Preparation, X-ray structure, and dynamic solution behaviour of *N*,*N*′,*N*″-tris(2,6-diisopropylphenyl)-guanidine, and its reaction with molybdenum carbonyl

Robyn E. Boeré, René T. Boeré, Jason Masuda, and Gotthelf Wolmershäuser

Abstract: The reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide with lithium 2,6-diisopropylanilide, quenching with water and recrystallization from heptane produces the symmetric guanidine $[DipNH]_2C{=}NDip$ which crystallizes in the triclinic system, space group $P\bar{1}$, a = 10.6513(11), b = 10.8997(11), c = 16.2961(17) Å, α = 80.524(12), β = 78.921(13), γ = 70.060(12)°, V = 1735.2(3) Å^3, Z = 2. The molecule crystallizes with three perpendicular 2,6-diisopropylphenyl groups, which surround and shield the central CN_3 unit, and provide (almost) three-fold symmetry around the central atom. Its dynamic solution behaviour has been studied by VT NMR between –90 and +180°C, and is consistent with three distinct barriers to N—C_{Ar} rotation. Preliminary estimates of the Gibbs free energy of activation for the lower two barriers are 56 ± 2 and 73 ± 2 kJ mol^{-1}. Reaction of the title compound with $Mo(CO)_6$ in refluxing *n*-heptane produces $[DipNH]_2C{=}NDip{\cdot}Mo(CO)_3$, a complex in which $Mo(CO)_3$ is η^6-coordinated to one of the diisopropylphenyl rings.

Key words: crystal structure, diisopropylaniline, guanidine, bulky ligands.

Résumé : La réaction du *N*,*N*′-bis(2,6-diisopropylphényl)carbodiimide avec le 2,6-diisopropylanilure, suivie d'un piégeage avec de l'eau et d'une recristallisation à partir de l'heptane permet d'isoler la guanidine symétrique $[DipNH]_2C{=}NDip$ qui cristallise dans le système triclinique, groupe d'espace $P\bar{1}$, avec a = 10,6513(11), b = 10,8997(11) et c = 16,2961(17) Å, α = 80,524(12), β = 78,921(13) et γ = 70,060(12)°, V = 1735,2(3) Å^3 et Z = 2. La molécule cristallise avec trois groupes 2,6-diisopropylphényles perpendiculaires qui entourent et protègent l'unité CN_3 centrale et qui assurent une symétrie pratiquement ternaire autour de l'atome central. On a étudié son comportement dynamique en solution à l'aide de la RMN à température variable entre –90 et 180°C et il est en accord avec trois barrières distinctes pour la rotation autour de la liaison N—C_{Ar}. Sur la base d'évaluations préliminaires, les énergies libres d'activation de Gibbs des deux barrières les plus faibles sont respectivement de 56 ± 2 et 73 ± 2 kJ mol^{-1}. La réaction des composés mentionnés dans le titre avec du $Mn(CO)_6$ dans l'heptane au reflux conduit à la formation de $[DipNH]_2C{=}NDip{\cdot}Mo(CO)_3$, un complexe dans lequel le $Mo(CO)_3$ est η^6-coordiné à l'un des noyaux diisopropylphényles.

Mots clés : structure cristalline, diisopropylaniline, guanidine, ligands encombrants.

[Traduit par la Rédaction]

Introduction

We have recently reported the synthesis of a series of superamidines (**1**) and their molybdenum carbonyl adducts (**2**) (1, 2), which contain the sterically demanding 2,6-diisopropylphenyl (Dip) substituent on nitrogen. The reactions of carbodiimides with nucleophiles is a well-established organic synthetic route for the preparation of amidines, and in particular for amidinate anions used in coordination chemistry (3), and we are interested in exploring this route to amidines and related compounds bearing Dip substituents using the known *N*,*N*′-bis-(2,6-diisopropylphenyl)carbodiimide.

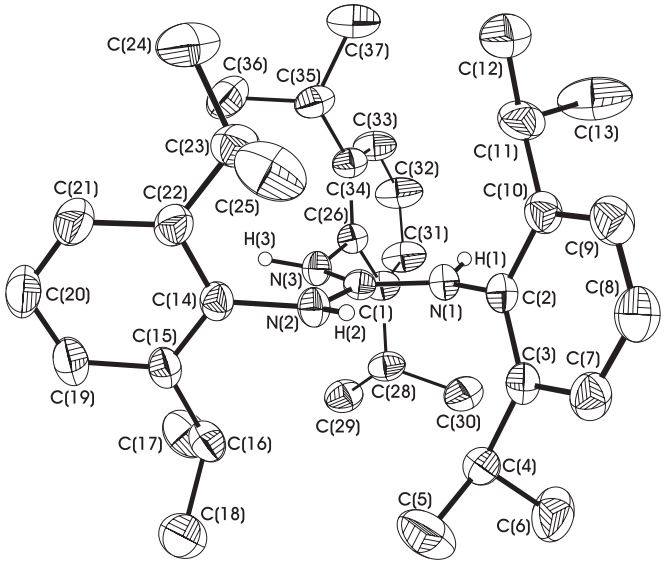
There is currently a strong interest in the use of guanidines (4) and guanidinate anions (5, 6) as ligands in coordination chemistry. Symmetrically trisubstituted guanidines are the nitrogen analogues of carbonic acid. In this work we report on the preparation of a guanidine (**3**) with a Dip substituent on all three nitrogen atoms using the carbodiimide route. Thermal reaction of the guanidine with $Mo(CO)_6$ leads to a single product (**4**) in which $Mo(CO)_3$ is coordinated in an η^6 fashion by one of the Dip groups, which is the dominant reaction previously observed for Dip-substituted amidines (1, 2).

Received September 10, 1999. Published on the NRC Research Press website on November 27, 2000.

R.E. Boeré, R.T. Boeré[1], and J. Masuda. Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, AB T1K 3M4, Canada.
G. Wolmershäuser. Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Straβe, D-67663 Kaiserslautern, Germany.

[1]Author to whom correspondence may be addressed. Telephone: (403) 329-2045. Fax: (403) 329-2057. e-mail: boere@uleth.ca

Fig. 1. ORTEP diagram (50% probability) of the structure of **3** as found by X-ray crystallography, with the atom numbering scheme. Hydrogen atoms on carbon are omitted for clarity. The occupancy of H(1) is 30%, and of H(2) 70%.



Results and discussion

Synthesis and structure of 3

Bis-(2,6-diisopropylphenyl)carbodiimide was prepared from *N*,*N*′-2,6-diisopropylphenylisocyanate according to a literature method (7). Attempts to prepare the guanidine by direct addition of the carbodiimide with 2,6-disopropyl aniline in refluxing toluene or xylenes failed, although this is precisely how *N*,*N*′,*N*″-triphenylguanidine is prepared (5). However, when the lithium anilide is prepared in situ in THF (rxn. [1]), it reacts quantitatively with the carbodiimide (rxn. [2]), to provide, after quenching, the desired guanidine (rxn. [3]).

[1] $DipNH_2 + n\text{BuLi} \rightarrow DipNH^-Li^+ + n\text{BuH}$

[2] $DipNH^-Li^+ + DipN{=}C{=}NDip \rightarrow [DipN]_2CNHDip^-Li^+$

[3] $[DipN]_2CNHDip^-Li^+ + H_2O \rightarrow [DipNH]_2C{=}NDip + LiOH$

The guanidine **3** is easily purified by recrystallization from acetonitrile, which removes coloured impurities. Since these crystals tend to retain solvent, we performed a second recrystallization from *n*-heptane to give solvent-free colourless crystals that have been fully characterized by elemental analysis, mass spectrometry, and solution NMR.

The structure of **3** has been determined in the solid state by X-ray diffraction (Figs. 1 and 2, Tables 1 and 2). The side view of the structure shown in Fig. 1 is particularly instructive, showing the three Dip groups arranged almost perpendicular to the planar central CN_3 unit. A similarly rotated aryl group disposition was observed previously in the structure of 2-(2,6-dichlorophenyl)-1-methylguanidine, and seems to be a feature of *ortho*-disubstituted aryl amidine or guanidine derivatives (8). Figure 2 shows the central triazamethane unit in **3** with directly attached atoms. Noteworthy is the similarity of all the C—N distances [from 1.316(2) to 1.357(2) Å]. A representative C=N bond distance has been established as 1.283(3) Å (9), and a value close to this has been obtained for the neutral guanidine (*E*)-*N*,*N*′-dicyclohexyl-4-morpholinecarboxamidine for which the C=N distance was measured as 1.276(3) Å (10). The related C—N single bonds in the latter guanidine were measured as 1.414(2) and 1.381(2) Å. Häfelinger and Kuske (11) have defined the parameter $\Delta_{CN} = d(C{-}N) - d(C{=}N)$ for the central N-C-N linkage found in all amidines (including guanidines). We have previously found that two almost identical Dip-substituted amidine structures, (**1**, R = 4-$CH_3C_6H_4$ and R = 4-$CH_3OC_6H_4$) possessed the very different Δ_{CN} values of 0.027(6) and 0.057(3) (1). In the former case, i.e., where the difference in interatomic distance in the supposed "double" and "single" bonds was very small, we were able to detect the presence of two N—H hydrogen atom positions, and refined a disorder model with 72 and 28% occupancy of the two structures. We propose that a similar positional disorder is operative in the crystal structure of **3**, for which $\Delta_{CN} = 0.032(6)$ Å. Indeed, peaks corresponding

Fig. 2. ORTEP diagram of the central triazamethane fragment in **3** with directly attached atoms. The disordered H atoms were located on a difference Fourier map, and correspond to positional disorder in the crystal packing of the molecule.

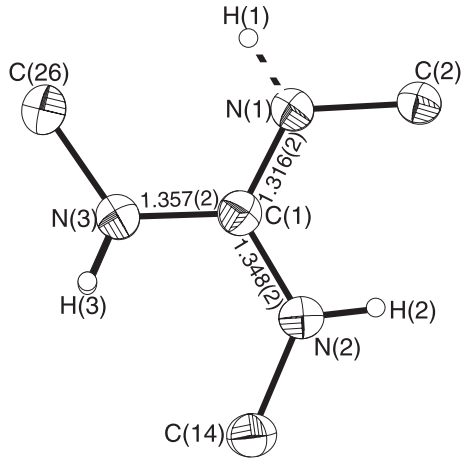


Table 1. Selected interatomic distances and angles for **3**.

Bond lengths	(Å)
N(1)-C(1)	1.3163(19)
N(1)-C(2)	1.4295(18)
N(2)-C(1)	1.3480(19)
N(2)-C(14)	1.421(2)
N(3)-C(1)	1.3567(18)
Bond angles	**(°)**
C(1)-N(1)-C(2)	120.16(12)
C(1)-N(2)-C(14)	124.30(12)
C(1)-N(3)-C(26)	122.81(14)
N(1)-C(1)-N(2)	121.99(13)
N(1)-C(1)-N(3)	119.52(13)
N(2)-C(1)-N(3)	118.47(14)

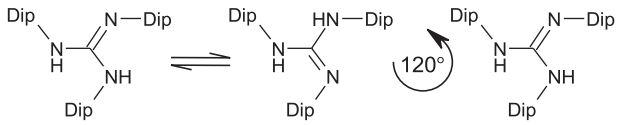
Table 2. Crystal data for **3**.[a]

Formula	$C_{37}H_{53}N_3$
Fw	539.82
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	10.6513(11)
b (Å)	10.8997(11)
c (Å)	16.296(17)
α (deg)	80.542(12)
β (deg)	78.921(13)
γ (deg)	70.060(12)
V (Å^3)	1735.2(4)
Z	2
d_{calc} (g cm^{-3})	1.033
Crystal dim. (mm)	0.52 × 0.32 × 0.21
Radiation, MoK$_\alpha$ (Å)	0.71073
Temperature (K)	293
μ (cm^{-1})	0.60
Absorption correction	none
Total reflections	20 256
Unique reflections	5206
Parameters refined	382
R (all data)	0.0586
R_w (all data)	0.1268
g.o.f. (all data)	1.052
Largest Δ/σ	0.01
Final diff. map [e Å^{-3}]	0.152, –0.104

[a]Weighting scheme used: $w = 1/[\sigma^2(Fo^2) + (0.0135P)^2]$ where $P = (Fo^2 + 2Fc^2)/3$.

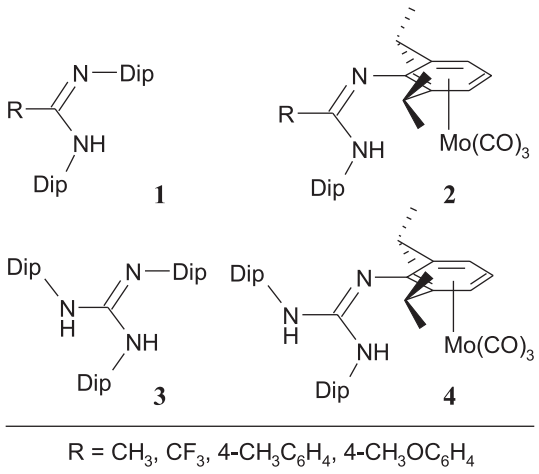
to the three N—H hydrogen atom locations were observed on a difference Fourier map, and their occupancies were allowed to vary. Convergence was achieved with H(3) as 100, H(2) 70, and H(1) 30%. In a structure so large we do not put a great deal of weight in the refinement of these occupancies, and our disorder model is based primarily on the metric parameters. As Fig. 2 clearly shows, the atoms in the triazamethane fragment are well-defined with almost spherical thermal ellipsoids.

Tautomeric disorder was postulated (without location of the H atoms) in the 2-(2,6-dichlorophenyl)-1-methylguanidine mentioned above (8). In this system, the three C···N distances are 1.364(5), 1.339(4), and 1.308(4) Å, only a slightly larger range than that found in the structure of **3**. These authors conclude only that the tautomer that identifies the 1.308(4) Å distance as the C=N bond "is predominant." In **3**, unlike our previously determined amidine structure (**1**, R = 4-$CH_3C_6H_4$) (1), the tautomeric forms are degenerate, and the apparent bond length averaging can be achieved by simple positional disorder in the crystal packing, as shown in the following graphic:



What these results emphasize is that the large Dip groups dominate the crystal packing and small variations in position of the remaining atoms can be tolerated with little cost to the lattice energy.

Scheme 1.



Reaction of 3 with $Mo(CO)_6$

The reaction of **3** with $Mo(CO)_6$ in refluxing *n*-heptane, conditions that were identical to our previous reactions of superamidines with molybdenum carbonyl (1, 2), resulted in a slow reaction that deposited yellow crystalline solid at the reflux temperature. Careful cooling of the solution resulted in the formation of essentially pure **4**, which has been characterized by solution IR, NMR and mass spectroscopies, and combustion analysis. The similarity in the NMR and IR spectroscopic parameters with those observed previously for type **2** complexes strongly suggests that the metal is coordinated in an η^6 fashion to the aromatic ring of one of the Dip groups. A parent ion for the complex is observed in the high-resolution mass spectrum. In the ^{1}H NMR spectrum, the aromatic C—H signals of *one* of the three Dip rings (a pseudo doublet and a pseudo triplet) are shifted ~1.5 ppm upfield as a consequence of π-coordination to the molybdenum atom. One of the two N—H signals is shifted ~2 ppm downfield (as observed for **2**), while the other retains a chemical shift similar to that in free **3**. The ν(C≡O) bands in the solution IR spectra are diagnostic of a "piano stool" coordination geometry for the $Mo(CO)_3$ group. Almost certainly it is the *imino* Dip group that attaches to the metal, as seen in all the superamidine complexes. Moreover, among the three X-ray structures previously determined for type **2** complexes, the ligand environment is extremely similar, and we note that this same arrangement can be obtained in **4** with the ligand in the conformation obtained for **3** in the solid state. This proposed structure is indicated in Scheme 1.

If we compare the solution IR data of **4** with those of **2** (Table 3), a distinct pattern emerges (1, 2). The electron withdrawing CF_3 group in **2** (R = CF_3) despite being three bonds removed from the diisopropylphenyl ring, nevertheless reduces the electron density at the ring. This leads to weaker back-bonding to Mo, and hence to about 5 cm^{-1} higher ν(C≡O) frequencies than in the methyl- and aryl-substituted amidine complexes **2** (R ≠ CF_3). In **4**, where an electron-donating DipNH group is attached to the amidine backbone, the ν(C≡O) frequencies are about 3 cm^{-1} lower in energy than in the methyl- and aryl-substituted amidine complexes **2** (R ≠ CF_3) consistent with stronger back-bonding by a more electron-rich aromatic ring.

Table 3. Solution IR data for **3**, **4**, and related compounds.[a]

Compound	ν(N-H) (cm^{-1})	ν(N-C-N) (cm^{-1})	ν(C≡O) (cm^{-1})	Reference
3	3415, 3392	1650	—	this work
1 (R = CH_3)	3391, 3378, 3366, 3350	1643	—	(1)
1 (R = CF_3)	3453, 3356	1657	—	(2)
1 (R = 4-$CH_3C_6H_4$)	3431, 3366	1620	—	(1)
1 (R = 4-$CH_3OC_6H_4$)	3431, 3366	1620	—	(1)
4	3403, 3272 br[b]	1640	1963, 1893, 1870	this work
2 (R = CH_3)	3193 br[b]	1640	1966, 1896, 1876	(1)
2 (R = CF_3)	—	1665	1971, 1906, 1883	(2)
2 (R = 4-$CH_3C_6H_4$)	3216 br[b]	1615	1966, 1896, 1879	(1)
2 (R = 4-$CH_3OC_6H_4$)	3216 br[b]	1615	1966, 1896, 1879	(1)

[a] *n*-Heptane solution in 0.2 mm NaCl solution cell.
[b] $CHCl_3$ solution in 0.2 mm NaCl solution cell; these weak bands are not observed in *n*-heptane because of limited solubility of the complexes.

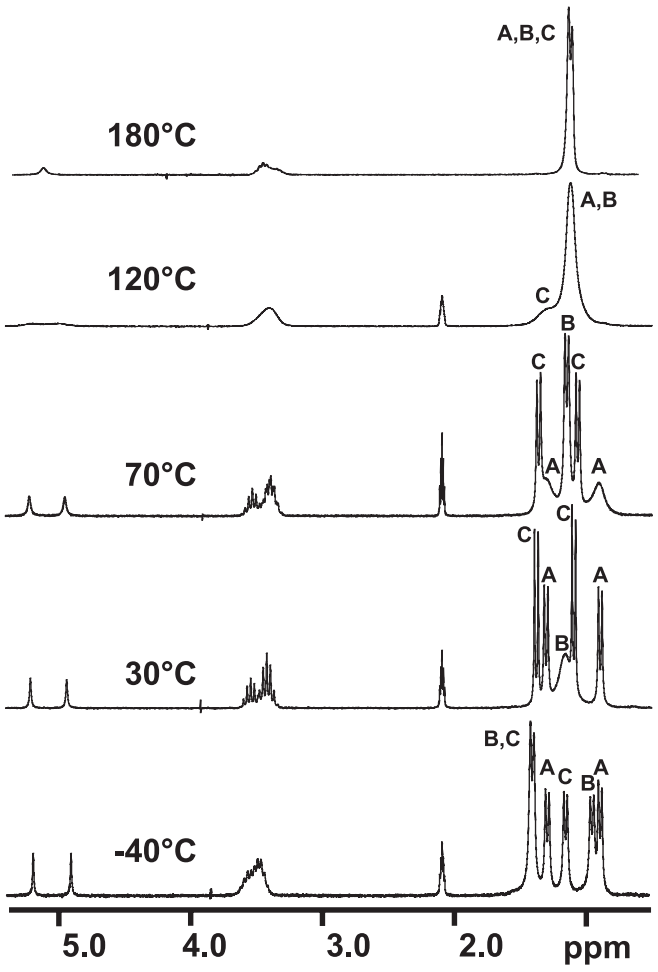
The large difference in NH environments observed for **4** in the NMR spectrum (δ 5.06 and 7.28) is also seen in solution IR spectra. Thus there is a broad band at 3272 cm^{-1} quite similar to the NH bands found in **2**, but there remains a sharp NH stretch at 3403 cm^{-1} for the additional DipNH group. In summary, the spectroscopic evidence for similarity with the previously characterized superamidine adducts strongly supports the proposed structure of **4** shown in Scheme 1.

Dynamic processes in solution

The room temperature ^1H NMR spectra of both the guanidine **3** and its metal complex **4** contain exchange-broadened signals as well as many sharp peaks. The room temperature ^{13}C spectrum of **3** also contains exchange-broadened peaks. Thus, there is some sort of dynamic process operative in both the guanidine and its complex with $Mo(CO)_3$. In this respect, the Dip-substituted guanidine differs from the Dip-substituted amidines **1** and their metal complexes **2**. The predominant isomers of **1** and the sole isomers of **2** have sharp, nonexchanging room temperature NMR signals. We have undertaken a preliminary VT-NMR study of the ^1H NMR spectra of **3** to try and sort out the complexities in the spectra. No attempt has been made to analyze the VT ^{13}C spectra of this compound; the RT spectrum is reported in the experimental section. Metal complex **4** is far too unstable in $CDCl_3$ solution to allow for VT-NMR studies.

The room temperature ^1H NMR spectrum of **3** in $CDCl_3$ solution as reported in the experimental section, or in $CD_3C_6D_5$ as shown in Fig. 3 at 30°C, is quite complex. Two very distinct NH proton signals, each integrating to one, are observed at δ 5.00 and 4.76. The isopropyl CH protons occur as three different septets, two of which have almost coincident chemical shifts, upfield of the remaining set. The most unusual feature is the isopropyl CH_3 protons, which exist as four sharp doublets in a 1:1:1:1 ratio, as well as a large exchange-broadened singlet between the inner two sharp doublets. These data strongly suggest that **3** exists in solution as a single isomer in which some sort of internal exchange is occurring that is slow on the NMR timescale. The NMR parameters of **3** closely resemble the predominant *Z-anti* isomer found for **1** (this conformation is that drawn in Scheme 1). This is the predominant solid-state form when H-bonding is not involved, as well as the lowest energy isomer by gas-phase computation (AM1 method) (1). Moreover, this is the geometry uniquely adopted by the $Mo(CO)_3$ adducts **2** in the solid-state and in solution (1, 2). Indeed, the solid-state structure of **3** can be considered as an amidine in the *Z-anti* geometry, with an additional DipNH group attached as the "R" group on the C atom of the backbone.

Fig. 3. NMR spectra of **3** at various temperatures (–40°C to +120°C in $CD_3C_6D_5$, 180°C in 1,2-$Cl_2C_6H_4$). Spectra were monitored at 10 degree intervals, and in the intervening spectra to those displayed here, smooth transitions between the peaks were observed.



Our VT-NMR spectroscopic study was conducted in a variety of solvents, namely CD_2Cl_2 and $CDCl_3$ for the low-temperature range, $CD_3C_6D_5$ for the intermediate, and 1,2-$Cl_2C_6H_4$ for the high-temperature range. There is indeed some solvent dependence of the chemical shifts of the signals, but the general process seems to be the same, and is clearly of an intramolecular nature. The solvent that covers the widest temperature range is $CD_3C_6D_5$. We independently checked the low-temperature range of this solvent by using the less viscous deuterated halocarbons, and find that essentially the same effects occur in all solvents studied. For simplicity we discuss the dynamic NMR behaviour using the data collected in $CD_3C_6D_5$ (except at the highest temperatures beyond the boiling point of this solvent, where 1,2-$Cl_2C_6H_4$ is used.)

Consider the representative NMR spectra presented in Fig. 3. At –40°C, rotational exchange of the Dip groups is frozen out, and in $CD_3C_6D_5$ solution there are five sharp methyl doublets in 2:1:1:1:1 ratio corresponding to two sets of two symmetry equivalent methyl groups of the imino Dip groups labeled "C" in the figure (δ 1.15 and 1.41), as well as two sets of two for each of the *amino* Dip groups, labeled "A" (δ 0.89 and 1.29) and "B" (δ 0.95 and 1.41). These data are consistent with three different Dip environments and a single plane of symmetry in the molecule, as seen in the solid-state structure. The shift equivalence of the deshielded B and C resonances is accidental (in CD_2Cl_2 their shifts are different). We note also that over the temperature range –90 to +80°C, the NH resonances remain sharp and distinct, with remarkably temperature-independent chemical shifts. This also agrees with the structure of **3** shown in Fig. 1 in which there are two different kinds of NH environments [i.e., H(2) and H(3)], and supports the notion that there is only a single geometrical isomer in solution over the whole temperature range that we have studied. There are of course several possible conformations that **3** may adopt in solution. We have modeled several of these by gas-phase AM1 calculations, and find that the geometry found in our crystal structure is indeed the lowest energy isomer we could find, lying 26.5 kJ mol^{-1} below the next higher form. Since this structure is fully consistent with the dynamic NMR data we will for the sake of argument consider this to be the isomer in solution, though we recognize that the actual solution geometry has not been proven.

Rotation of an amino Dip group exchanges the "inner" and "outer" methyl groups of the ^{i}Pr substituents, which appear to possess quite distinct shielding environments. On warming to 30°C, the two doublets labeled B have coalesced to a broad singlet at δ 1.15, indicating slow rotation of a single amino Dip group. This leaves four sharp doublets labeled A and C now in a 1:1:1:1 ratio for the shielded and deshielded methyl groups of the remaining amino and imino Dip groups, respectively. Spectra were obtained at 10 deg. intervals, and the changes in peak intensities and locations between the selected spectra presented in Fig. 2 underwent smooth transitions in the intermediate stages. At 70°C the coalesced signal B has grown into a sharp doublet at δ 1.14 (effectively the average of the two separate signals at –40°C) due to the four methyl groups on the rapidly rotating Dip substituent, while the second amino Dip CH_3 signals have collapsed into two exchange-broadened singlets labeled A. The two doublets C remain sharp, which we assign to the more rigid imino ring. Thus there are again five different CH_3 environments, integrating in a 1:1:2:1:1 ratio. At 120°C, line broadening of the NH signals to produce two extremely broad lines has (finally) set in, indicating the onset of slow NH tautomerism. This exchange process interconverts the amino and imino Dip sites, breaking down the rigidity of the latter. Now wholesale exchange of all the CH_3 *and* the CH environments sets in, the latter signals having remained sharp at lower temperatures, and all resonances are either coalesced or almost coalesced. Finally, at 180°C, NH tautomerism and rotation of the Dip groups are all fast on the NMR time-scale, and a simple high-symmetry spectrum containing a single Dip environment occurs. These changes are also reflected in the aromatic region, but we have not interpreted the observed patterns in detail; they are partly obscured by the residual toluene signals, and have thus been omitted from Fig. 3 for the sake of clarity.

An important piece of additional evidence for the interpretation of the dynamic phenomena put forth above for **3** is the RT spectrum in $CDCl_3$ of the metal complex **4**. The NMR signals that are sharp are virtually identical to those obtained for the two Dip groups of the type **2** amidine complexes, i.e., a coordinated imino and an uncoordinated amino group (1, 2). The CH_3 resonances of the third DipNH group are exchange-broadened at RT. This suggests that one amino DipNH group is undergoing slow rotation on the NMR time-scale, while the other is not, and that it must be the DipNH group on the amidine backbone that is dynamic. Sample instability has prevented us from performing the same kind of VT studies with **4** that were done with **3**. Ligand fluxionallity in a Pt{COD} complex of the dianion of *N*,*N*′,*N*″-triphenylguanidine has recently been reported, but the mechanism of intramolecular motion in this complex is not directly comparable to that observed in **4** (6).

A preliminary estimate of the activation energies for some of these dynamic processes can be obtained from the half-height line widths of the NMR signals at the coalescence temperature, using the classical expression of Gutowsky and Holm (12). Eyring absolute rate theory (13) leads to a value of $\Delta G^{\ddagger} = 56 \pm 2$ kJ mol^{-1} for the interconversion of the A set of signals, which we have attributed to the rotation of one of the Dip groups about an N—C_{Ar} bond. Similarly, $\Delta G^{\ddagger} = 73 \pm 2$ kJ mol^{-1} for the interconversion of the B set of signals. The final process that interconverts A, B, and C signals at the highest temperature is too complex to analyze by simple coalescence-point measurement. Although a full understanding of the dynamic processes that operate in **3** will require complete line-shape analysis and spectral simulation, we note that similar free energies of activation have been measured for hindered rotation about P—C_{Ar} bonds bearing the related bulky supermesityl substituent. Thus in Mes*P=C=PMes*, $\Delta G^{\ddagger} = 59 \pm 1$ kJ mol^{-1} (14), while in Mes*As=C=PMes*, $\Delta G^{\ddagger} = 57$ kJ mol^{-1} (15).

In conclusion, an *N*,*N*′,*N*″-trisubstituted guanidine bearing super-bulky Dip substituents has been prepared by the carbodiimide route, and shows interesting conformational effects due to hindered rotation in solution as shown by NMR spectroscopy. It forms a piano stool complex with $Mo(CO)_3$, in which the imino aryl ring acts as a six-electron donor to the organometallic fragment.

Experimental section

Starting materials and general procedures

All experimental procedures were performed under a nitrogen atmosphere using modified Schlenk techniques. 2,6-Diisopropylaniline and *n*-butyllithium (Aldrich) were commercial products and used as received. Bis-2,6-diisopropylphenylcarbodiimide was prepared using the published procedure (7). Solvents were reagent grade, or better, and were used as received (acetonitrile) or dried and distilled under a nitrogen atmosphere from $LiAlH_4$ (*n*-heptane) and sodium–benzophenone (tetrahydrofuran). ^1H and ^{13}C NMR spectra were recorded on a Bruker AC250/Tecmag Macspect spectrometer operating at 250.13 and 62.90 MHz, respectively. The ^1H and ^{13}C chemical shifts δ (ppm) for $CDCl_3$ solutions are referenced to TMS, while $CD_3C_6D_5$ solutions were referenced to the residual CHD_2 signal at δ 2.09. VT-NMR spectra were recorded using the Bruker VT accessory, and temperatures are considered accurate to ±2° below RT and ±1° above RT. IR spectra were recorded on a Bomem MB-100 spectrometer as KBr pressed pellets (solids) or in NaCl solution cells. Mass spectra were undertaken in the Department of Chemistry, University of Alberta and elemental analyses by MHW Laboratories, Phoenix, AZ.

Preparation of *N,N′,N″*-tris(2,6-diisopropylphenyl)guanidine (3)

A solution of 0.495 g (2.75 mmol) 2,6-diisopropylaniline in 10 mL of anhyd THF was treated with 3.03 mmol of 2.25 M *n*BuLi in hexanes at 0°C, and stirred for an additional 20 min at the same temperature. After warming to RT, 1.00 g (2.75 mmol) of *N,N′*-bis(2,6-diisopropylphenyl)carbodiimide in 6 mL of THF was added dropwise to the orange solution, whereupon the mixture was refluxed for 2 h. After cooling to RT, 1 mL H_2O was added, the mixture dried with anhyd $MgSO_4$ and evaporated to dryness. Crystallization from CH_3CN afforded 1.05 g (1.94 mmol, 70.5% yield) of **3**, mp 261–262°C. Additional product could be won from the mother liquor, but this tended to be slightly discoloured. Analytical material and data crystals were obtained by recrystallization from *n*-heptane. MS (70 eV): *m/z* 539.42351 (M^+ within 0.8 ppm, 100%), 524 ($M - CH_3^+$, 8%); 496 ($M - {}^iPr^+$, 92%). IR (KBr) cm^{-1}: ν(N-H) 3407, 3398; ν(C=N) 1646. ^1H NMR ($CDCl_3$): δ 0.98 (d, *J*(H-H) = 6.8 Hz, 12H), 1.09 (br s, 12H), 1.31 (d, *J*(H-H) = 6.8 Hz, 6H), 1.36 (d, *J*(H-H) = 6.8 Hz, 6H), 3.26 (sept, *J*(H-H) = 6.8 Hz, 2H), 3.31 (sept, *J*(H-H) = 6.8 Hz, 2H), 3.46 (sept, *J*(H-H) = 6.8 Hz, 2H), 4.77 (s, 1 H), 5.00 (s, 1 H), 6.93–7.30 (m, 9H). ^{13}C NMR δ: 22.55, 23.00, 24.31 (br), 24.88, 26.04, 28.66, 28.80, 28.89, 122.54, 123.07, 124.09, 127.30, 128.76, 132.47, 133.92, 141.15, 144.15, 145.63, 147.09, 147.92. Anal. calcd. for $C_{37}H_{53}N_3$ (539.9): C 82.32, H 9.90, N 7.78%; found: C 82.12, H 9.89, N 7.93%.

Preparation of *N,N′N″*-tris(2,6-diisopropylphenyl)guanidinotricarbonylmolybdenum(0) (4)

A mixture of **3** (0.482 g, 0.895 mmol) and $Mo(CO)_6$ (0.236 g, 0.895 mmol) was heated in *n*-heptane (24 mL) to reflux. After 18 h, a solid precipitate formed. On cooling, the solid was filtered off, and recrystallized from a minimum quantity of boiling heptane, hot filtering, and cooling to –35°C to give small, bright yellow crystals of **4** which were analytically pure. Yield: 0.17 g, (0.24 mmol, 26%), mp 210°C dec. ^1H NMR ($CDCl_3$) δ: 0.91 (d, *J*(H-H) = 6.8 Hz, 6H), 1.1 (br s, 12H), 1.20 (d, *J*(H-H) = 6.8 Hz, 6H), 1.29 (d, *J*(H-H) = 6.8 Hz, 6H), 1.39 (d, *J*(H-H) = 6.8 Hz, 6H), 2.87 (sept, *J*(H-H) = 6.8 Hz, 2H), 3.11 (sept, *J*(H-H) = 6.8 Hz, 2H), 3.49 (sept, *J*(H-H) = 6.8 Hz, 2H), 5.06 (s, 1 H), 5.50 (d, *J*(H-H) = 6 Hz, 2 H), 5.77 (t, *J*(H-H) = 6 Hz), 1 H), 7.06–7.37 (m, 6H), 7.28 (s, 1 H). ^{13}C NMR spectrum not obtained due to sample instability. MS (70 eV) reported on ^{98}Mo isotopomers: *m/z* 721.31377 (M^+ within 1.8 ppm, 2%), 635.31446 ($M - 3CO - 2H^+$ within 0.2 ppm, 17%); 539 (ligand$^+$, 62%), 496 (ligand–$^iPr^+$, 100%). IR (KBr) (cm^{-1}): ν(N-H) 3400, 3252 br; ν(C≡O) 1952, 1882, 1833; ν(C=N) 1635. Anal. calcd. for $C_{40}H_{53}MoN_3O_3$ (719.83): C 66.74, H 7.42, N 5.84%; found: C 67.00, H 7.16, N 5.95%.

X-ray analysis

The crystal structure of **3** was determined using a Stoe IPDS diffractometer. 277 Frames with an angle increment of 1.3° were measured. Therefore the full φ range of 360° was covered and each reflection was thus measured twice. Experimental details are summarized in Table 1. The structure was solved by direct methods using SHELXS-97 (16) and refined by full-matrix least-squares on F^2 using SHELXL-97 (17) using all reflections. The non-hydrogen atoms were refined anisotropically, and although most of the H atoms on C were located on the difference map, they were refined using a riding model (C—H = 0.95 Å). For CH_3 groups, a geometrically fixed trigonal pyramidal unit was fitted to the electron density for H by refining a torsion angle that defined the rotation of the group on the C—C bond (a standard procedure in SHELXL). The H atoms attached to N were refined freely. Isotropic *U* values were bound to 1.2 times the *U* values of the corresponding N atoms. Disorder is encountered with respect to the position of one such H atom. The disorder ratio was freely refined (the sum was fixed to 1). The refinement converged with occupancy of 0.3 for the hydrogen attached to N(1) and 0.7 for N(2). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited.[2]

Electronic structure calculations

All calculations were performed using the AM1 method as implemented in HyperChem 5.1 running on a Pentium III computer under Windows NT 4.0 (18).

[2] A detailed structure report including atom positions and the anisotropic temperature factors has been deposited. Copies of materials on deposit may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON, Canada K1A 0S2 (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). Crystal data, atomic coordinates, bond lengths and angles, and hydrogen coordinates of the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support (RTB), and the University of Lethbridge for purchase of the NMR spectrometer and the Macspect controller.

References

1. R.T. Boeré, V. Klassen, and G. Wolmershäuser. J. Chem. Soc. Dalton Trans. 4147 (1998).
2. R.T. Boeré, V. Klassen, and G. Wolmershäuser. Can. J. Chem. **78**, 583 (2000).
3. Y. Zhou and D.S. Richeson. Inorg. Chem. **36**, 501 (1997).
4. P.J. Bailey, K.J. Grant, S. Pace, S. Parsons, and L.J. Stewart. J. Chem. Soc. Dalton Trans. 4263 (1997).
5. P.J. Bailey, L.A. Mitchell, and S. Parsons. J. Chem. Soc. Dalton Trans. 2839 (1996).
6. M.B. Dinger, W. Henderson, and B.K. Nicholson. J. Organomet. Chem. **556**, 75 (1998).
7. G. Himbert and W. Schwickerath. Liebigs Ann. Chem. 85 (1984).
8. A. Carpy, J.-M. Leger, C.-G. Wermuth, and G. Leclerc. Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. **B37**, 885 (1981).
9. G. Argay, A. Kalman, A. Karpor, and B. Ribar. Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. **B36**, 363 (1980).
10. F. Bellucci, V. Bertolasi, V. Ferretti, and G. Gilla. Acta Crystallogr. Sect. C: Cryst. Struct. Commun. **C41**, 544 (1985).
11. G. Häfelinger and K. H. Kuske. *In* The chemistry of amidines and imidates. Vol. 2. *Edited by* S. Patai and Z. Rappoport. Wiley, Chichester. 1991. Chap. 1. pp. 1–100.
12. H.S. Gutowsky and C.H. Holm. J. Chem. Phys. **25**, 1228 (1956).
13. J. Sandström. *In* Dynamic NMR spectroscopy. Academic Press, London. 1982.
14. M. Yoshifuji, S. Sasaki, T. Niitsu, and N. Inamoto. Tetrahedron Lett. **30**, 187 (1989).
15. H. Ranaivonjatovo, H. Ramadane, H. Gornitzka, J. Escudié, and J. Satgé. Organometallics, **17**, 1631 (1998).
16. G. Sheldrick. SHELXS-97. University of Göttingen, Göttingen, Germany. 1997.
17. G. Sheldrick. SHELXL-97. University of Göttingen, Göttingen, Germany. 1997.
18. HyperChem Pro Release 5.1, HyperCube. Waterloo, ON.