationship holds true for all solvents, including DMSO-d_6 (see below).

These shift analogies were supported by the spectral changes upon dissolution of crystals, which also aided in the assignments. Dissolution of crystals of **3** (R = isobutyl) in $CDCl_3$ gave NMR features (Supporting Information, Table S2) similar to those observed for **2**. A ^{1}H NMR spectrum recorded in 5 min contained mostly one

large set of peaks of the *E* isomer, identified by NMR shifts that closely resemble those of the *E* isomer of **2**. Dissolution of crystals of **3** in CD_2Cl_2 also gave NMR features similar to those observed for **2** (Supporting Information, Tables S1 and S2), for which three distinct sets of signals were observed, with features expected for the three isomers.

A ^{1}H NMR spectrum of **4** (R = *tert*-butyl) initially recorded within 5 min of dissolution in $CDCl_3$ showed signals for the three isomers, with the *E* and *E*′ isomers in abundance. With time, peaks assignable to the *Z* isomer grew. However, the spectrum obtained upon dissolution of **4** in CD_2Cl_2 has only two sets of signals. The peaks clearly assignable to the *Z* isomer were sharp, and these grew with time. Although the signals attributable to the *E*′ isomer were broad at 25 °C, all signals in the regions characteristic of the *E* and *E*′ isomers, including the informative H6/6′ signal, were sharp at 0 °C; these results are consistent with the absence of the *E* isomer in this solvent (Supporting Information, Tables S1 and S2).

Dependence of the *E*′:*E* and the *E*′:*Z* Ratios on Solvent and Remote N Group Steric Bulk. Some *E*′:*E*:*Z* equilibrium ratios have been mentioned above for different solvents. In this section we discuss the data further (Supporting Information, Table S2). Because the situation is complicated, we begin with a brief summary. The *E*′ isomer is favored by high steric bulk and polar solvents. The *E* isomer is insensitive to steric bulk but favored by low solvent polarity. The *Z* isomer is favored by low steric bulk and low solvent polarity.

For **2**, *E*′:*E*:*Z* equilibrium ratios in $CDCl_3$ (5:32:63) versus CD_2Cl_2 (19:19:62) show that while the percentage of the *E*′ isomer has increased, the abundance of the *Z* isomer has remained more or less constant. In other words, *E*′ has increased and *E* has decreased as the dielectric constant of the solvent increased from 4.8 ($CDCl_3$) to 9.1 (CD_2Cl_2). This same relationship is valid for **3**, and as mentioned above, signals for the *E* isomer of **4** are no longer observed even in the relatively low polarity solvent, CD_2Cl_2 (Supporting Information, Table S2). For all $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ compounds, the *E*′ isomer is least abundant in $CDCl_3$ (5−15%). As shown in Supporting Information, Table S2, the abundance of the *E*′ isomer (64−82%) was greater in the higher dielectric constant (37.5) solvent, acetonitrile-d_3, and even higher in DMSO-d_6 (dielectric constant = 47.2). Although we do not discuss the NMR studies in DMSO-d_6 in detail, the isomer and signal assignments followed the methods discussed for other solvents. For example, an NMR spectrum of **2** recorded in DMSO-d_6 showed mostly one set of signals (*E*′) initially, and a second set of peaks grew with time, reaching equilibrium within 30 min (*E*′:*Z* = 78:22). The N4H signals of both the *E*′ and *Z* isomers appear more downfield in DMSO-d_6 than in acetonitrile, consistent with the good H-bonding and solvation properties of DMSO.

Compared to all solvents used for **2**, **3**, and **4**, the abundance of the *Z* isomer was lowest (13−22%) in DMSO-d_6 (Supporting Information, Table S2). The *Z* isomer was favored most in $CDCl_3$ (57−64% abundance). Thus, a low dielectric solvent favors the *Z* isomer for all $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ compounds studied.

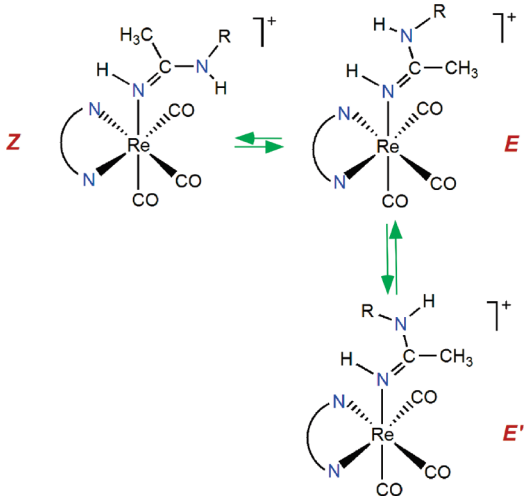

Figure 9. Scheme relating the identified isomers of $[Re(CO)_3(L)(HNC(CH_3)NHR)]^+$ cations. The figure illustrates the likely pathway between the *Z* and the *E*′ isomers, passing through the *E* isomer. Faster interconversion occurs between *E* and *E*′ isomers, as rotation about the bond between the amidine C and the remote N is expected to be faster compared to rotation about the bond between the amidine C and the N bound to Re.

***Z*′ Isomer.** While we have observed evidence for the presence of *E*′, *E*, and *Z* isomers for complexes **2** and **3** in $CDCl_3$ and CD_2Cl_2, the *Z*′ isomer appears not to be present in several solvents ranging from $CDCl_3$ to DMSO-d_6. The *Z*′ isomer is probably destabilized by interligand steric clashes involving the basal plane defined by the 5,5′-Me_2bipy N atoms and the trans carbonyl C atoms (Supporting Information, Figure S7). Such clashes are likely to be severe in octahedral complexes but less important in square-planar complexes, and the *Z*′ isomer has been reported for Pt^{II} complexes.[14] Complexes with the *fac*-$\{Re^{I}(CO)_3\}$ core are generally sterically undemanding compared to other octahedral complexes because Re^{I}−N bonds are longer than typical M−N bonds for metal ions in an octahedral environment, and the CO ligands are relatively non sterically bulky. Nevertheless, even in this favorable case, steric clashes appear to preclude formation of significant amounts of the *Z*′ isomer.

The unstable nature of the *Z*′ isomer suggests that the pathway for the interconversion of the *E*′ to *Z* isomers passes through the *E* isomer and not through the *Z*′ isomer. Furthermore, the findings for **2** in $CDCl_3$, namely, that the *E*′/*E* ratio remained constant while the amount of *Z* increased with time and that only *E*′-to-*E* EXSY cross-peaks were present in the ROESY spectrum, suggest that the *E*′-to-*E* interconversion is facile. Thus, the slow steps in the *E*′-to-*Z* interconversion are the *E*-to-*Z* steps. A likely reaction pathway scheme is illustrated in Figure 9.

NMR Studies of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)\text{-}NH_2)]BF_4$ (7). NMR spectra of **7** in acetonitrile-d_3 at 25 °C recorded at 15 min and 1 day were very similar, containing two very broad NH signals (6.30 and 5.93 ppm) and one fairly sharp NH signal at 5.45 ppm (each integrating to one proton) for the major *Z* isomer (Table 3). Sharp H6/6′ signals were observed, with the smaller signal downfield, suggesting that ~12% *E*′ isomer was also present. The signal at 5.45 ppm did not shift with temperature and can be assigned to N3H of the *Z* isomer. At 5 °C, the two broad

NH signals of equal intensity became sharp (6.60 and 5.81 ppm). At 35 °C, the broad signals merged to give one peak (6.09 ppm), the total intensity remaining the same. These results indicate that the signals are from the $-NH_2$ group of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NH_2)]BF_4$ and that elevated temperature increases the rate of rotation around the $C-NH_2$ bond. The NH peaks of the minor E' isomer could not be identified. The H6/6′ and amidine CH_3 signals were used to obtain the ratio of the E' and Z isomers (Table 4).

Structural analysis of *fac*-$[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)OCH_3)]BF_4$, an iminoether analogue of the amidine complexes in this study, has revealed that the iminoether ligand has the Z configuration in the solid state.[26] The oxygen of the iminoether ligand is less sterically bulky than the NHR group of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ complexes. Combining these findings for $[Re(CO)_3(5,5'\text{-}Me_2bipy)(ligand)]BF_4$ complexes in which the ligand is an amidine or an iminoether, we suggest that the Z configuration is favored electronically, but the E' configuration is favored by steric effects.

Robustness of the Isopropylamidine Ligation. When $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**) in acetonitrile-d_3 or in $CDCl_3$ was treated with a 5-fold excess of the basic 4-dimethylaminopyridine ligand, no major changes in spectral features of the amidine complex were observed, even up to 2 months, indicating that the isopropylamidine ligand is not readily replaced. The NMR signals of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(4\text{-dimethylaminopyridine})]BF_4$, synthesized as a control, did not change with time in acetonitrile-d_3 or in $CDCl_3$.

Conclusions

The $[Re(CO)_3(5,5'\text{-}Me_2bipy)(CH_3CN)]BF_4$ complex (**1**) readily forms $[Re(CO)_3(5,5'\text{-}Me_2bipy)(amidine)]BF_4$ complexes upon treatment with amines. The facility of this reaction for a low-oxidation-state, third-row transition metal complex very likely reflects the fact that the CO ligands reduce the electron density on the metal via π back-bonding. In these complexes, the amidine ligand is attached robustly, but it does not exhibit a trans influence.

Because the amidine grouping is not in a ring and the ligand is monodentate, the configuration is not constrained. Furthermore, there is no interligand hydrogen bonding possible to influence the stereochemistry. Thus, the configuration is influenced primarily by electronic and steric effects. The E' isomer crystallized for $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ (R = methyl, isopropyl, isobutyl, *tert*-butyl, and benzyl), whereas the Z isomer crystallized for $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NH_2)]BF_4$. Increased steric bulk of the R group favors the E' configuration of the amidine ligand because the alkyl group projects away from the basal plane. The Z configuration is favored electronically, as evidenced by the structure of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NH_2)]BF_4$ and also by the structure of several $[Re(CO)_3(L)(iminoether)]BF_4$ complexes analyzed in unpublished work.[26]

The exchange reaction between the E' and Z isomers of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ (R = isopropyl, isobutyl and *tert*-butyl) complexes is too slow to be observed on the NMR time scale. The isomerization rate is slow because there is double-bond character in the bond between the amidine C and the N bound to Re. However, the isomerization rate between the E' and E isomers is fast because there is less double-bond character in the bond between the amidine C and the remote N. Exchange between the E' and Z isomers is likely to follow a pathway through the E isomer because the Z' isomer (not observed) is likely to be unstable as a result of strong steric clashes between the R group and the basal ligands in this isomer.

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Supporting Information Available: Crystallographic data for $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**), $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH_2CH(CH_3)_2)]BF_4$ (**3**), $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHC(CH_3)_3)]BF_4$ (**4**), $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH_2C_6H_5)]BF_4$ (**5**), and $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NH_2)]BF_4$ (**7**) in CIF format; ORTEP plot of the cation in $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH_3)]BF_4$ (**6**); ROESY spectra of **2** in acetonitrile-d_3 and $CDCl_3$; figure depicting stacking in **5**; and tables of selected ^1H NMR shifts for **2**, **3**, and **4** in $CDCl_3$ and CD_2Cl_2 and of the distribution of E, E', and Z isomers of **2**, **3**, and **4** in several solvents compared to the distribution in acetonitrile-d_3. This material is available free of charge via the Internet at http://pubs.acs.org.