DALTON

Guanidines as neutral monodentate ligands; syntheses and crystal structures of $[Co\{PhN{=}C(NHPh)_2\}_2Cl_2]$ and $[Ag\{PhN{=}C(NHPh)_2\}]$-$[SO_3CF_3]$

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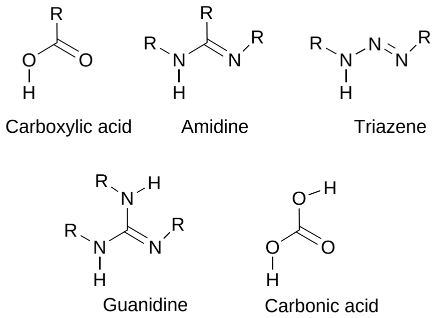
Two complexes exhibiting monodentate metal co-ordination of a neutral guanidine have been synthesized and structurally characterised. Treatment of $CoCl_2$ with 1,2,3-triphenylguanidine in tetrahydrofuran solution produced the tetrahedral complex $[Co\{(PhN)C(NHPh)_2\}_2Cl_2]$ **1** in which the guanidine ligands are co-ordinated through their imine nitrogen atoms alone. Similarly, treatment of the guanidine with $Ag[SO_3CF_3]$ in toluene provided the linear complex $[Ag\{(PhN)C(NHPh)_2\}_2][SO_3CF_3]$ **2** in which the triflate counter ion remains unco-ordinated, but is hydrogen bonded to the guanidine hydrogen atoms. Both complexes have been characterised by X-ray crystallography.

The nitrogen analogues of carboxylic acids, amidines (RN=CR−NHR) and triazenes (RN=N−NHR), have been shown to be excellent ligands for transition metals, in particular as anionic chelating or bridging amidinates and triazenates.[1] However, their behaviour as neutral monodentate ligands is comparatively uncommon, although a number of such complexes have been characterised.[2–5] The increased basicity (donor strength) of the nitrogen donors over oxygen, and the added flexibility provided by manipulation of the electronic and steric properties of the R groups, are features of these ligands which have been exploited on many occasions. In particular, the potential of complexes in which the sterically demanding bis(trimethylsilyl)benzamidinate ligand $[PhC(NSiMe_3)_2]^-$ replaces a cyclopentadienyl ligand to provide new unsaturated complexes has attracted considerable attention over recent years.[6] Guanidines $[RN{=}C(NHR)_2]$ bear the same relationship to carbonic acid as amidines and triazenes do to carboxylic acids, and as such should be excellent ligands given the above considerations. Furthermore, there exists the possibility of a second deprotonation to provide a dianionic ligand $[C(NR)_3]^{2-}$, the nitrogen analogue of carbonate,[7] which is unavailable to the carboxylic acid analogues. Carbonate is a highly versatile ligand which has been structurally characterised in a multitude of mono-, di- and tri-hapto co-ordination modes,[8] and it is therefore surprising that the potential of guanidines as ligands with a diverse co-ordination chemistry is only now beginning to be appreciated.

Our initial interest in the potential of guanidines and their anions as ligands was prompted by the prospect that the $[C(NR)_3]^{2-}$ dianion might exhibit an η^3-co-ordination mode in which all three nitrogen donors are bound to a single metal ion.[7] This is a co-ordination mode unknown for the carbonate ligand, but its ubiquity for the trimethylenemethane ligand $[C(CH_2)_3]^{2-}$, the carbon analogue of this system,[9] fuelled our expectation that it might also be observed for the nitrogen ligand. Although we have yet to demonstrate the existence of such a co-ordination mode for the guanidine dianion, we have now developed the co-ordination chemistry of guanidines to a considerable extent. We have previously reported ruthenium and rhodium complexes containing chelating guanidinate ligands,[10] and the redox pair $[Mo_2\{\mu\text{-}\eta^2\text{-}(NPh)_2CNHPh\}_4]^{0/+}$ which gave the first indications of the flexible donor properties of these ligands.[11] In addition we have characterised a number of main-group complexes containing both guanidine mono- and di-anions.[12] Here we report the syntheses and structural characterisation of rare examples of complexes containing a guanidine co-ordinated as a neutral monodentate ligand. To our knowledge there are only two previous examples of complexes containing monodentate guanidine ligands which have been structurally characterised,[13,14] and in both of these the ligand is a 1,1,3,3-tetrasubstituted guanidine $[(R_2N)_2C{=}NH]$. The ligand reported here is, in contrast, a 1,2,3-trisubstituted guanidine $[(NHR)_2C{=}NR]$.



Results and Discussion

Our previous observations of the reactivity of 1,2,3-triphenylguanidine with the metal halide complexes $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ and $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)Cl_2\}_2]$ had shown that, in addition to cleaving the chloro-bridges, the guanidine also acts as a base to provide a chelating guanidinate ligand with concomitant formation of the guanidinium chloride.[10] Indeed, treatment of these dimers with 4 molar equivalents of the guanidine in toluene solution rapidly leads to precipitation of the salt and formation of the guanidinate complexes in good yield at room temperature. Given the observation that amidines and triazenes can act as neutral imine donors to provide tetrahedral complexes with transition-metal dihalides,[2,3] we were interested to investigate the possibility that guanidines could behave in a similar fashion.

$[Co\{(PhN)C(NHPh)_2\}_2Cl_2]$ 1

Treatment of $CoCl_2$ with 2 molar equivalents of 1,2,3-triphenylguanidine in tetrahydrofuran (thf) under reflux provides a bright blue solution of $[Co\{(PhN)C(NHPh)_2\}_2Cl_2]$ **1**

Table 1 Selected bond lengths (Å) and angles (°) for molecule 1 of [Co{(PhN)C(NHPh)$_2$}$_2$Cl$_2$] **1**

Co(1)–N(11)	2.014(6)	C(11)–N(21)	1.342(8)
Co(1)–N(12)	2.013(5)	C(11)–N(31)	1.384(8)
Co(1)–Cl(11)	2.280(2)	C(12)–N(12)	1.295(8)
Co(1)–Cl(21)	2.284(2)	C(12)–N(22)	1.375(8)
C(11)–N(11)	1.312(8)	C(12)–N(32)	1.361(8)
N(11)–Co(1)–N(12)	113.2(2)	N(11)–C(11)–N(21)	120.3(6)
Cl(11)–Co(1)–Cl(21)	105.32(8)	N(11)–C(11)–N(31)	121.3(6)
N(11)–Co(1)–Cl(11)	109.3(2)	N(21)–C(11)–N(31)	118.4(6)
N(12)–Co(1)–Cl(11)	111.0(2)	N(12)–C(12)–N(22)	118.5(6)
N(12)–Co(1)–Cl(21)	109.3(2)	N(12)–C(12)–N(32)	124.2(6)
N(11)–Co(1)–Cl(21)	109.3(2)	N(22)–C(12)–N(32)	117.3(6)

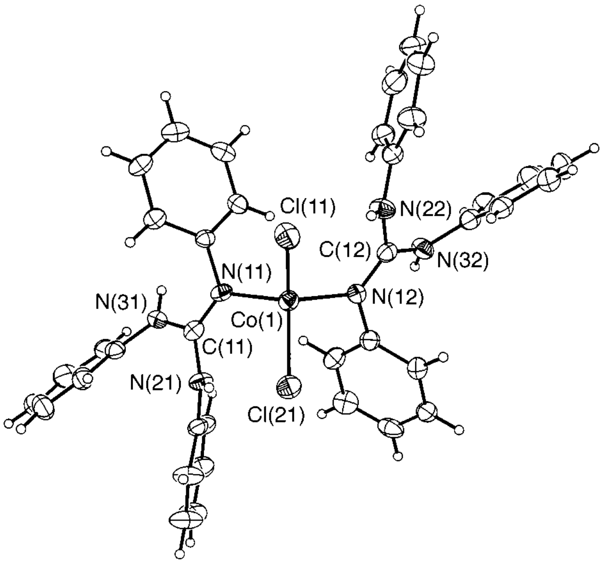


Fig. 1 Thermal ellipsoid plot of [Co{(PhN)C(NHPh)$_2$}$_2$Cl$_2$] **1** showing the atom numbering scheme. A second molecule in the unit cell, which is not shown, has similar metrical parameters

which may be obtained as the crystalline bis(dichloromethane) solvate in 77% yield by slow evaporation of a dichloromethane–hexane solution. The infrared spectrum of this complex as a Nujol mull shows the ν(C=N) mode of the co-ordinated guanidine at 1626 cm^{-1} which compares with a value of 1637 cm^{-1} for the free guanidine. Previous studies of transition-metal guanidine complexes have shown a similar reduction in C=N stretching frequency.[14,15] Thus, a low-energy shift of between 60 and 67 cm^{-1} has been observed for the 1,1,3,3-tetramethylguanidine (L) complexes [ML$_4$][ClO$_4$]$_2$ (M = Co, Cu or Zn) and this was interpreted as indicating co-ordination through the imine rather than an amine nitrogen. The ν(N–H) modes of the ligand appear as a rather broad unresolved band at 3351 cm^{-1} in the spectrum of **1** which contrasts with the sharp band at 3382 cm^{-1} observed in the spectrum of the free guanidine.

A crystal structure determination shows that complex **1** contains two independent molecules per unit cell, solvated by two molecules of CH$_2$Cl$_2$. In all cases, the differences in bond lengths for the two molecules are not crystallographically significant at the 3σ level and therefore only data for the molecule containing Co(1) will be discussed; this is however not the case for bond angles. The molecular structure of **1** is shown in Fig. 1, and selected bond lengths and angles are provided in Table 1. The Co–Cl bond lengths are only slightly (*ca.* 0.01 Å) longer than in the analogous compound with *N*,*N′*-di(*p*-tolyl)formamidine ligands,[2] but significantly longer than those found in [CoCl$_2$(NC$_5$H$_4$OMe-2)$_2$][16] and [CoCl$_2$(NC$_5$H$_4$Me-4)$_2$][17] (*ca.* 0.06 and 0.21 Å respectively), however the Co–N bond lengths [2.014(6) and 2.013(5) Å] do not differ significantly from those for the formamidine complex. Significant differences between the bond angles around the cobalt are however observed for the guanidine and formamidine complexes; whilst the N–Co–N angles for the two complexes are almost identical [113.2(2) and 113.0(2)° respectively], the Cl–Co–Cl angles differ markedly [105.32(8) and 115.10(6)° respectively]. However, the chemical significance of these observations is questionable since the corresponding angles for the second molecule of **1** in the unit cell differ significantly [N–Co(2)–N 108.1(2), Cl–Co(2)–Cl 107.35(8)°] thus indicating that the effects of crystal packing may account for considerable distortions of geometry about the cobalt ion in these tetrahedral CoCl$_2$L$_2$ complexes. The NH hydrogens were located in Fourier-difference maps and their attachment to the non-ligating nitrogens clearly indicates that it is the imine nitrogen atoms of the guanidine ligands which are co-ordinated to cobalt as suggested by the infrared evidence. This is confirmed by the observation that the C–N bonds between the central guanidine carbons and the ligating nitrogens [1.312(8) and 1.295(8) Å] are significantly shorter than the remaining bonds to these carbons [range 1.342(8)–1.384(8) Å]. As far as we are aware **1** represents the first structurally characterised example of a guanidine acting as a neutral monodentate ligand towards a transition metal.

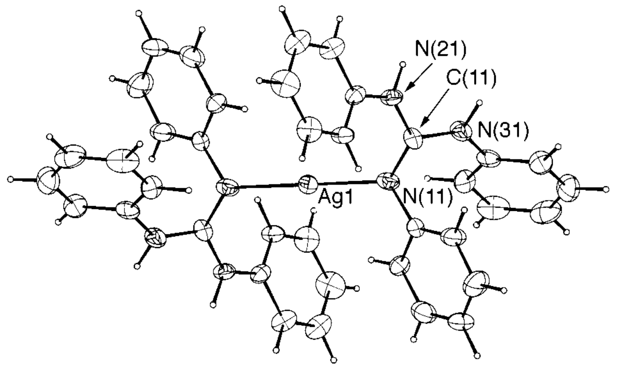


Fig. 2 Thermal ellipsoid plot of [Ag{(PhN)C(NHPh)$_2$}$_2$][SO$_3$CF$_3$] **2** showing the atom numbering scheme. The silver ion is located at an inversion centre which relates the two ligands. A second molecule in the unit cell, which is not shown, has similar metrical parameters

Following our characterisation of the M–M bonded dimers [Mo$_2${μ-η^2-(NPh)$_2$CNHPh}$_4$]$^{0/+}$, our intention in preparing complex **1** was as a precursor to the corresponding cobalt dimer. We have found that **1** does indeed react with methyllithium, mimicking the preparation of the corresponding iron formamidinate dimers [Fe$_2${μ-η^2-(PhN)$_2$CH}$_4$][18] and [Fe$_2${μ-η^2-(PhN)$_2$CH}$_3$][19] from [Fe(PhNCHNHPh)$_2$Cl$_2$], but we have as yet been unable to cleanly isolate any product from this reaction. However, we are confident that it should be possible to synthesize such a dimer since both the formamidinate- and benzamidinate-bridged dimers [Co$_2${μ-η^2-(PhN)$_2$CR}$_4$][20] (R = H or Ph) and their reduced analogues [Co$_2${μ-η^2-(PhN)$_2$CR}$_3$][21] have been synthesized by this route. The triazenate-bridged complex [Co$_2${μ-η^2-(*p*-MeC$_6$H$_4$N)$_2$N}$_4$] has also been characterised.[22] We are therefore continuing our work in this area.

[Ag{(PhN)C(NHPh)$_2$}$_2$][SO$_3$CF$_3$] 2

The reaction of silver triflate with 1,2,3-triphenylguanidine proceeds at reflux in toluene to provide the toluene-soluble complex [Ag{(PhN)C(NHPh)$_2$}$_2$][SO$_3$CF$_3$] **2** which may be crystallised as well formed colourless blocks by layering with hexane. The infrared spectrum of **2** shows the C=N stretching band at 1618 cm^{-1} and the ν(N–H) modes as two sharp absorptions at 3366 and 3304 cm^{-1}. A crystal structure determination shows the crystals of **2** to contain two independent molecules per unit cell each consisting of a linear [AgL$_2$]$^+$ complex with an associated triflate counter ion. Complex **2** is illustrated in Fig. 2 and selected bond lengths and angles are given in Table 2. Both

Table 2 Selected bond lengths (Å) and angles (°) for [Ag{(PhN)C(NHPh)$_2$}$_2$][SO$_3$CF$_3$] **2**

Ag(1)–N(11)	2.135(8)	Ag(2)–N(12)	2.146(8)
C(11)–N(11)	1.32(1)	C(12)–N(12)	1.29(1)
C(11)–N(21)	1.36(1)	C(12)–N(22)	1.35(1)
C(11)–N(31)	1.36(1)	C(12)–N(32)	1.36(1)
Ag(1)–N(11)–C(11)	122.5(6)	Ag(2)–N(12)–C(12)	117.5(6)
N(11)–C(11)–N(21)	120.7(8)	N(12)–C(12)–N(22)	123.7(9)
N(11)–C(11)–N(31)	125.7(8)	N(12)–C(12)–N(32)	125.3(9)
N(21)–C(11)–N(31)	113.5(7)	N(22)–C(12)–N(32)	111.0(9)

complexes possess an inversion centre at silver which relates the two ligands, and although the differences in some of the metrical data for these two complexes is crystallographically significant the essential features are the same for the two, and consequently only the complex containing Ag(1) is discussed in detail. The Ag–N distances in the two independent molecules [2.135(8) and 2.146(8) Å] of **2** are intermediate between those found for the bis(ammine) complex [Ag(NH$_3$)$_2$][ClO$_4$] [2.112(6) and 2.117(6) Å)][23] and the polymeric ethane-1,2-diamine complex [{Ag(en)}$_n$][ClO$_4$]$_n$ [2.17(1) Å],[24] both of which also exhibit essentially linear co-ordination of the silver ion. As far as the ligand is concerned, the most closely related, structurally characterised complex is the recently reported three-coordinate silver formamidine complex [Ag(PhN=CH–NHPh)$_2$(O$_3$SCF$_3$)] in which the Ag–N distances were found to be 2.179(4) and 2.206(4) Å,[4] significantly longer than those in **2**. Although in this complex, as in **2**, the silver is co-ordinated by two Ph–N=C imine nitrogen atoms, the difference in Ag–N distances between the two may be attributed to the change in geometry brought about by the weak co-ordination of triflate in the formamidine complex (N–Ag–N 142°) rather than by any difference between the nitrogen ligands. This is supported by our observation that the Co–N distances in the two tetrahedral complexes **1** and [CoCl$_2${HC(=NR)NHR}$_2$] (R = *p*-tolyl) do not differ significantly (see above). The anticipated similarity of the donor properties of the imine nitrogen atoms of the formamidine (PhN=CH–NHPh) and guanidine [PhN=C(NHPh)$_2$] ligands would suggest that the reason for the difference in coordination environments for the silver ions in the two complexes is steric rather than electronic in origin. Indeed, it is clear from the structure of **2** that the silver is shielded from further co-ordination by two flanking phenyl groups on unco-ordinated nitrogens.

Although the NH hydrogens in complex **2** were not directly located in the crystallographic study, co-ordination of the imine rather than an amine nitrogen to the silver is indicated by comparison of the central C–N bond distances within the ligands. For molecule 1 these distances are 1.32(1) Å for the carbon to co-ordinated nitrogen and 1.39(1) Å for the two bonds to the unco-ordinated nitrogens. The corresponding distances for molecule 2 are 1.29(1), 1.35(1) and 1.36(1) Å respectively. The [SO$_3$CF$_3$]$^-$ counter ion in **2** is hydrogen bonded *via* two S=O oxygens to the NH hydrogens of the guanidine ligands. The N–O distances in these N–H···O systems range from 2.912(12) to 3.109(13) Å and the N–H–O angle from 128.5 to 145.3°.

Experimental

General

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques and solvents which were dried and distilled under nitrogen immediately prior to use. The 1,2,3-triphenylguanidine was prepared by condensation of aniline with diphenylcarbodiimide in toluene solution. The CoCl$_2$ (Aldrich) was dried by heating to reflux with an excess of thionyl chloride for 30 min followed by drying at 50 °C under dynamic vacuum for 1 h. The NMR spectra were recorded on a Bruker AC 250 spectrometer and the infrared spectra on a Perkin-Elmer Paragon 1000 spectrometer from samples as Nujol mulls and mass spectra on a Kratos MS50 TC instrument in positive-ion FAB mode using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Elemental analyses were conducted by the microanalytical service of this department.

Syntheses

[Co{(PhN)C(NHPh)$_2$}$_2$Cl$_2$] 1. Anhydrous CoCl$_2$ (1.854 g, 12.27 mmol) and 1,2,3-triphenylguanidine (8.199 g, 28.53 mmol) were heated together to reflux in thf (90 cm^3) for 89 h. The resulting bright blue solution was reduced to dryness and the residue dissolved in CH$_2$Cl$_2$ (50 cm^3) and the solution filtered through a pad of Celite. Hexane was added until precipitation commenced and the precipitate was then dissolved by adding CH$_2$Cl$_2$ dropwise. Crystallisation by slow evaporation provided well formed needles of complex **1**·2CH$_2$Cl$_2$ (8.20 g, 77%) (Found: C, 63.61; H, 4.75; N, 11.82. C$_{40}$H$_{38}$Cl$_6$CoN$_6$ requires C, 54.92; H, 4.35; N, 9.61%). This is consistent with solvent loss by the crystals of approximately 1.8 molecules of CH$_2$Cl$_2$ per molecule of **1** (**1**·0.2CH$_2$Cl$_2$ requires C, 63.58; H, 4.77; N, 11.65%). IR (Nujol mull): 3351 (N–H) and 1626 cm^{-1} (C=N). Positive-ion FAB mass spectrum: *m/z* (%) 704 (0.1, *M*$^+$), 668 (1.1, *M* − Cl), 633 (0.4, *M* − 2Cl), 612 (3.3, *M* − NHPh) and 288 (100, triphenylguanidine). UV/VIS (CH$_2$Cl$_2$): $\tilde{\nu}$/cm^{-1} = 40 000 (ε = 24 550) and 15 360 (ε = 345 dm^3 mol^{-1} cm^{-1}).

[Ag{(PhN)C(NHPh)$_2$}$_2$][SO$_3$CF$_3$] 2. Silver triflate (427 mg, 1.66 mmol) and 1,2,3-triphenylguanidine (955 mg, 3.32 mmol) were placed in a Schlenk tube under nitrogen and aluminium foil was wrapped around the tube to exclude light. Toluene (40 cm^3) was added and the mixture heated to reflux for 1 h. The resulting mixture was filtered through a Celite pad to remove a small amount of pale brown material and the resulting very pale pink solution was reduced to *ca.* 10 cm^3 under vacuum. The solution was layered with hexane (20 cm^3) and allowed to stand overnight to yield a crop of colourless crystals suitable for X-ray crystallography (720 mg, 52%) (Found: C, 57.67; H, 4.51; N, 10.54. C$_{39}$H$_{34}$AgF$_3$N$_6$O$_3$S requires C, 56.32; H, 4.12; N, 10.11%). IR (Nujol mull): 3366 (m, N–H), 3304 (m, N–H) and 1618 cm^{-1} (s, C=N). ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.37 (br, 2 H, NH and 7.25–6.92 (m, 15 H, C$_6$H$_5$. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 152.7 (CN$_3$), 129.1, 124.6, 122.8 (C$_6$H$_5$). Positive-ion FAB mass spectrum: *m/z* 684 (*M*$^+$), 394 (*M*$^+$ − triphenylguanidine), 288 (triphenylguanidine) and 194 (diphenylcarbodiimide).

X-Ray crystallography

Crystals of complex **1** were grown from saturated dichloromethane–hexane solutions by slow evaporation at room temperature, while those of **2** were obtained by slow diffusion of hexane into a toluene solution.

Crystal data. For **1**·2CH$_2$Cl$_2$: C$_{40}$H$_{38}$Cl$_6$CoN$_6$, *M* = 874.40, monoclinic, space group *P*2$_1$/*n*, *a* = 13.080(2), *b* = 29.624(3), *c* = 21.925(3) Å, β = 91.467(12)°, *U* = 8492(2) Å^3 (from 46 reflections, 15 < θ < 16° measured at ±ω, λ = 0.710 73 Å), *Z* = 8, *D*$_c$ = 1.368 g cm^{-3}, *F*(000) = 3592, blue columnar block, 0.58 × 0.29 × 0.29 mm, *T* = 220 K, μ(Mo-Kα) = 0.818 mm^{-1}. For **2**: C$_{39}$H$_{34}$AgF$_3$N$_6$O$_3$S, *M* = 831.66, triclinic, space group $P\bar{1}$, *a* = 9.802(5), *b* = 13.760(7), *c* = 15.464(7) Å, α = 66.81(2), β = 81.65(2), γ = 75.39(3)°, *U* = 1852.73 Å^3 (from 26 reflections, 12 < θ < 13° measured at ±ω, λ = 0.710 73 Å), *Z* = 2 (two independent molecules lying on crystallographic inversion centres), *D*$_c$ = 1.49 g cm^{-3}, *F*(000) = 846.24, colourless block, 0.33 × 0.23 × 0.19 mm, *T* = 220 K, μ(Mo-Kα) = 0.65 mm^{-1}.

Data collection, solution and refinement. Data were collected using Mo-Kα radiation in the range $5 \leqslant 2\theta \leqslant 50°$ for complex **1** and $5 \leqslant 2\theta \leqslant 45°$ for **2** on a Stoe Stadi4 diffractometer equipped with an Oxford Cryosystems low-temperature device[25] using ω–θ scans. An absorption correction based on ψ scans was applied for **1** (maximum and minimum transmission coefficients: 0.540 and 0.498), $R_{int} = 0.1958$ (based principally on a weak high-angle data). Owing to rather low crystal quality, characterised by poor peak shapes and high backgrounds, a consistent set of ψ scans could not be obtained for **2**, leaving little option but to apply a correction during refinement (DIFABS, correction applied to F_c maximum and minimum corrections 1.347 and 0.683, respectively).[26] Both structures were solved by direct methods (SIR 92).[27] Complex **1** was refined against F^2 (SHELXTL)[28] with anisotropic displacement parameters for all non-H atoms, and H atoms placed in calculated positions, although those attached to nitrogen were discernible in a difference map. The refinement converged to $R1 = 0.0759$ [based on F and 7721 data with $F > 4\sigma(F)$] and $wR2 = 0.2013$ (based on F^2 and all 14 784 data) for 956 parameters). The final difference-synthesis maximum and minimum were +0.51 and −0.50 e Å^{-3}, respectively. Complex **2** was refined against F using 2895 data with $F > 4\sigma(F)$ (out of a total of 4264 unique data, CRYSTALS).[29] Hydrogen atoms were placed in calculated positions, and anisotropic displacement parameters were refined for all other atoms, giving a final R of 0.0639, $R' = 0.0704$ for 481 parameters. The final difference-map extrema were 0.81 and −1.32 e Å^{-3}.

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