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PAPER

Synthesis and coordination chemistry of tri-substituted benzamidrazones†

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A series of N^1,N^1,N^3-tri-substituted benzamidrazones of the general formula [PhC(NHR)═NNMe$_2$] (R = Me, *n*-Pr, *i*-Pr, *n*-Bu, Bn, Ph; **1a–f**) was synthesized *via* condensation of 1,1-dimethylhydrazine with the corresponding imidoyl chloride, [PhC(Cl)═NR]. Multinuclear NMR data, and zero-point energy DFT calculations conducted with the B3LYP functional and 6–31G+(d,p) basis set, suggest that these compounds exist as a single tautomer in solution; possessing a weak intramolecular hydrogen bond and a structure dominated by the localised resonance structure ArC(NHR)═N–NMe$_2$. An X-ray crystallographic study upon PhC(NHPh)═NNMe$_2$ (**1f**) demonstrated that this compound adopts an identical tautomer in the solid state. Reactions of [PhC(NHMe)═NNMe$_2$] (**1a**) with [LMCl$_2$]$_2$ (M = Ru, L = cymene; M = Rh, Ir, L = Cp*) results in the stoichiometric formation of products of the formula [LM{PhC(═NMe)NHNMe$_2$}Cl]$^+$Cl$^-$ (**2a–c**) in which the amidrazone chelates the metal in a κ^2-N^1,N^3-coordination mode. Formation of this five-membered chelate occurs with a concomitant tautomerisation of the amidrazone ligand to an alternative tautomer, *i.e.* [PhC(═NMe)NHNMe$_2$], the latter tautomer is expected to be readily energetically accessible based upon the aforementioned DFT calculations. This series of salts may be deprotonated with lithium hexamethyldisilazide to form the corresponding charge neutral complexes [LM{PhC(NMe)═NNMe$_2$}] (**3a–c**). In contrast, the reaction of N^1,N^1,N^3-tri-substituted benzamidrazones with [(cymene)RuCl$_2$]$_2$ in the presence of NaOAc yielded a mixture of cyclometallation (C–H activation) and amidrazone chelation/deprotonation (N-H activation) products. Reaction of **1a** yielded an inseparable mixture of products, whilst the reaction of **1c** resulted in formation of the cyclometallated product [LM{C$_6$H$_5$C(═N^{i}Pr)NHNMe$_2$}] (L = cymene, M = Ru; **4a**) in a modest 62% yield. This latter complex could be isolated as a crystalline orange solid, full characterisation including single crystal X-ray diffraction demonstrated that the amidrazone coordinates in a κ^2-N^2,C-coordination mode.

Introduction

Neutral and mono-anionic *N*,*N*-chelating ligands that form five-membered metallacycles upon binding to metal centres have found extensive applications in transition metal mediated processes. Whilst potentially redox active, α-diimine based ligands (**I**) have been employed in alkene polymerisation catalysis,[1–4] mono-anionic ligands derived from chiral diamines (**II**) have been used in the catalytic asymmetric hydrogenation of unsaturated substrates.[5–6] Although simple diamine ligands (**III**) such as tetramethylethylene diamine (TMEDA) have a pedigree in the stabilisation of reactive s-block complexes, more recently these ligands have been applied to the stabilisation of bimetallic metallation reagents.[7] Along with these ethylene and *ortho*-phenylene bridged systems (**I–III**), a number of ligands containing additional heteroatoms within the back-bone have been reported, including tetrazacyclopentadienes,[8] azoimines,[9] pyridinine-phosphinimes and imidazole-phosphinimines.[10]

Perhaps the least well studied of existing *N*,*N*-chelating ligands that have the potential to form 5-membered metallocycles are amidrazones (**IV**). Amidrazones, sometimes referred to as hydrazidines or hydrazide-hydrazones, are unsaturated open-chain nitrogen containing compounds of the general formula [R^{1}C(NR^{2}R^3)(N-NR^{4}R^5)].[11] Whilst the parent amidrazone (R^1 = R^2 = R^3 = R^4 = R^5 = H) has been shown to form upon metal templated condensation of hydrazine and hydrogen cyanide within the coordination sphere of octahedral phosphite-substituted Group VIII complexes[12] and a number of keto-substituted amidrazones have been shown to form complexes with gold and vanadium metals,[13] assignment of the coordination chemistry of **IV** in

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existing metal complexes remains ambiguous. Of perhaps the most relevance to the current work, Krajete and co-workers have demonstrated the coordination of nickel(II) bromide to an N^1,N^1-dimethyl-N^3-aryl benzamidrazone.[14]

Directing group mediated C–H activation of aryl rings of organic substrates, either *via* oxidative addition of low-valent transition metal fragments or base-mediated electrophilic addition of organometallic complexes, may be considered a key reaction in the controlled and selective functionalisation of carbon–hydrogen bonds.[15] Although numerous functional groups, including ketones, imines, pyridines, diazocompounds, hydroxylimines and nitriles, have been shown to direct this C–H activation reaction, examples of directing groups containing more than two heteroatoms with the potential to bind the organometallic reagent through chelation remain scarce.[16] Indeed, despite a number of tridentate cyclometallated complexes having been prepared, the vast majority of these contain symmetrical pincer type ligands with the cyclometallated carbon as the central atom of the array.[17] A number of cyclometallated complexes with oxygen, sulfur or nitrogen atom containing side chains coordinated to the metal centre have also been reported.[18]

We now report the synthesis and solution conformation of a series of N^1,N^2,N^3-benzamidrazones along with coordination studies with late-transition metal complexes $[LMCl_2]_2$. These studies demonstrate that although the latter substrates may act as neutral or mono-anionic κ²-*N*,*N*-chelating ligands, under certain reaction conditions benzamidrazones may act as directing groups for electrophilic C–H activation forming κ²-*N*,*C*-chelated complexes.

Experimental

General experimental

Unless otherwise indicated, operations were performed under anhydrous conditions and inert atmosphere employing standard Schlenk-line and glovebox techniques. Glassware was dried in an oven at 160 °C overnight or flame-dried prior to use. NMR spectra were acquired using Bruker AV-300, AVQ-400 and AVB-400 spectrometers. Chemical shifts are reported as part per million (ppm, δ) and ^{1}H and ^{13}C chemical shifts are referenced to the corresponding residual protic solvent resonance. Mass spectral data were obtained at the QB3 Mass Spectrometry Facility operated by the College of Chemistry, University of California, Berkeley. Fast atom bombardment mass spectra were recorded on a Micromass ZAB2-EQ magnetic sector instrument. Infrared spectral data were recorded on a Thermo Scientific Nicolet iS10 spectrometer fitted with a Smart OMNI-transmission or Smart iTR device as either KBR discs, neat solids or thin films. Elemental analyses were recorded by the UC Berkeley micro-mass facility. Solvents were dried through a push-still system *via* passage through alumina. $[(cymene)RuCl_2]_2$ was purchased from Sigma-Aldrich and used without further purification. $[Cp^*MCl_2]_2$ (M = Rh, Ir) were synthesised by literature methods.[19] NaOAc was purchased from Sigma-Aldrich and used as received and lithium hexamethyldisilazide (LiHMDS) was freshly prepared from *n*-BuLi and hexamethyldisilazane and recrystallised before use. Whilst compounds **1e** and **1f** are literature known, for completion, detailed characterisation data are provided in the supporting information.[20]

Representative procedure for synthesis of N^1,N^2,N^3-benzamidrazones

On a Schlenk-line, a Schlenk-tube was flame-dried under vacuum and *N*-methylbenzamide (6.25 g, 46.6 mmol) was added under a purge of argon. Dry toluene (30 mL) was added *via* cannula, and solid PCl_5 (9.72 g, 46.6 mmol) was added to the resultant slurry. The reaction mixture was warmed until homogeneous and stirred for 2 h at room temperature, after which the solvent was removed *in vacuo*. Additional dry toluene (2 × 20 mL) was added and removed under reduced pressure to distil any remaining $POCl_3$. *N*-Methylbenzimidoyl chloride was obtained as a slightly yellow oil and used directly. A solution of the imidoyl chloride in dry toluene (20 mL) was added to a mixture of triethylamine (7.1 g, 69.9 mmol) and 1,1-dimethylhydrazine (2.80 g, 46.6 mmol) in toluene solution (20 mL) in a separate Schlenk-tube. Upon addition, an exothermic reaction was observed, and noticeable warming of the Schlenk tube occurred along with the precipitation of a colourless solid from solution. The tube was sealed and after 48 h at room temperature the reaction was quenched by dilution with toluene (100 mL) and H_2O (100 mL). The phases were separated and the aqueous layer back-extracted with DCM (100 mL), the combined organics were dried over magnesium sulfate, and the solvent was removed under vacuum to give the crude product as viscous yellow oil. Purification by short-path distillation 100–105 °C at 0.25 mmHg gave pure **1a** (5.13 g, 29.0 mmol, 62%) as a yellow oil. ^{1}H NMR (300 MHz, 298 K, CD_2Cl_2) δ 2.41 (s, 6H, -NMe_2), 2.71 (d, 3H, J = 5.4 Hz, -NHMe), 6.02 (broad s, 1H, -NHMe), 7.38–7.45 (m, 5H, ArH); ^{13}C (75.5 MHz, 298 K, CD_2Cl_2) δ 31.0, 46.9, 128.3, 128.6, 129.3, 134.3, 162.4; Infrared (thin film, cm^{-1}) 3327, 3059, 2976, 2945, 2853, 1603, 1570; *m*/*z* (ESI, +ve) 178 (100%, $[M + H]^+$), 163 (20%, $[M + H - CH_3]^+$); HR-MS (ESI, +ve) calcd. for $C_{10}H_{16}N_3$ 178.1339 found 178.1337.

Compound 1b

Isolation by distillation gave **1b** (5.40 g, 26.3 mmol, 86%) as a viscous light yellow oil b.p. 140–143 °C at 0.25 mmHg. ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ 0.63 (t, 3 H, J = 7.2 Hz, -NHCH$_2$CH$_2$CH_3), 1.15 (tq, 2 H, J = 7.2, 6.8 Hz, -NHCH$_2$CH_2CH$_3$), 2.57 (s, 6H, -NMe_2), 2.80 (dt, 2H, J = 6.9, 6.8 Hz, -NHCH_2CH$_2$CH$_3$), 6.20 (broad s, IH, -NHCH$_2$CH$_2$CH$_3$), 7.12–7.16 (m, 3H, ArH), 7.62–7.64 (m, 2H, ArH); ^{13}C NMR (100 MHz, 298 K, C_6D_6) δ 11.5, 25.3, 46.3, 47.5, 128.6, 129.3, 129.6, 135.5, 162.5; Infrared (solid, cm^{-1}) 3307, 2944, 2856, 1600, 1570; *m*/*z* (ESI, +ve) 206 (100%, $[M + H]^+$), 161 (5%, $[M - C_3H_8]^+$); HR-MS (ESI, +ve) calcd. for $C_{12}H_{20}N_3$ 206.1652 found 206.1650.

Compound 1c

Isolation by distillation gave **1c** (2.13 g, 10.4 mmol, 68%) as a viscous light yellow oil b.p. 135–137 °C at 0.25 mmHg. ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ 0.83 (d, 6H, J = 6.4 Hz, -NHCHMe_2), 2.54 (s, 6H, -NMe_2), 3.43 (d hept, 1H, J = 6.4, 5.1 Hz, -NHCHMe$_2$), 6.03 (d, 1H, J = 5.1 Hz, -NHCHMe$_2$), 7.15–7.19 (m, 3H, ArH), 7.63–7.65 (m, 2H, ArH); ^{13}C NMR (100 MHz,

298 K, C_6D_6) δ 24.6, 45.5, 47.5, 129.1, 129.7, 135.8, 162.3; Infrared (solid, cm^{-1}) 3289, 2944, 2855, 1597, 1569; *m/z* (ESI, +ve) 206 (100%, $[M + H]^+$), 164 (80%, $[M - C_3H_5]^+$); HR-MS (ESI, +ve) calcd. for $C_{12}H_{20}N_3$ 206.1652 found 206.1647.

Compound 1d

Isolation by distillation gave **1d** (4.25 g, 19.3 mmol, 69%) as a viscous light yellow oil b.p. 158–160 °C at 0.25 mmHg. ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ 0.70 (t, 3H, *J* = 7.2 Hz, -NH$(CH_2)_3CH_3$), 1.02–1.18 (m, 4H, -NHC$H_2(CH_2)_2CH_3$), 2.58 (s, 6H, -NMe_2), 2.85 (dt, 2H, *J* = 6.9, 6.8 Hz, -NHC$H_2(CH_2)_2CH_3$), 6.19 (broad s, 1H, -N$H(CH_2)_3CH_3$), 7.15–7.20 (m, 3H, Ar*H*), 7.64–7.67 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, 298 K, C_6D_6) δ 14.2, 20.3, 34.2, 44.4, 47.5, 128.6, 129.3, 129.6, 135.5, 162.5; Infrared (solid, cm^{-1}) 3310, 2944, 2855, 1600, 1570; *m/z* (ESI, +ve) 220 (100%, $[M + H]^+$), 205 (5%, $[M + H - CH_3]^+$), 177 (15%, $[M - C_3H_7]^+$); HR-MS (ESI, +ve) calcd. for $C_{13}H_{22}N_3$ 220.1808 found 220.1802.

Synthesis of [LM{PhC(=NMe)NHNMe$_2$}Cl]$^+$Cl$^-$ (2a–c)

In a glovebox, **1a** (57 mg, 0.32 mmol, 2 equiv.) and the corresponding metal complex $[LMCl_2]_2$ (L = cymene, M = Ru; L = Cp*, M = Rh, Ir; 0.16 mmol, 1 equiv.) were weighed separately, each dissolved in 2.5 mL of dichloromethane and the solutions combined. The resulting reaction mixture was transferred to a 20 mL vial and stirred for 48 h at room temperature. The solvent volume was then concentrated to *ca.* 1 mL under reduced pressure, this mixture was then added to 15–20 mL of pentane upon which point the product precipitated from solution (the mixture may then be triturated for a further 4 h if oiling out of solution occurs). Isolation by filtration, followed by washing with pentane (2 × 5 mL) yielded **2a–c** as yellow, orange or red solids which are tolerant of both moisture and air.

Compound 2a

Isolated as an orange solid (103 mg, 0.208 mmol, 66%). X-Ray quality crystals were grown from slow diffusion of pentane into a dichloromethane solution. ^{1}H NMR (400 MHz, 298 K, CD_2Cl_2) δ 1.36 (d, 6H, *J* = 8.0 Hz, ArCHMe_2), 2.35 (s, 6H, Ar*Me*), 3.00 (hept, 1H, *J* = 8.0 Hz, ArC*H*Me$_2$), 3.37 (s, 3H, -NMe_2), 3.51 (s, 3H, -NMe_2), 3.81 (s, 3H, -N*Me*), 5.32 (d, 1H, *J* = 6.0 Hz, Ar*H*), 5.39 (d, 1H, *J* = 6.0 Hz, Ar*H*), 5.51 (d, 1H, *J* = 6.0 Hz, Ar*H*), 5.60 (d, 1H, *J* = 6.0 Hz, Ar*H*), 7.27–7.29 (m, 2H, Ar*H*), 7.44–7.48 (m, 3H, Ar*H*), 11.40 (broad s, 1H, N*H*); ^{13}C NMR (100 MHz, 298 K, CD_2Cl_2) δ 18.8, 22.5, 22.7, 32.0, 45.1, 56.8, 62.3, 81.3, 82.9, 85.5, 87.2, 96.7, 107.0, 126.8, 129.0, 129.1, 131.6, 165.2; Infrared (solid, cm^{-1}) 3370, 3109, 2963, 2855, 1620, 1600, 1578; *m/z* (ESI, +ve) 448 (70%, $[M - Cl]^+$), 412 (10%, $[M - H - 2Cl]^+$); HR-MS (ESI, +ve) calcd. for $C_{20}H_{29}N_3{}^{35}Cl^{102}Ru$ 448.1088 found 448.1103; Elemental analysis calcd. for $C_{20}H_{29}N_3Cl_2Ru$: C 49.69, H 6.00, N 8.69 found: C, 48.85, H 5.95, N 8.37.

Compound 2b

Isolated as a brown-red solid (113 mg, 0.232 mmol, 72%). ^{1}H NMR (400 MHz, 298 K, CD_2Cl_2) δ 1.68 (s, 15H, C_5Me_5), 3.13 (s, 3H, -N*Me*), 3.38 (broad s, 3H, -NMe_2), 3.57 (broad s, 3H, -NMe_2), 7.35–7.37 (m, 2H, Ar*H*), 7.45–7.51 (m, 3H, Ar*H*), 11.75 (broad s, 1H, -N*H*); ^{13}C NMR (100 MHz, 298 K, CD_2Cl_2) δ 9.7, 41.0, 95.9 (d, $^1J_{^{103}Rh-^{13}C}$ = 8.2 Hz), 127.5, 129.1, 129.2, 131.5, 164.9 (remaining ^{13}C resonances could not be observed); Infrared (solid, cm^{-1}) 3376, 3111, 2984, 1626, 1600, 1578; *m/z* (ESI, +ve) 450 (100%, $[M - Cl]^+$), 414 (25%, $[M - H - 2Cl]^+$); HR-MS (ESI, +ve) calcd. for $C_{20}H_{30}N_3{}^{35}Cl^{103}Rh$ 450.1178 found 450.1170.

Compound 2c

Isolated as a yellow solid (123 mg, 0.214 mmol, 86%). ^{1}H NMR (400 MHz, 298 K, CD_2Cl_2) δ 1.65 (s, 15H, C_5Me_5), 3.21 (s, 3H, -N*Me*), 3.54 (broad s, 3H, -NMe_2), 3.73 (broad s, 3H, -NMe_2), 7.39–7.41 (m, 2H, Ar*H*), 7.47–7.50 (m, 3H, Ar*H*), 12.10 (broad s, 1H, -N*H*); ^{13}C NMR (100 MHz, 298 K, CD_2Cl_2) δ 9.6, 41.8, 87.7, 126.7, 129.1, 129.2, 131.6, 166.8 (remaining ^{13}C resonances could not be observed) Infrared (solid, cm^{-1}) 3368, 3109, 2916, 1624, 1600, 1540; *m/z* (ESI, +ve) 540 (80%, $[M - Cl]^+$), 504 (100%, $[M - H - 2Cl]^+$); HR-MS (ESI, +ve) calcd. for $C_{20}H_{30}N_3{}^{35}Cl^{191}Ir$ 538.1729 found 538.1742.

Synthesis of [LM{PhC(=NMe)NNMe$_2$}Cl] (3a–c)

In a glovebox, to a stirred suspension of **2a–c** (0.20 mmol, 1 equiv.) in toluene (10 mL) was added dropwise a solution of lithium hexamethyldisilazide (0.20 mmol, 1 equiv.) as a solution in the same solvent (5 mL). The resulting reaction mixture quickly changed appearance, becoming homogeneous and changing in colour. After 2 h at room temperature the mixture was filtered, the solid was washed with toluene (5 mL) and the resulting filtrate concentrated to approximately 3 mL. The product was precipitated from solution by addition of 15–20 mL of pentane. Isolation by filtration, followed by washing with pentane (2 × 5 mL) yielded **3a–c**.

Compound 3a

Isolated as a red solid (9.7 mg, 0.021 mmol, 53% based upon 0.040 mmol of **2a**) ^{1}H NMR (300 MHz, 298 K, CD_2Cl_2) δ 1.34 (d, 6H, *J* = 6.9 Hz, ArCHMe_2), 2.29 (s, 6H, Ar*Me*), 2.99 (hept, 1H, *J* = 6.9 Hz, ArC*H*Me$_2$), 3.13 (s, 6H, -NMe_2), 3.21 (s, 3H, -N*Me*), 5.00 (m, 2H, Ar*H*), 5.32 (m, 2H, Ar*H*), 7.16–7.19 (m, 2H, Ar*H*), 7.27–7.29 (m, 2H, Ar*H*); ^{13}C NMR (75.5 MHz, 298 K, CD_2Cl_2) δ 18.7, 22.7, 31.9, 45.2, 81.7, 85.9, 94.7, 104.5, 128.3, 128.4, 129.0, 134.4, 170.9 (remaining ^{13}C resonances not observed); Infrared (solid, cm^{-1}) 2978, 2916, 1540, 1449, 1384; *m/z* (FAB, +ve) 448 (60%, $[M]^+$), 412 (100%, $[M - H - Cl]^+$); HR-MS (FAB, +ve) calcd. for $C_{20}H_{29}N_3{}^{35}Cl^{104}Ru$ 450.1148 found 450.1104.

Compound 3b

Isolated as a deep-red solid (70.9 mg, 0.158 mmol, 77%). ^{1}H NMR (400 MHz, 298 K, CD_2Cl_2) δ 1.65 (s, 15H, C_5Me_5), 2.92 (s, 3H, -N*Me*), 2.99 (s, 6H, -NMe_2), 7.22–7.30 (m, 5H, Ar*H*); ^{13}C NMR (100 MHz, 298 K, CD_2Cl_2) δ 9.6, 41.3, 57.0, 94.0 (d, $^1J_{^{103}Rh-^{13}C}$ = 7.7 Hz), 128.2, 128.3, 129.1, 134.9, 171.3; Infrared (solid, cm^{-1}) 2908, 1542, 1445, 1374; *m/z* (FAB, +ve) 450 (45%, $[M + H]^+$), 414 (65%, $[M - H - Cl]^+$); HR-MS (FAB, +ve) calcd. for $C_{20}H_{30}N_3{}^{35}Cl^{103}Rh$ 450.1178 found 450.1189.

Table 1 Selected X-ray diffraction acquisition data

	1f	2a	3c	4a
Molecular formula	$C_{15}H_{17}N_3$	$C_{20}H_{29}Cl_2N_3Ru{\cdot}CH_2Cl_2$	$C_{20}H_{29}ClN_3Ir$	$C_{22}H_{32}ClN_3Ru$
Formula weight (g mol^{-1})	239.32	568.34	539.11	475.03
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
a (Å)	8.8213(14)	10.3261(7)	9.7105(11)	9.437(5)
b (Å)	9.2284(15)	13.8183(9)	12.4005(13)	10.703(5)
c (Å)	9.3398(15)	17.4025(12)	16.6567(18)	11.940(5)
α (°)	80.219(2)	90	90	110.278(5)
β (°)	75.043(2)	90	90	90.291(5)
γ (°)	62.591(2)	90	90	106.338(5)
V (Å^3)	650.94(18)	2483.1(3)	2005.7(4)	1078.5(9)
Z	2	4	4	2
μ (mm^{-1})	0.074	1.075	6.798	0.862
ρ (g cm^{-3})	1.221	1.514	1.785	1.463
Θ range (°)	2.49–25.34	1.88–25.38	2.05–25.35	1.83–25.37
R_1, wR_2 [$I > 2\sigma(I)$]	0.0377, 0.1155	0.0515, 0.1053	0.0301, 0.0599	0.0257, 0.0976
R_1, wR_2 (all data)	0.0548, 0.1280	0.0638, 0.110	0.0350, 0.0624	0.0265, 0.0997
Measured/independent reflections/R_{int}	2340/1837/0.0161	4566/3933/0.0549	27219/3660/0.0655	23597/3909/0.0237

Compound 3c

Isolated as an orange solid (67.2 mg, 0.125 mmol, 64%). X-Ray quality crystals were grown from slow diffusion of pentane into a toluene solution at –35 °C. ^{1}H NMR (400 MHz, 298 K, CD_2Cl_2) δ 1.66 (s, 15H, C_5Me_5), 3.14 (s, 3H, -NMe), 3.31 (s, 6H, -NMe_2), 7.18–7.32 (m, 5H, ArH); ^{13}C NMR (100 MHz, 298 K, CD_2Cl_2) δ 11.3, 43.0, 60.2, 87.4, 130.0, 130.1, 131.0, 135.9, 176.4; Infrared (solid, cm^{-1}) 2967, 2911, 1544, 1445, 1388; m/z (FAB, +ve) 540 (40%, [M]$^+$), 504 (100%, [M – H – Cl]$^+$); HR-MS (FAB, +ve) calcd. for $C_{20}H_{30}N_3{}^{35}Cl^{193}Ir$ 540.1743 found 540.1758.

Synthesis of [(cym)Ru{PhC(NH^{i}Pr)=NMe$_2$}Cl] (4a)

In a glovebox, a solution of **1c** (26.0 mg, 0.127 mmol) in CD_2Cl_2 (2 mL) was added to $[(cym)RuCl_2]_2$ (50 mg, 0.063 mmol). In a separate 20 mL vial, sodium acetate (25.9 mg, 0.316 mmol, 5 equiv.) was weighed out and the reaction mixture added. The reaction mixture was stirred for 4 days and the reaction monitored by removing aliquots and analysing by ^{1}H NMR spectroscopy. The product **4a** (0.078 mmol, 62%) was observed and the yield recorded against tetrakis(trimethylsilyl)silane as an internal standard. Although unstable on the benchtop for extended periods, **4a** could be isolated in pure form, albeit with significant decomposition occurring during isolation, by chromatography upon silica gel using a 10 cm column with 2.5 cm diameter employing a 10 : 1 mixture of hexanes : ethylacetate. X-Ray quality crystals were grown by recrystallisation from hexanes. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 0.59 (d, 3H, J = 6.8 Hz, ArCHMe_2), 1.06 (d, 3H, J = 6.8 Hz, ArCHMe_2), 1.13 (d, 3H, J = 6.4 Hz, -NHCHMe_2), 1.29 (d, 3H, J = 6.4 Hz, -NHCHMe_2), 2.18 (s, 3H, ArMe), 2.38 (hept, 1H, J = 6.8 Hz, ArCHMe$_2$), 2.57 (s, 3H, -NMe_2), 2.74 (s, 3H, -NMe_2), 4.23 (d hept, 1H, J = 6.8 and 6.4 Hz), 4.80 (d, 1H, J = 6.0 Hz, ArH), 4.94 (d, 1H, J = 5.6 Hz, ArH), 5.65 (d, 1H, J = 6.0 Hz, ArH), 6.16 (d, 1H, J = 5.6 Hz, ArH), 6.92–694 (m, 2H, ArH + -NH), 7.13 (dd, 1H, J = 7.5 and 7.1 Hz), 7.50 (d, 1H, J = 7.7 Hz, ArH), 8.16 (d, 1H, J = 7.5 Hz); ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 18.6, 19.9, 24.4, 24.7, 25.0, 30.5, 44.8, 45.4, 47.4, 73.4, 82.0, 90.3, 90.5, 104.8, 104.9, 121.4, 126.4, 128.8, 137.2, 139.5, 171.4, 183.1; Infrared (solid, cm^{-1}) 3247, 2958, 2866, 1585, 1569, 1462; LR-MS (FAB, +ve) 475 (60%, [M]$^+$), 440 (100%, [M – Cl]$^+$); HR-MS (FAB, +ve) calcd. For $C_{22}H_{32}N_3{}^{35}Cl^{102}Ru$ 475.1323 found 475.1338.

X-Ray crystallographic data

All single crystal X-ray diffraction experiments were conducted at UC Berkeley CheXray facility using a SMART APEX diffractometer equipped with a fine-focus sealed tube, Mo K/α source and Bruker APEX-I CCD detector. Structure solution, followed by full-matrix least squares refinement was performed using the WinGX-1.70 suite of programs. A multi-scan absorption correction was applied, whilst structures were solved with SHELXS-97 and refined in SHELXL-97.[21]

DFT calculations

Calculations were implemented in Gaussian03 using the restricted B3LYP functional and 6,31G+(d,p) basis set.[22] All minima were confirmed by frequency calculations and, for **1f**, metrical outputs were compared against the solid-state data.

Results and discussion

Synthesis and conformation of tri-substituted amidrazones

Whilst the structurally related, but diverse, series of compounds referred to by the generic term amidrazone have numerous methods of preparation and applications in synthesis,[11] reports of the synthesis and study of N^1,N^1-dimethyl-N^3-alkylbenzamidrazones and N^1,N^1-dimethyl-N^3-arylbenzamidrazones remain limited to a handful of examples.

Thus, in 1971 Smith and co-workers reported that the reaction of N-phenylbenzimidoyl chloride with an excess of 1,1-dimethylhydrazine yielded the corresponding amidrazone.[20a] In 1972, Walter and Weiss provided an analysis of N^1,N^3-disubstituted and N^1,N^1,N^3-trisubstituted amidrazones by infrared spectroscopy and concluded that these compounds exist in solution as a single tautomer containing an intramolecular hydrogen bond (Fig. 2, tautomer **A**).[23] In contrast, Smith and co-workers

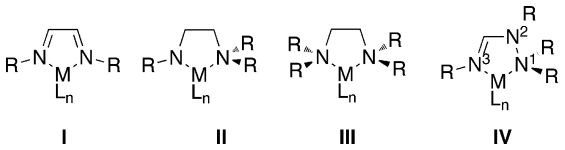


Fig. 1 Representative *N*,*N*-chelating ligands (the numbering scheme in **IV** is used throughout).

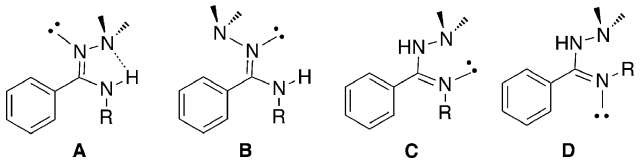
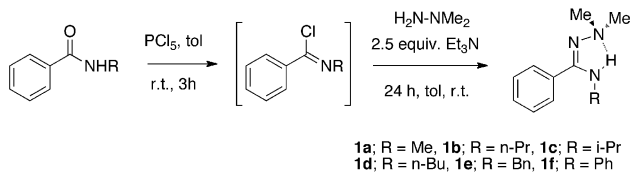


Fig. 2 Four possible tautomers of N^1,N^2,N^3-benzamidrazones **1a–f**.

argued that, although N^1,N^1-dimethyl-N^3-alkylbenzamidrazones exist in this conformation, based upon resonance arguments, tautomerisation to an alternative hydrazide imide form may occur for N^1,N^1-dimethyl-N^3-phenylbenzamidrazones (Fig. 2, tautomer **C** or **D**).[20a,b]

Following literature precedent,[20] the reaction of 1,1-dimethylhydrazine with *N*-alkyl or *N*-aryl benzimidoyl chlorides in the presence of two equivalents of triethylamine proceeded to yield the corresponding amidrazones (Scheme 1). The latter compounds could be purified by vacuum distillation or flash column chromatography upon silica gel using a mixture of dichloromethane, methanol and ammonium hydroxide as the eluent (for experimental details see ESI†).



Scheme 1 Synthesis of N^1,N^2,N^3-benzamidrazones.

In line with the expectations[23] furnished by Walter and Weiss, ^{1}H NMR experiments upon compounds **1a–f**, in either $CDCl_3$ or d_8-toluene solution, demonstrated significant $^3J_{H-H}$ coupling constants (5.1–6.9 Hz) between the N–H proton and the α-methyl, methylene, or α-methine protons of the group at the N^3-position. In the case of the N^1,N^1,N^3-trimethylbenzamidrazone **1a** the N^3-methyl resonance, apparent as a sharp doublet at 2.71 ppm ($^3J_{H-H}$ = 6.2 Hz), collapsed to a broadened singlet upon addition of a single drop of D_2O. These data are suggestive of the predominance of tautomer **A** in solution.

Due to a lack of α-protons, the structural assignment of compound **1f** is more convoluted (*vide supra*). Whilst the literature precedent provides two contrasting views of the bonding in this molecule, we now provide a more comprehensive account of the ground-state tautomer of these compounds.

Our understanding of the solution structures of **1a–f** was further enhanced by a single crystal X-ray diffraction experiment upon **1f** in combination with gas phase DFT calculations. Readily crystallised from a concentrated hexanes solution, compound **1f** exists as tautomer **A** in the solid state. Important bond lengths and angles are listed in Table 3 and the structure is represented in Fig. 3.

Table 2 Relative sum of thermal and zero-point energies (kcal mol^{-1}) for the possible tautomers of **1a**, **1c** and **1f** calculated using the B3LYP functional and 6,31G+(d,p) basis set

Confomer	A	B	C	D
R = Me	0	+4.0	+6.9	+7.4
R = ^{i}Pr	0	+3.5	+1.8	+2.8
R = Ph	0	+5.2	+5.1	+5.8

Table 3 Selected bond angles (°) and bond lengths (Å) within **1f**, **2a**, **3c** and **4a**

	1f	2a	3c	4a
N^1–M	—	2.180(5)	2.162(6)	—
N^2–M	—	—	—	2.106(2)
N^3–M	—	2.081(5)	2.065(6)	—
C_{ipso}–M	—	—	—	2.039(3)
N^1–N^2	1.4496(15)	1.449(7)	1.474(8)	1.446(3)
C–N^2	1.2942(16)	1.337(7)	1.302(9)	1.315(4)
C–N^3	1.3690(17)	1.295(7)	1.339(9)	1.357(4)
N^3–C–N^2	123.23(13)	119.1(6)	124.8(6)	122.4(2)
N^1–N^2–C	112.49(11)	115.9(5)	110.5(6)	112.7(2)
N^1–M–N^3	—	75.80(19)	75.8(2)	—

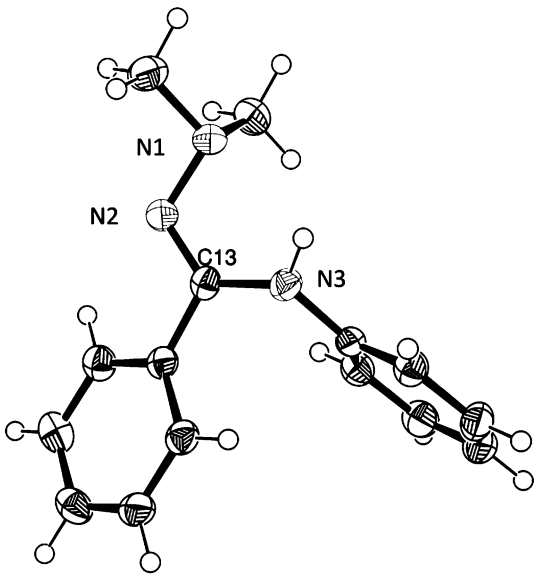


Fig. 3 ORTEP representation of **1f**, thermal ellipsoids at 50% probability.

Whilst the N^1–N^2, N^3–C and N^2–C bond lengths of 1.4496(15), 1.3690(17) and 1.2942(16) Å, respectively, are consistent with the localised resonance structure of tautomer **A**, the presence of a weak intramolecular hydrogen bond is suggested by the short N^3–H distance of 2.259 Å and the degree of pyramidalisation at N^1 (DP = 39%).[24]

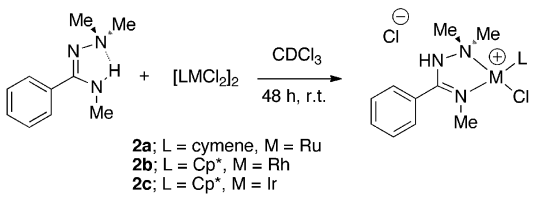
As the solid state data are not necessarily representative of the solution structure, a series of DFT studies were conducted using the B3LYP functional employing the 6,31G+(d,p) basis set. The results of this study are presented in Table 2 and the competency of the model was confirmed by comparison of the calculated bond angles and bond lengths of tautomer **A** of compound **1f** to that acquired from the X-ray crystallography study (see ESI, Fig. S1†).

In all instances, tautomers **B–D** proved energetically unfavourable in comparison to tautomer **A**. Despite some relatively small energy differences (R = ^{i}Pr) it is noteworthy that for the

series of compounds characterised (**1a–f**) both solution and solid state data support this finding. Whilst it has been previously suggested that for R = Ph the tautomeric species **C** or **D** may become energetically favourable due to resonance considerations, calculations put these tautomers some 5–6 kcal mol^{-1} higher in energy than **A**. Although gas-phase computational data match experimental (R = Ph, see ESI, Fig. S1†), it is noteworthy that, despite being reasonably well modelled, the calculated N^1–H intramolecular hydrogen bond is some 0.1 Å longer than recorded experimentally.

Reactions of 1a with [(cymene)RuCl]$_2$ and [Cp*MCl$_2$]$_2$ (M = Rh, Ir)

N^1,N^1,N^3-Trimethylbenzamidrazone **1a** reacts stoichiometrically with [(cymene)RuCl$_2$]$_2$, [Cp*RhCl$_2$]$_2$ or [Cp*IrCl$_2$]$_2$ in CDCl$_3$ solution to yield the corresponding κ^2-N^1,N^3-chelate complexes in which a chloride ion has been displaced from the metal coordination sphere (Scheme 2). Salts **2a–c** were readily isolated by precipitation from chloroform solutions by addition of a mixture of diethyl ether and hexanes and were isolated in 67–86% yield as orange, red or yellow solids (see experimental section for details). Whilst reactions in CDCl$_3$ solution were most notably characterised by the formation of a low-field broad resonance between 10 and 12 ppm, assigned to the N–H of the chelated amidrazone, upon binding, the quarternary ^{13}C NMR resonance of the amidrazone shifts downfield (**2a**, 165.2 ppm; **2b**, 164.9 ppm; **2c**, 166.8 ppm) relative to that of the free ligand (**1a**, 162.3 ppm). Thus, multinuclear NMR data are suggestive of a change in the tautomer of the ligand within complexes **2a–c**.



Scheme 2 Reaction of **1a** with [LMCl$_2$]$_2$.

In all instances, the cationic fragments [LM{PhC(=NMe)-NHNMe$_2$}Cl]$^+$ (L = cym, M = Ru; L = Cp*, M = Rh, Ir) could be observed by electrospray ionisation mass spectrometry with further fragmentation occurring with loss of chloride from the parent ion. Although infrared spectroscopy demonstrated the expected N–H stretch (3350–3380 cm^{-1}) implied by the NMR data, ultimately the coordination mode of the amidrazone **1a** was confirmed by a single crystal X-ray diffraction study upon **2a**.

Represented in Fig. 4 with important bond angles and bond lengths listed in Table 3, compound **2a** crystallises with a single molecule of dichloromethane in the unit cell. Most importantly these data demonstrate that **1a** provides a κ^2-N^1,N^3-chelate to ruthenium and that coordination occurs with a concomitant tautomerisation of the ligand to the hydrazide imide resonance form, *i.e.* tautomer **C**, a structure that is expected to be some 6–7 kcal mol^{-1} less stable than the ground-state **A** based upon DFT calculations.

For **2a** the coordination sphere of the metal is completed by coordination to the π-system of cymene and a single chloride ion. The additional chloride counter-ion exists in the secondary coordination sphere and forms a close contact with the proton

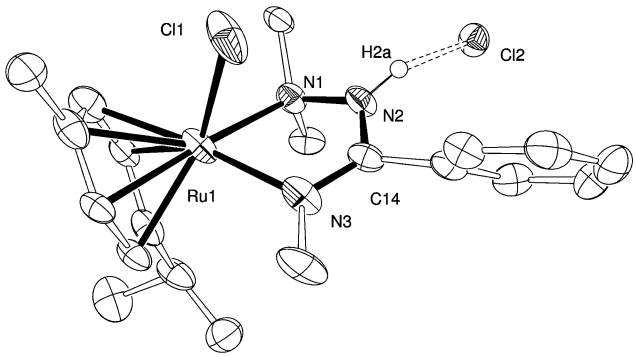
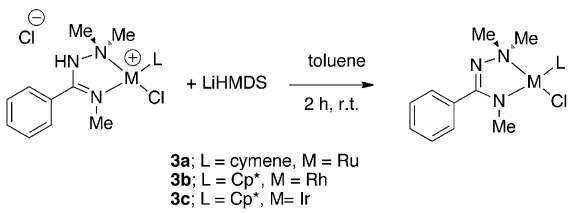


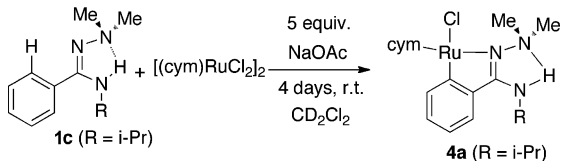
Fig. 4 ORTEP representation of **2a**. Thermal ellipsoids at 50% probability. H-atoms with the exception of the N–H proton and dichloromethane solvent molecules omitted for clarity.

of the amidrazone ligand with the H(2a)–Cl(2) bond length being 2.540 Å. The metal–nitrogen bond lengths (2.081(5)–2.180(5) Å) and metal–chlorine bond length (2.4132(17) Å) of **2a** are consistent with literature known 6-coordinate ruthenium amidinate complexes containing similar coordination geometry at the metal.[25] Most importantly, the tautomerisation of the amidrazone to **C** is apparent by N^2–C and N^3–C bond lengths of 1.337(7) and 1.295(7) Å, respectively.

Despite complexes **2a–c** displaying limited solubility in hexane or toluene solutions, they could be deprotonated in the presence of one equivalent of lithium bis(trimethylsilyl)amide (LiHMDS) in toluene solution to give the neutral analogues **3a–c** (Scheme 3). These latter compounds demonstrated improved solubility in hydrocarbon solvents and, in all cases, the progress of the reaction was evidenced by the disappearance of ν(N–H) in the infrared spectrum and the disappearance of the heavily deshielded N–H resonance in the ^{1}H NMR spectrum.



Scheme 3 Deprotonation of **2a–c** with [Li{N(SiMe$_3$)$_2$}] (LiHMDS).



Scheme 4 Cyclometallation of **1c** with [(cym)RuCl$_2$]$_2$ mediated by NaOAc.

Compared to the parent amidrazone (**1a**, 162.4 ppm) and cationic metal complexes **2a–c** (*vide supra*), ^{13}C NMR resonances of the quaternary carbon centre of the ligand shift downfield significantly upon deprotonation (**3a**, 170.9 ppm; **3b**, 171.3 ppm; **3c**, 176.4 ppm). The former data compare well to those reported for ruthenium amidinate complexes of the formula [(η^6-C$_6$H$_5$R)Ru{η^2-^{t}BuNC(Ph)=N^{t}Bu}X] (R = H, Me, OMe, F;

X = Cl, PF_6). These complexes contain a similar monoanionic ligand coordinated to a Group VIII metal, albeit *via* a four-membered *N*,*N*-chelate, and demonstrate characteristic resonances in the ^{13}C NMR between 170 and 175 ppm.[25]

Once again the coordination mode of the chelated amidrazone was provided by an X-ray diffraction experiment. Thus, single crystals of **3c** grown from slow diffusion of pentane into a toluene solution proved suitable for a single crystal diffraction experiment, and selected bond angles and bond lengths are listed in Table 3 whilst the structure is represented in Fig. 5. Although structural features of the iridium(III) centre warrant little discussion, it is important to note that upon deprotonation the amidrazone ligand readily tautomerises back to a monoanionic version of tautomer **A**, as evidenced by the N^1–N^2, N^2–C and C–N^3 bond lengths of 1.474(8), 1.302(9) and 1.339(9) Å with the metal effectively taking the place of the proton in the structure represented in Fig. 2. It is noteworthy that, despite the N^2–C bond length being approximately equal to that recorded for the free ligand **1f**, not only is the N^1–N^2 distance significantly longer but the N^3–C bond length is significantly shorter than observed in **1f** (see Table 3). These data are consistent with effective charge localisation across the N^3–C–N^2 moiety of the chelated, deprotonated amidrazone ligand.

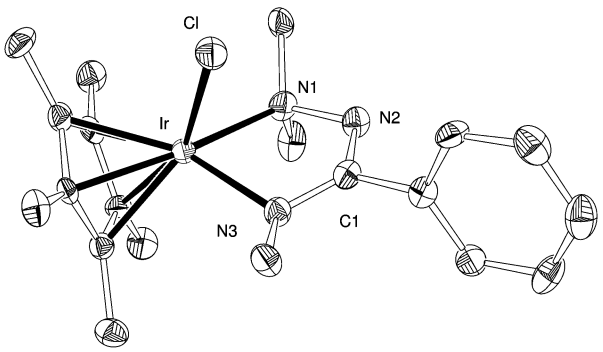


Fig. 5 ORTEP representation of **3c**. Thermal ellipsoids at 50% probability. H-atoms omitted for clarity.

Reactions of 1a and 1c with *in situ* generated [(cymene)Ru(OAc)Cl]

In contrast, the reaction of amidrazone **1a** with $[(cymene)RuCl_2]_2$ in the presence of sodium acetate provided a mixture of products. Despite the complex expected from coordination and deprotonation being present, *i.e.* **3a**, among the mixture a new ruthenium containing species was readily apparent from ^1H NMR spectroscopic data. The latter complex was characterised by a diagnostic four proton spin system (characterised by 1D and 2D-experiments), characteristic of an *ortho*-metallated aromatic ring and, based upon comparison to similarly cyclometallated ruthenium complexes of benzylamines reported by Pfeffer and co-workers, was assigned as the product derived from cyclometallation of the amidrazone ligand.[26]

Davies, MacGregor and co-workers have recently published a series of papers demonstrating and rationalising electrophilic C–H activation of imines, 2-phenylpyridines and oxazolines by a $[LMCl_2]_2$ (L = cymene, M = Ru; L = Cp*, M = Rh, Ir) and sodium acetate reaction mixture.[27–28] Through both experimental and computational studies it has been hypothesised that the reaction proceeds by *in situ* formation of the metal acetate [LM(OAc)Cl], with subsequent simultaneous activation of the C–H bond by the metal and intramolecular deprotonation by the acetate group.[28] In related studies, Jones and co-workers have expanded the scope of this electrophilic C–H cyclometallation reaction to include electron-rich and electron-poor imines.[29]

Of particular relevance to the current study, it was found that the reaction of $[Cp^*IrCl_2]_2$, NaOAc and pyrrole imine substrates containing acidic N–H protons yielded a mixture of N–H and C–H activation products.[27b] The N–H activation product **3a** derived from κ^2-N^1,N^3-chelation observed during the reaction **1a** with $[(cymene)RuCl_2]_2$ and NaOAC could be avoided by employing an amidrazone substrate possessing a bulky group at the N^3-terminus. Thus, reaction of **1c** under the same reaction conditions gave the cyclometallated product **4a** in 62% yield as evidence by NMR spectroscopy. The selectivity in this reaction is consistent with the idea that the bulky iso-propyl group disfavours coordination of N^3 to the hindered metal centre and favours instead coordination to N^2 followed by electrophilic cyclometallation of the *ortho*-position of the phenyl ring.

Multinuclear NMR spectra of isolated samples of **4a** provided diagnostic data. Thus, whilst the four proton spin system of the metallated aromatic apparent from the *in situ* NMR data of reactions of **1c** was readily observable in the aromatic region of the ^1H NMR spectrum in CD_2Cl_2 6.92–694 (m, 2H), 7.13 (dd, 1H, J = 7.5 and 7.1 Hz), 7.50 (d, 1H, J = 7.7 Hz), 8.16 (d, 1H, J = 7.5 Hz), resonances consistent with the intact amidrazone ligand were also apparent. Most notably the methine position of the iso-propyl group could be observed as a doublet of heptets at 4.23 ppm ($^3J_{H-H}$ = 6.8 and 6.4 Hz) with coupling occurring to the acidic N–H of the amidrazone moiety. These data are consistent with those observed for the parent organic fragment which demonstrates a similar resonance at 3.43 ppm ($^3J_{H-H}$ = 6.4 and 5.1 Hz). The *ipso*-carbon of the cyclometallated ligand also provided a characteristic resonance in the ^{13}C NMR at 183.1 ppm, which being shifted some 30 ppm downfield of that in the free ligand, compares well with values reported for cyclometallated complexes containing the same "[(cymene)RuCl]" fragment. For instance [(*p*-cymene)RuCl-{$(C_6H_4)C(H)$═$N(CH_2)_2OCH_3$}], a complex which contains a cyclometallated imine ligand exhibiting a κ^2-*N*,*C*-coordination mode, demonstrates a ^{13}C NMR chemical shift at 188.5 ppm assigned to the carbon directly attached to the metal centre.[27a]

Whilst infrared spectroscopic data are consistent with the proposed formulation with ν(N–H) observed as a sharp peak at 3247 cm^{-1} (*cf.* **1c**, 3289 cm^{-1}), fast-atom bombardment mass spectrometry provided additional support for the cyclometallated product and M^+ was observed at 475 and 477 m/z with fragmentation occurring with loss of chloride to form the corresponding cation at 440 m/z.

Despite strong evidence for the proposed formulation, the coordination geometry of compound **4a** was ultimately elucidated by a single crystal X-ray diffraction experiment. The results of this experiment are represented in Fig. 6 and important bond angles and bond lengths are listed in Table 3. Whilst the N^1–N^2 and C–N^3 bond lengths of 1.446(3) and 1.357(4) Å, respectively, are consistent with those in the free ligand **1f**, the C–N^2 bond length of 1.315(4) Å is significantly longer due to the augmented coordination number of the N^2-position. These data are consistent with the isolation of a cyclometallation product in which the amidrazone exists as tautomer **A**. In addition, the N^2–Ru and C_{aryl}–Ru bond lengths of 2.106(2) and 2.039(3) Å, respectively, are similar to

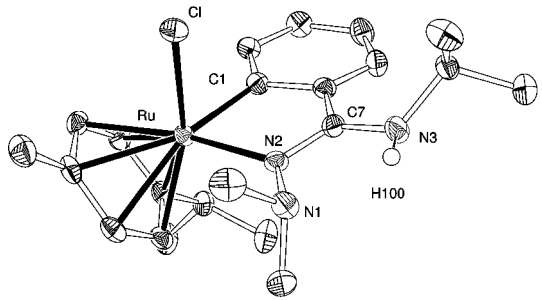


Fig. 6 ORTEP representation of **4a**. Thermal ellipsoids at 50% probability. H-atoms, with the exception of the N–H proton, omitted for clarity.

those of 2.080(2) and 2.043(2) Å, respectively, reported by Davies and co-workers for the aforementioned cyclometallated complex [(*p*-cymene)RuCl{$(C_6H_4)C(H)$=$N(CH_2)_2OCH_3$-κ^2C,N}].[27a]

Summary and conclusions

The synthesis and solution conformation of a series of N^1,$N^2$$N^3$-benzamidrazones along with coordination studies with late-transition metal complexes $[LMCl_2]_2$ has been investigated. These studies demonstrate that although the latter substrates may act as neutral or mono-anionic κ^2-*N*,*N*-chelating ligands, under suitable reaction conditions benzamidrazones may act as directing groups for electrophilic C–H activation forming κ^2-*N*,*C*-coordinated complexes. We are continuing to study the applications of amidrazones as directing groups for C–H activation and functionalisation.

Acknowledgements

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