Superamidines 2. Synthesis of the bulky ligand *N,N′*-bis-(2,6-diisopropylphenyl)-trifluoroacetamidine and its molybdenum carbonyl complex[1]

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Abstract: *N,N′*-bis-(2,6-diisopropylphenyl)trifluoroacetamidine has been prepared for the first time from 2,6-diisopropylaniline and the trifluoroacylation reagent TFAP via the imidoylchloride. The crystal structure of the amidine was determined, indicating that it crystallizes in the *Z-anti* tautomer, in contrast to the nonfluorinated analogue, which is *E-anti* in the solid state. In solution, as indicated by NMR spectroscopy, it exists in two isomeric forms. The amidine reacts with $Mo(CO)_6$ to produce a coordination complex with $Mo(CO)_3$ in which the ligand is also in the *Z-anti* geometry, the metal is η^6-coordinated to the imino-2,6-diisopropylphenyl ring, and the amino N-H unit is directed towards the metal, as determined by a single-crystal X-ray structure. Unlike the analogous nonfluorinated acetamidine, there is no indication of an intermediate in which the neutral amidine is coordinated in a monodentate fashion to an $Mo(CO)_5$ unit, which we now attribute to the predominant geometry of the ligand, both in the solid state and in solution, being *Z-anti*. The high steric bulk of this superamidine ligand apparently prevents the formation of a metal–metal bonded $Mo_2(amidinate)_4$ as observed previously in a redox reaction between *N,N′*-diphenylbenzamidine and $Mo(CO)_6$ under similar thermal reaction conditions.

Key words: trifluoromethyl, superamidine, amidine, molybdenum, carbonyl, coordination.

Résumé : On a réalisé la première synthèse de la *N,N′*-bis-(2,6-diisopropylphényl)-trifluoroacétamidine à partir de la 2,6-diisopropylaniline et du réactif de trifluoroacétylation, TFAP, par le biais du chlorure d'imidoyle. On a déterminé la structure cristalline de l'amidine qui indique qu'elle cristallise sous la forme du tautomère *Z-anti*, qui diffère de la situation avec l'analogue non fluoré qui, à l'état solide, existe sous la forme *E-anti*. Sur la base des données de R.M.N., en solution, il existe dans les deux formes isomères. L'amidine réagit avec le $Mo(CO)_6$ pour donner un complexe de coordination avec le $Mo(CO)_3$ dans lequel, selon la structure déterminée par diffraction des rayons X sur un cristal unique, le ligand est aussi dans une géométrie *Z-anti*, le métal forme une η^6-coordination avec le noyau imino-2,6-diisopropylphényle et l'unité N-H de l'amino est orientée vers le métal. Contrairement à ce qui a été observé avec l'acétamidine analogue non fluorée, il ne semble pas exister d'intermédiaire dans lequel l'amidine neutre serait coordinée de façon monodentate avec une unité de $Mo(CO)_5$; on attribue maintenant cette situation à la géométrie prédominante du ligand qui est *Z-anti* tant à l'état solide qu'en solution. Le grand encombrement stérique qui l'on retrouve dans ce ligand superamidine empêche la formation d'un $Mo_2(amidinate)_4$ avec liaison métal-métal comme on l'a observé antérieurement dans une réaction redox entre la *N,N′*-diphénylbenzamidine et le $MO(CO)_6$ dans des conditions de réactions semblables.

Mots clés : trifluorométhyle, superamidine, amidine, molybdène, carbonyle, coordination.

Introduction

Amidines and amidinate anions are useful ligands in the general development of coordination chemistry (1, 2), and their complexes with the Group 13 elements catalyze the polymerization of ethylene (3–5). We have recently reported the preparation of the first *N,N′*-disubstituted amidines containing the 2,6-diisopropylphenyl (Dip) substituent on nitrogen (6). Such "super-bulky" substituents were originally developed to stabilize low-coordinate main-group elements of the third and subsequent periods. It is our contention that the use of super-bulky substituents with conventional nitrogen-based ligands will lead to unique patterns of reactivity. So far, we have demonstrated that it is possible to synthesize

Received June 24, 1999. Published on the NRC Research Press website on May 10, 2000.

This paper is dedicated to Professor Christopher J. Willis on the occasion of his 65th birthday.

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[1]Part of this work was presented at the 15th International Symposium on Fluorine Chemistry, UBC, Vancouver, B.C., August 2–7, 1997.

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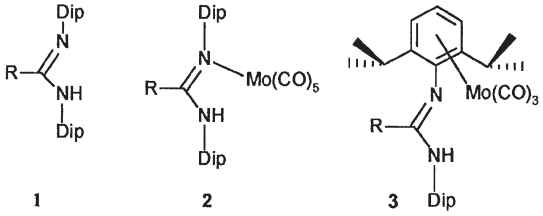
amidines **1a-c** with Dip groups on nitrogen. The ligands dissolve in typical NMR solvents ($CDCl_3$) as at least two isomeric forms, and so far, three different isomers have been detected in the solid state by X-ray crystallography (6). However, whereas analogous nonbulky amidines such as *N*,*N*′-diphenylbenzamidine produce quadruply bonded dimolybdenum(II) compounds (7) in thermal reactions with $Mo(CO)_6$ in hydrocarbon solvents, under these conditions the superamidines have only provided two different kinds of neutral coordination compounds. Thus superamidine **1a** reacts with molybdenum carbonyl in hot *n*-heptane to produce an N-coordinated $LMo(CO)_5$ complex **2a**, but on further reaction this complex loses two further CO molecules to form the half-sandwich $LMo(CO)_3$ complex **3a**. By contrast, amidines **1b**, **c** form $LMo(CO)_3$ complexes **3b**, **c** with no detectable intermediates in thermal reactions with $Mo(CO)_6$ (6).



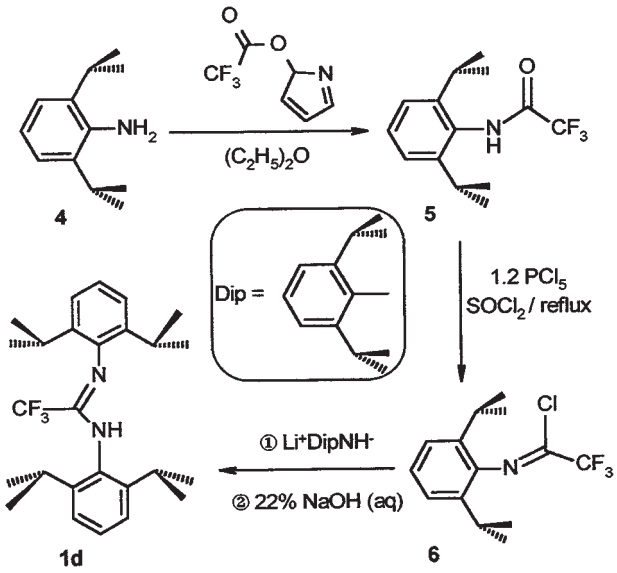
In this work we report results on a further superamidine with Dip groups on N and a trifluoromethyl substituent on the central carbon atom, **1d**. The structure and reactivity of this compound is distinct from that of its unfluorinated analogue **1a**, and more closely resembles that of the aryl derivatives **1b**, **c**, apparently for structural rather than electronic reasons. In thermal reactions of **1d** with $Mo(CO)_6$ the only observed product is the $LMo(CO)_3$ complex **3d**.

Results and discussion

Ligand synthesis

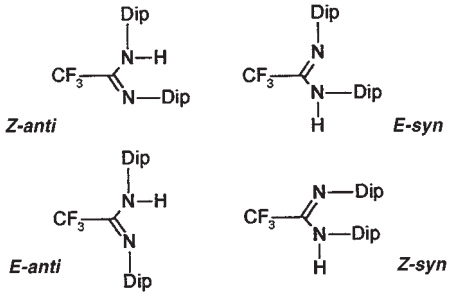
Our synthesis follows the basic methodology outlined by Maringgele and Meller (8) for the synthesis of several *N*,*N*′-diaryl-*N*′-trimethylsilyltrifluoroacetamidines (i.e., with the remaining hydrogen on N being replaced with an $Si(CH_3)_3$ group). Each step of the procedure required extensive optimization, and in particular, differed significantly from that of the nonfluorinated analogues **1a-c**. The synthetic route is outlined in Scheme 1, and the particulars of each step are detailed in the Experimental section. Commercially available 2,6-diisopropylaniline, **4**, was converted to the corresponding amide of trifluoroacetic acid, **5**, using the trifluoroacylation reagent 2-(trifluoroacetoxy)pyridine (TFAP) (9). Dehydration and chlorination using 1.2 equiv of PCl_5 in refluxing $SOCl_2$ produced the imidoylchloride, **6**, which was isolated and purified by vacuum distillation in 63% yield. Maringgele and Meller (10) obtained a variety of *N*-aryltrifluoromethylimidoyl chlorides as byproducts in only 10–20% yield from reactions of amides with BCl_3. The ^{19}F NMR chemical shifts of these imidoyl chlorides are found at $\delta = -71.0$ to -72.0 ppm, in excellent agreement with the –71.48 ppm we find in the NMR spectrum of **6**.

Scheme 1.



The imidoylchloride does not react directly with a second equiv of **4** as the nonfluorinated analogues do (6). Instead, the lithium anilide was produced, and this reacted with the imidoyl chloride to produce the desired amidine directly. However we have found that to purify this raw product conversion first to the hydrochloride, followed by reforming the free amidine, **1d**, using 23% sodium hydroxide solution was required. All of these compounds are new, and have been fully characterized by elemental analysis, mass spectroscopy as well as ^1H and ^{13}C NMR spectroscopy. The details are given in the Experimental section.

Scheme 2.



Isomers and tautomers

In $CDCl_3$ solution, **1d** exists in two isomeric forms as shown by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. Previously reported trifluoroacetamidines with a variety of nonbulky aryl groups also show isomerism in solution (8). For example, an amidine with a 2,6-dimethylphenyl group on one nitrogen and a phenyl group on the other displays two singlets at $\delta = -61.9$ and -60.4 ppm in the ^{19}F NMR spectrum (8). Similarly in **1d** there are two closely spaced singlets at $\delta = -67.24$ and -66.84 ppm. The difference in absolute shift is attributable to protonation vs. silylation at the amino nitrogen.

We have previously shown that superamidines can exist in a variety of isomeric and tautomeric forms (6). The four possible isomers of the trifluoromethyl derivative are shown in Scheme 2, using the nomenclature devised by Perrin (11)

Fig. 1. PLUTO diagram of **1d**, showing the atom numbering scheme. The ligand is in the *Z-anti* conformation. The rotationally disordered CF_3 group has been modeled by two trigonal F_3 units with occupancy of 0.85, F(1)-F(3), and 0.15, F(4)-F(6).

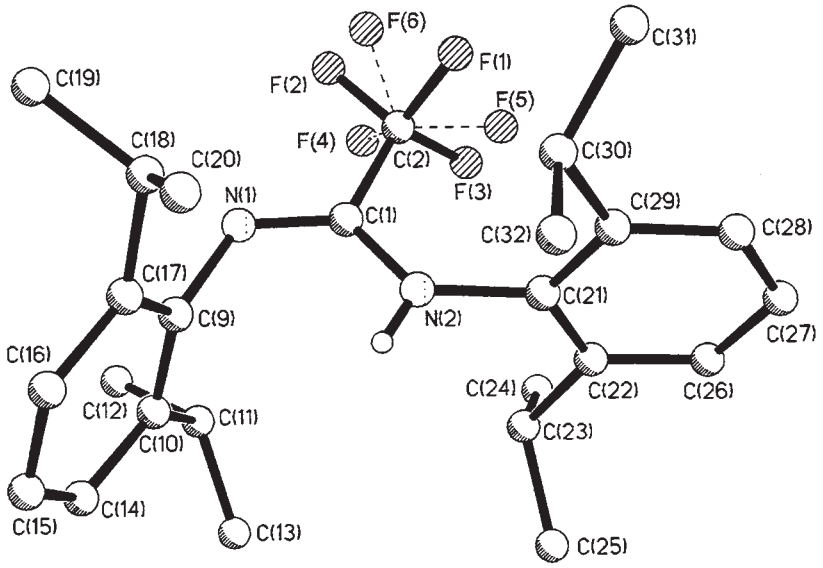


Table 1. Crystal data and structure refinement.[a]

Compound	**1d**	**3d**
Formula	$C_{26}H_{35}F_3N_2$	$C_{29}H_{35}F_3MoN_2O_3$
FW	432.56	612.53
T (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	C2/*c*	$P2_1/n$
a (Å)	17.4663(17)	12.0559(11)
b (Å)	14.6527(12)	16.5327(10)
c (Å)	20.7594(15)	15.3228(14)
β (°)	106.654(10)	95.270(11)
V (Å^3)	5090.1(7)	3041.2(4)
Z	8	4
D_c (mg/m^3)	1.129	1.338
Crystal	colourless block	yellow plate
Size (mm)	0.40 × 0.34 × 0.30	0.60 × 0.26 × 0.08
Rfl. Collected (R_{int})	21505 (0.0403)	26067 (0.0338)
Data / restraints / parameters	3871 / 30 / 301	4787 / 0 / 364
Final *R* [$I > 2\sigma(I)$]	*R*1 = 0.0421, *wR*2 = 0.0943	*R*1 = 0.0287, *wR*2 = 0.0653
Gof (all data)	0.992	0.946

[a]Weighting schemes used: **1d**, $w = 1/[\sigma^2(Fo^2) + (0.0500P)^2]$; **3d**, $w = 1/[\sigma^2(Fo^2) + (0.0420P)^2]$ where $P = (Fo^2 + 2Fc^2)/3$.

based on the Cahn–Ingold–Prelog sequence rules. The lowest-energy isomer of **1d**, as minimized in an AM1 calculation, is the *Z-anti* form. Relative to this, the tautomeric *E-syn* isomer lies only 1.2 kJ mol^{-1} higher in energy, while the *Z-syn* isomer lies 11.0, and the *E-anti* 26.7 kJ mol^{-1} higher in energy. Calculations on **1a**, however, indicate that the *E-anti* isomer for the methyl ligand **1a** lies only 15.5 kJ mol^{-1} higher than *Z-anti*. These calculations do not factor in the energy of hydrogen bonding, which apparently can stabilize the *E-anti* form as seen in the solid state for the methyl analogue **1a**. The typical energy of a single H-bond is ~20 kJ mol^{-1} (12). We have determined the single-crystal X-ray structure of **1d** (see Fig. 1), which indicates that it crystallizes preferentially as the *Z-anti* isomer. There are no short intermolecular contacts in the crystal. Apparently the steric bulk of a trifluoromethyl group is sufficiently large to cancel out the energetic advantage for the formation of an H-bonded dimer, which is possible only in the *E-anti* conformation. Important bond distances and angles are listed in Table 1.

Häfelinger and Kuske (13) have defined the parameter $\Delta_{CN} = d(C—N) - d(C=N)$ for the central N—C—N linkage found in all amidines, using crystallographic structural data. This parameter ranges from 0 in the structure of **1a**, to 0.178 Å in 2,6-*cis*-dimethylpiperidyl-*N*-phenyl-2,2-dimethylpropionamidine, an amidine where conjugation is minimized due to bulky substituents on nitrogen and carbon (d(C—N) = 1.441(5); d(C=N) = 1.263(5) Å), and which crystallizes in

Table 2. Selected interatomic distances and angles.

Distances (Å)		Angles (°)	
1d			
N(1)—C(1)	1.270(2)	C(1)-N(1)-C(9)	119.49(15)
N(2)—C(1)	1.364(2)	C(1)-N(2)-C(21)	128.55(15)
Δ_{CN}[a]	0.094	N(1)-C(1)-N(2)	126.85(16)
N(1)—C(9)	1.426(2)	N(1)-C(1)-C(2)	115.45(17)
N(2)—C(21)	1.444(2)	N(2)-C(1)-C(2)	117.68(18)
C(1)—C(2)	1.509(3)		
N(2)—H(2)	0.92(2)		
3d			
N(1)—C(1)	1.270(3)	N(1)-C(1)-N(2)	128.1(2)
N(2)—C(1)	1.343(3)	N(1)-C(1)-C(2)	113.5(2)
Δ_{CN}[a]	0.073	N(2)-C(1)-C(2)	118.4(2)
C(1)—C(2)	1.527(3)	C(1)-N(1)-C(9)	126.6(2)
N(1)—C(9)	1.402(3)	C(1)-N(2)-C(21)	128.3(2)
N(2)—C(21)	1.454(3)	C(33)-Mo(1)-C(34)	83.63(13)
N(2)—H(2)	0.88(3)	C(33)-Mo(1)-C(35)	82.96(14)
Mo(1)—C(33)	1.940(3)	C(34)-Mo(1)-C(35)	85.77(16)
Mo(1)—C(34)	1.912(4)	Mo(1)-H(1)-N(1)	
Mo(1)—C(35)	1.947(4)		
Mo(1)—H(2)	3.14(3)		

[a] $\Delta_{CN} = d(\text{C-N}) - d(\text{C=N})$.

the rarely observed *Z-syn* form (14). In the crystal structure of **1d**, $\Delta_{CN} = 0.094$, the largest we have yet observed for a superamidine structure. The metric parameters of **1d** otherwise closely parallel those of **1c**, the only other superamidine so far which crystallizes exclusively in the *Z-anti* form, for which $\Delta_{CN} = 0.057$ (6). The C—N single bonds in **1c** and **1d** are identical within experimental error at 1.364 Å. Thus the origin of the larger Δ_{CN} value in **1d** is the *shorter* C=N double bond, which at 1.270(2) is almost 0.04 Å shorter in the fluorinated amidine. However, these values are not unprecedented. In the structure of *N′-p*-bromophenyl-*N*-(*p*-tolyl)acetamidine, which crystallizes in the *E-anti* isomer, *d*(C–N) = 1.366(8) and *d*(C=N) = 1.273(8) Å, leading to a $\Delta_{CN} = 0.093$ (15).

Reaction with $Mo(CO)_6$

Amidine **1d** was heated with $Mo(CO)_6$ in refluxing *n*-heptane under an atmosphere of N_2. The course of the reaction was easily monitored by solution infrared spectroscopy and we observed that **1d** reacted slowly, with no observable evidence by solution IR spectroscopy of any intermediate, to the final product, a bright yellow crystalline solid, which was produced in 25% yield. The structure of the compound was indicated by ^{1}H NMR and IR spectroscopy to be a half-sandwich "piano-stool" complex of $Mo(CO)_3$, in which the metal is coordinated to one of the electron-rich aromatic rings of the ligand rather than through nitrogen. In the ^{1}H NMR spectrum, the signals due to the aromatic hydrogen atoms of one of the diisopropylphenyl groups are shifted 1.45–1.49 ppm upfield, while the other signals remain at the same chemical shift. In the free ligand, the *meta* and *para* hydrogen resonances are not distinguishable, but in the complex, the upfield-shifted signals show a resolved pseudo-triplet for the *para* and a resolved pseudo-doublet for the *meta* hydrogen atoms, in the expected 1:2 intensity ratio. The magnitude of these shifts are typical of those observed for η^6-arenes coordinated to an $Mo(CO)_3$ unit. The solution IR spectrum (Table 3) showed three bands in the carbonyl-stretching region, a very strong singlet at about 1966 cm^{-1}, and a slightly less intense doublet centred at about 1885 cm^{-1}. This is the pattern expected for a *fac*-octahedral tricarbonyl metal complex with highly asymmetric coligands (16).

Table 3. Solution IR data.[a]

Compound	ν(N-H) (cm^{-1})	ν(N-C-N) (cm^{-1})	ν(C≡O) (cm^{-1})
1d	3453, 3356	1657	—
3d		1665	1971, 1906, 1883

[a] *n*-Heptane solution in 0.2 mm NaCl solution cell.

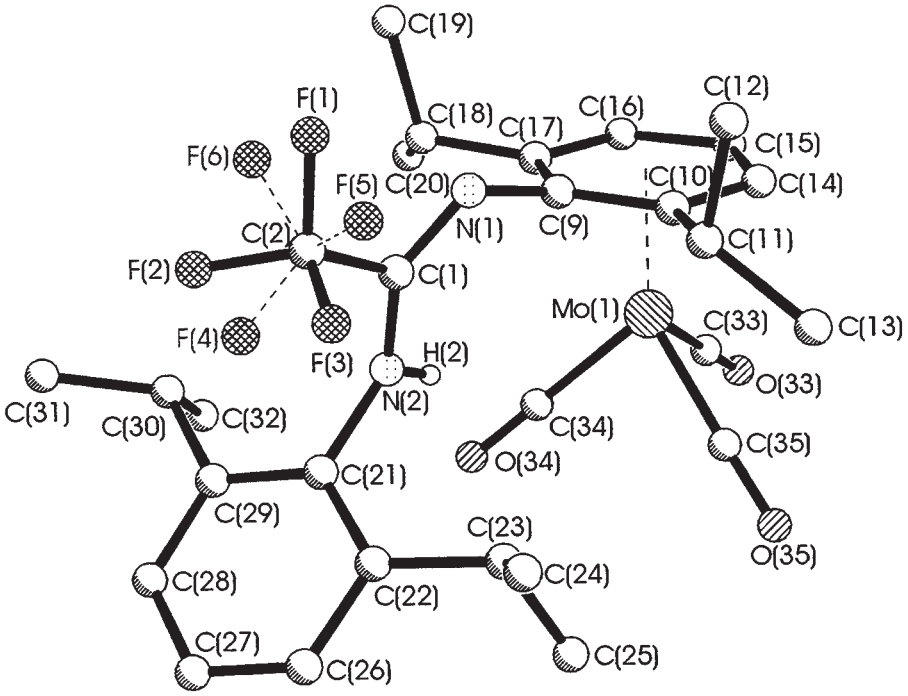
The single-crystal X-ray structure of **3d** is presented in Fig. 2. The same "baseball catcher's mitt," structure is observed as previously obtained for the methyl **3a** and tolyl **3b** structures, in which the amidine ligand, itself in the *Z-anti* tautomer, has "caught" the $Mo(CO)_3$ fragment with the inside face of the imino-bearing ring. With respect to the C(1)=N(1) double bond, the metal complex also has *Z* symmetry. The N-H of the amino group corresponds to the "catcher's thumb," and there is a close contact of 3.14(3) Å between H(1) and Mo, less than a reasonable guess at the sum of their van der Waals' radii (the van der Waals radius for molybdenum is not contained in standard compilations; we have used values of neighbouring elements to provide this estimate). The similarity in structures of **3d**, **3a**, and **3b** is striking. The amidine unit in **3d** is bent further away from the molybdenum atom than in **3a**. This is evidenced by a 5° larger N(1)-C(1)-N(2) angle, and a 3° smaller N(1)-C(1)-C(2) angle. Other metric parameters between the two structures are extremely similar.

Progress of reaction with $Mo(CO)_6$

The thermal reactions with $Mo(CO)_6$ of all the superamidines that we have studied do not go on to the formation of bridged multiply bonded dimolybdenum species (6, 7). This is undoubtedly due to the high steric bulk of the Dip groups. The question that remains, however, is why **1d** reacts more like the aryl amidines **1b** and **1c**, in going directly to an η^3-$Mo(CO)_3$ complex, than the methyl amidine **1a**, which first forms an N-bonded $Mo(CO)_5$ complex, and only on further heating produces the η^3-$Mo(CO)_3$ complex?

We believe that this difference in reactivity can be traced to the structural forms of the free ligand in the solid state and in solution. Only **1a** crystallizes in the *E-anti* form as an H-bonded dimer, unlike **1b**, **1c**, and **1d**. Furthermore, **1a** is much less soluble in *n*-heptane than the others, undoubtedly due to the dimer structure. Thus visual inspection of the thermal reaction of **1a** with $Mo(CO)_6$ clearly shows that undissolved ligand is present during much of the course of the reaction. This is different from what is observed for the other three superamidines, which dissolve readily as the temperature of the solvent is increased. We hypothesize that if the three more soluble amidines dissolve in the *Z-anti* geometry they have in the solid, reaction of ligand in this configuration promotes conversion to the η^6-$Mo(CO)_3$ complex. On the other hand, if the hexacarbonyl reacts with a

Fig. 2. PLUTO diagram of **3d**, showing the atom numbering schemes. The ligand is also in the *Z-anti* conformation, with the Mo atom coordinated to the inside of the aryl ring attached to the imino nitrogen atom. The rotationally disordered CF_3 group has been modeled by two trigonal F_3 units with occupancy of 0.87, F(1)-F(3), and 0.13, F(4)-F(6).



hydrogen-bonded dimer in the *E-anti* geometry before this can isomerize to the *Z-anti* form, it forms a metal complex in which this geometry is preserved. We have previously shown that conversion of the η^1-$Mo(CO)_5$ complex to the η^6-$Mo(CO)_3$ complex is accompanied by *E* to *Z* ligand isomerism (6).

Is there any evidence that the amidines exist in solution in the *Z-anti* form? Consider the combined NMR spectroscopic parameters presented in Table 4 for all the species we have so far prepared. The proton (and ^{19}F, where applicable) NMR parameters of the *dominant* species in $CDCl_3$ solution for the free amidines in each case are strikingly similar to those of the metal tricarbonyl derivatives. If, as seems likely, the latter dissolve in the *Z-anti* geometry found in the solid state, the correspondence of the NMR spectoscopic parameters supports this isomer as the predominant form of the free ligand in $CDCl_3$ as well. Furthermore, this is also the lowest energy form in the gas phase as indicated by MO calculations.

The differences that do exist between the NMR spectroscopic parameters of free ligand and complex are readily attributed to variations in ring shielding effects. Thus the ^1H signal of the amino NH atom is further upfield in the ligand, where in the *Z-anti* form it experiences ring current shielding from the Dip group on the imino nitrogen. Similarly, one CH_3 group is significantly further upfield than the rest. Assuming that the Dip group on the amino nitrogen rocks back and forth on the C—N bond, one set of methyl groups would also experience ring current shielding from the ring attached to the imino nitrogen. In the $Mo(CO)_3$ complexes, both types of anomalously shielded protons revert to more normal chemical shifts. This is consistent with the metal carbonyl unit blocking the aromatic ring that is responsible for the shielding effect.

Experimental section

General

2,6-diisopropylaniline, 2-hydroxypyridine, trifluoroacetic anhydride, thionyl chloride, phosphorus pentachloride, *n*-butyl lithium (Aldrich), and molybdenum carbonyl (Strem) were commercial products, and used as received, except that the aniline was vacuum distilled and stored under nitrogen before use. Solvents were reagent grade, and distilled from sodium wire (toluene, THF), P_2O_5 (CH_2Cl_2), or $LiAlH_4$ (*n*-heptane). 2-(Trifluoroacetoxy)pyridine (TFAP) was prepared from 2-hydroxypyridine and trifluoroacetic anhydride by the literature method (9). Reactions involving metal carbonyl and organolithium reagents were performed under an atmosphere of purified N_2 using a dry-box, Schlenk ware, and vacuum-line techniques; all other procedures were performed in vessels open to the atmosphere but protected by $CaCl_2$ drying tubes. Infrared spectra were recorded on a BOMEM MB102 Fourier transform spectrometer, and are KBr pellets unless otherwise specified. NMR spectra were acquired at 250.13 (^1H) and 62.90 (^{13}C) MHz on a Bruker AC250-F spectrometer referenced to TMS, and on a Bruker AMX300 at 282.41 (^{19}F) MHz referenced to external C_6F_6 in C_6D_6 at –163.00 ppm on the $CFCl_3$ scale, and are in $CDCl_3$ unless otherwise specified. Mass spectra were recorded by the Mass Spectrometry Center, University of Alberta, Canada and in the Fachbereich Chemie, Universität Kaiserslautern. Elemental analyses were performed by MHW

Table 4. ^{1}H and ^{19}F NMR chemical shifts.

Compound	NH	Aromatic	X	^{i}Pr CH[a]	^{i}PrCH[a]	^{i}Pr CH_3[b]	^{i}Pr CH_3[b]	^{i}Pr CH_3[b]	^{i}Pr CH_3[b]
1a major[c,d]	5.40	7.29–7.04m	1.88[f]	3.23	3.21	1.32	1.26	1.19	1.04
1a minor[c,d]	5.51	buried	1.84[f]	3.31 br	2.95 br	buried between 1.35 and 1.15			
1b major[c]	5.67	7.29–6.97 m	2.27[g]	3.24	3.16	1.34	1.23	0.98	0.88
1b minor[c]	6.88	buried	buried	3.45 br	3.00 br	buried 1.4–1.2		buried 1.0–0.8[j]	
1c major[c]	5.66	7.35–6.70 m	3.74[h]	3.23	3.16	1.34	1.23	0.99	0.90
1c minor[c]	6.89	buried	buried	3.37 br	2.93 br	buried 1.1–1.3		buried	0.8
1d major[e]	5.50	7.34–7.06 m	–67.24[i]	3.18	3.03	1.34	1.27	1.20	1.00
1d minor[e]	6.05	buried	–66.84[i]	3.25 br	2.82 br	buried between 1.4–1.2			
2a[c]	7.37	7.4–7.16 m	1.42[f]	3.16	3.15	1.42	1.30	1.27	1.11
3a[c]	7.98	7.35–7.17 m, 5.82 tr, 5.60 d	1.79[f]	3.19	2.81	1.29	1.25	1.24	1.22
3b[c]	8.20	7.29–6.96 m, 5.79–5.66 m	2.27[g]	3.17	2.85	1.28	1.27	1.20	0.86
3c[c]	8.18	7.29–7.06 m, 6.69 d, 5.79–5.66 m	3.74[h]	3.17	2.84	1.28	1.27	1.20	0.88
3d[e]	8.07	7.37–7.17 m, 5.89 t, 5.57 d	–67.54[i]	3.14	2.72	1.28	1.27	1.26	1.22

[a]Heptet with J ≅ 7 Hz.
[b]Doublet with J ≅ 7 Hz.
[c]Ref. (6).
[d]There is evidence for a third species as well, with a single sharp ^{i}Pr CH signal, which could be the H-bonded dimer in solution.
[e]This work.
[f]δCH_3 group on amidine backbone.
[g]δCH_3 group on 4-position of phenyl ring.
[h]δCH_3O group on 4-position of phenyl ring.
[i]δCF_3 group, ^{19}F NMR.
[j]Upfield doublet is evident centred on 0.80 ppm.

Laboratories, Phoenix, AZ, U.S.A. and by the analytical services of the Fachbereich Chemie, Universität Kaiserslautern.

Preparation of $CF_3C\{O\}NH(2,6\text{-}^iPrC_6H_3)$, 5

2,6-Diisopropylaniline (90.9 g, 513 mmol) in 250 mL of dry diethyl ether was added drop wise to TFAP (98.0 g, 513 mmol) in 300 mL of the same solvent, with cooling to maintain 23°C. After stirring 20 h, the solvent was removed, and the residues extracted with 1.6 L of dH_2O by vigorous stirring for 2 h, filtering and drying to give 128.6 g of pure **5** (471 mmol, 92% yield), mp 158–159°C. An analytical sample was obtained by recrystallizing from ethanol. IR: ν(N-H) 3254, ν(C=O) 1709 cm^{-1}. ^{1}H NMR: 7.54 (s, 1 H, conc. depend.), 7.40–7.20 (m, 3 H), 2.95 (hept, 6.9 Hz, 2 H), 1.19 (d, 6.9 Hz, 12 H. ^{13}C NMR: 157.11 (quart, 37 Hz), 146.17, 129.63, 128.10, 123.98, 116.34 (quart, 289 Hz), 28.83, 23.58. ^{19}F NMR: –75.47 (s, CF_3). Mass spec: 272.8 (M^+, 34%), 258 (M–CH_3^+, 12%), 204 (M–CF_3^+, 100%). Anal. calcd. for $C_{14}H_{18}F_3NO$: C 61.5, H 6.6, N 5.1%; found: C 61.5, H 6.7, N 5.2%.

Preparation of $4\text{-}CF_3C\{Cl\}N(2,6\text{-}^iPr_2C_6H_3)$, 6

5 (20.0 g, 73.2 mmol) was refluxed in 15 mL of $SOCl_2$ (excess) for 0.5 h (oil bath at 80–90°C), after which one equiv of PCl_5 (15.2 g, 73.2 mmol) was added in small increments. After a further 1.5 h reflux and NMR monitoring of the reaction, a further 2.5 g (12 mmol) PCl_5 was added, which after 3 h led to complete consumption of **5**. The bath temperature was raised to 140°C and the remaining $SOCl_2$ was distilled off. The residues were fractionally distilled under vacuum, producing **6** as a colourless liquid, bp 48°C / 4 × 10^{-2} mbar (13.5 g, 46.3 mmol, 63% yield). IR (neat): ν(X=N) 1703, ν(X–Φ) 1287, 1217, 1165. ^{1}H NMR: 7.20–7.18 (m, 3 H), 2.62 (hept, 6.9 Hz, 2 H), 1.18 (d, 6.9 Hz, 12 H). ^{13}C NMR: 140.47, 135.93, 133.94 (quart, 49 Hz), 126.35, 123.47, 116.65 (quart, 277 Hz), 28.64, 22.97. ^{19}F NMR: –71.48 (s, CF_3). Mass spec: 290.7 (M^+ on ^{35}Cl, 29%), 256 (M–Cl^+, 75%), 240 (M–CH_4Cl), 177 ($C_6H_3{}^iPr_2NH_2^+$, 48%), 162 ($C_6H_3{}^iPr_2^+$, 100%). Anal. calcd. for $C_{14}H_{17}ClF_3N$: C 57.64, H 5.87, N 4.80%; found: C 57.57, H 5.85, N 5.00%.

Preparation of $CF_3C\{N\text{-}2,6\text{-}^iPr_2C_2H_3\}NH(2,6\text{-}^iPr_2C_6H_3)$, 1d

210 mL of 1.5 M *n*BuLi (hexane solution) was added via cannula to 44 mL (233 mmol) of 2,6-diisopropylaniline in 500 mL of THF in a 1 L flask equipped with a reflux condenser. After stirring a further 30 min, 68 g (233 mmol) of **6** in 200 mL THF was added dropwise with cooling. After stirring 30 min, the mixture was heated to reflux for 10 h, filtered, and the filtrate evaporated. The resulting oil was treated with 1 L of 95% ethanol followed by 600 mL *c*HCl. After evaporation to dryness, the residues were divided into five parts, each dissolved in 200 mL ethanol, reacted with 200 mL of 23% NaOH, and extracted three times with 100 mL of toluene. The toluene phase was washed with NH_4Cl and then water, and evaporated to an oil. Extended pumping on this oil produced crystals, which could be recrystallized from *n*-heptane, to give 16 g of colourless crystals of **1d** (38 mmol, 16% yield). An analytical sample was produced by recrystallizing a second time from *n*-heptane, mp 94–98°C. IR: ν(N-H) 3451, 3358, ν(N-C-N) 1655 cm^{-1}. ^{1}H NMR: 7.37–7.06 (m, 6H), 5.50 (s, 1 H), 3.18 (hept, 6.9 Hz, 2H), 3.03 (hept, 6.7 Hz, 2 H), 1.34 (d, 6.8 Hz, 6 H), 1.27 (d, 6.8 Hz, 6 H), 1.20 (d, 6.7, 6 H), 1.00 (d, 6.7 Hz, 6 H). ^{13}C NMR: 147.51, 143.28 (quart, 33 Hz),

140.62, 138.17, 131.18, 129.03, 123.46, 118.10 (quart, 279 Hz), 28.48, 25.32, 24.16, 22.41, 22.10. ^{19}F NMR: –67.24 (s, CF_3, major species), –66.84 (s, CF_3, minor species). Mass spec: 432.27486 (M^+, 57%), 389 (M–^{i}Pr$^+$, 79%), 256 (M-$C_6H_3{}^i Pr_2NH^+$, 100%), 214 ($CF_3NC_6H_3{}^i Pr^+$, 13%), 177 ($C_6H_3{}^i Pr_2NH_2^+$, 73%). Anal. calcd. for $C_{26}H_{35}F_3N_2$: C 72.19, H 8.16, N 6.48%; found: C 71.95, H 7.99, N 6.59%.

Preparation of η^6-[CF_3C{N-2,6-$^i Pr_2C_6H_3$}NH(2,6-$^i Pr_2C_6H_3$)]Mo(CO)$_3$, 3d

Three grams (6.9 mmol) of **7** and 1.83 g (6.9 mmol) of $Mo(CO)_6$ were loaded under N_2 into a side-arm flask under N_2. One hundred fifty millilitres of dry *n*-heptane was then added, and the mixture heated to reflux. Progress of the reaction was monitored by solution IR, and heating discontinued after 42 h. Removal of the solvent followed by recrystallization from *n*-heptane provided 1.02 g (1.7 mmol, 25% yield) of **3d** as bright yellow crystals, which were analytically pure, mp 145°C dec. IR: ν(N-H) 3462, 3208, ν(C=O) 1969, 1865, ν(N-C-N) 1665 cm^{-1}. ^{1}H NMR: 8.07 (s, 1 H), 7.37–7.17 (m, 3 H), 5.89 (t, 6.5 Hz, 1 H), 5.57 (d, 6.5 Hz, 2 H), 3.14 (hept, 6.8 Hz, 2 H), 2.72 (hept, 6.9 Hz, 2 H), 1.28 (d, 6.9 Hz, 6 H), 1.27 (d, 6.8 Hz, 6 H), 1.26 (d, 6.9, 6 H), 1.22 (d, 6.8 Hz, 6 H). ^{13}C NMR spectrum not obtained due to sample instability. ^{19}F NMR: –67.54 (s, CF_3). Mass spec: 614.16607 (M^+ based on ^{98}Mo, 31%), 558 (M–2CO$^+$, 4%), 530 (MoL$^+$, 100%), 486 (MoL–^{i}Pr$^+$, 2%), 432 (L$^+$, 36%), 389 (L–^{i}Pr$^+$, 62%), 256 (M-$C_6H_3{}^i Pr_2NH^+$, 72%), 177 ($C_6H_3{}^i Pr_2NH_2^+$, 56%). Anal. calcd. for $C_{26}H_{35}F_3MoN_2O_3$: C 56.86, H 5.76, N 4.57%; found: C 57.00, H 5.60, N 4.65%.

Crystallography

Data collected on a Stoe IPDS diffractometer using monochromated Mo K_α radiation (0.71073 Å) by the ϕ-oscillation method. An analytical absorption correction was carried for **3d**, but no correction was necessary for **1d**. Both structures were solved by direct methods using SHELXS-97 (17) and refined by full-matrix least-squares on F^2 using SHELXL-97 (18) using all reflections. For **1d** all the hydrogen atoms except the one attached to N were localized geometrically and a riding model was used for refinement. The CF_3 group is rotationally disordered and was modeled by two trigonal F_3 units with occupancies of 0.85 and 0.15. For **3d**, all the hydrogen atoms were localized, and a similar disorder model was applied to the F_3 unit, with refined occupancies of 0.87 and 0.13.[3]

Electronic structure calculations

All calculations were performed using the AM1 method as implemented in HyperChem 5.1 running on a Pentium II computer under Windows 95 (19).

Acknowledgments

The Natural Sciences and Engineering Research Council of Canada, the University of Lethbridge research fund, and the Alexander von Humboldt-Foundation supported this work. R.T.B wishes to thank Prof. Dr. O.J. Scherer and Dr. G. Wolmershäuser for their hospitality during a sabbatical leave at Kaiserslautern and acknowledges the access given to the facilities of the Fachbereich Chemie of the University. We thank staff at the Chemistry Department of the University of Calgary for acquiring the ^{19}F NMR spectra, and one of the referees for many helpful suggestions.

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[3] Detailed structure reports including the H-atom positions and the anisotropic temperature factors have been deposited. Copies of materials on deposit may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2.