

Guanidine anions as chelating ligands; syntheses and crystal structures of $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}]$ and $[\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr}^i\text{-p})\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}]$

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Treatment of the chloro-bridged dimers $[\{\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2]$ and $[\{\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr}^i\text{-p})\text{Cl}_2\}_2]$ with 1,2,3-triphenylguanidine in toluene solution led to the formation of $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}]$ **1** and $[\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr}^i\text{-p})\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}]$ **2** respectively. These represent the first examples of complexes containing guanidine anions as chelating ligands. Crystal structure analyses of both complexes have been performed.

Anionic 1,3-nitrogen analogues of carboxylates derived from amidines ($\text{RNHCR}=\text{NR}$)¹ and triazines ($\text{RNHN}=\text{NR}$)² are frequently encountered in both bridging and chelating co-ordination modes and are now firmly established as flexible ligands capable of co-ordination to a wide variety of metal centres. Indeed, bis(trimethylsilyl)benzamidates are now attracting renewed attention as alternatives to cyclopentadienyl in early transition-metal chemistry with a view to modification of α -alkene polymerisation catalysts.³ Until recently the related guanidines ($\text{R}_2\text{N})_2\text{C}=\text{NR}$ ($\text{R} = \text{H}$, alkyl or aryl) had only been characterised as monodentate ligands co-ordinating to Lewis-acidic centres through the imine nitrogen.⁴ However, two recent independent reports detail the structural characterisation of guanidine anions bridging terpyridineplatinum(II) units, the first complexes characterised to contain guanidine anion ligands.⁵ In an earlier paper we reported the synthesis and crystal structure of the dianion of 1,2,3-triphenylguanidine as its dilithiate.⁶ We now report the synthesis and characterisation of two complexes in which the monoanion of 1,2,3-triphenylguanidine is found to chelate metal centres.

Results and Discussion

Treatment of either $[\{\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2]$ or $[\{\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr}^i\text{-p})\text{Cl}_2\}_2]$ with 4 molar equivalents of 1,2,3-triphenylguanidine in toluene solution leads to precipitation of 2 molar equivalents of the guanidinium chloride salt $[\text{C}(\text{NHPh})_3]\text{Cl}$ and formation of the air-stable complexes $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}]$ **1** or $[\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr}^i\text{-p})\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}]$ **2** which may be crystallised from solution by concentration and cooling. Although no intermediates could be isolated, it is supposed that the reactions proceed through the intermediacy of the complexes derived by chloro-bridge cleavage and co-ordination of the guanidine through the imine nitrogen. Both ¹H and ¹³C NMR spectra indicate the presence of two types of phenyl group in the ratio 2:1 and are therefore consistent with these formulations.

Single-crystal structure determinations of complexes **1** and **2** were undertaken and the molecular structures are shown in Figs. 1 and 2 respectively. The structures are closely related, each containing an η -bonded aromatic ligand, a terminal chloride and the chelating triphenylguanidine anion. In each case the angles around the central carbon of the guanidine ligand total 360° indicating the strict planarity of the CN_3 unit, a feature also observed in our recent structure determination of the dilithiate of this ligand.⁶ In the rhodium complex **1** the dihedral

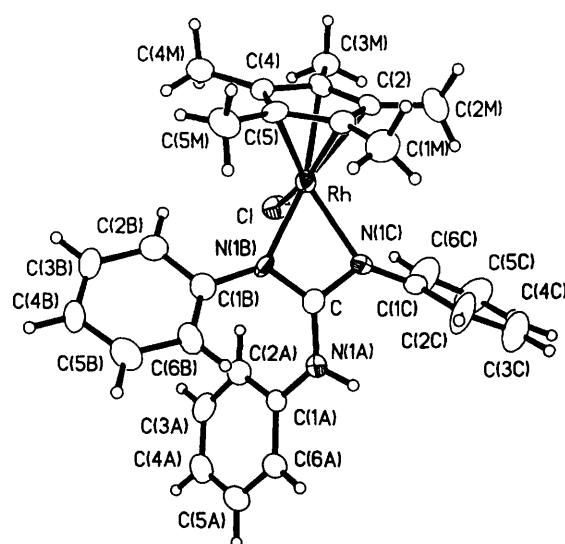


Fig. 1 Molecular structure of $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}]$ **1**

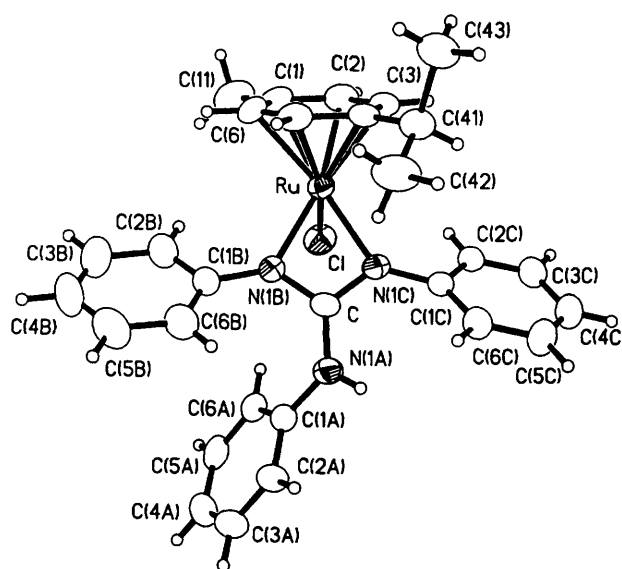


Fig. 2 Molecular structure of $[\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr}^i\text{-p})\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}]$ **2**

Table 1 Selected bond distances (Å) and angles and torsion angles (°) for $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}] \mathbf{1}$

Rh–N(1B)	2.085(6)	C–N(1A)	1.378(10)
Rh–N(1C)	2.136(8)	N(1A)–H(1A)	0.89(8)
Rh–Cl	2.420(2)	N(1A)–C(1A)	1.404(9)
Rh–C	2.568(7)	N(1B)–C(1B)	1.432(12)
C–N(1B)	1.309(9)	N(1C)–C(1C)	1.409(10)
C–N(1C)	1.331(10)		
N(1B)–Rh–N(1C)	61.4(2)	H(1A)–N(1A)–C(1A)	107(5)
C(2)–Rh–C(5)	65.6(3)	C–N(1A)–C(1A)	123.8(6)
N(1B)–Rh–Cl	88.4(2)	C–N(1B)–C(1B)	127.6(7)
N(1C)–Rh–Cl	91.4(2)	C–N(1B)–Rh	95.6(5)
N(1B)–C–N(1C)	109.4(7)	C(1B)–N(1B)–Rh	136.7(6)
N(1B)–C–N(1A)	127.6(7)	C–N(1C)–C(1C)	124.9(7)
N(1C)–C–N(1A)	123.0(7)	C–N(1C)–Rh	92.6(5)
H(1A)–N(1A)–C	120(5)	C(1C)–N(1C)–Rh	136.9(5)

N(1B)–Rh–N(1C)–C 6.1(4)

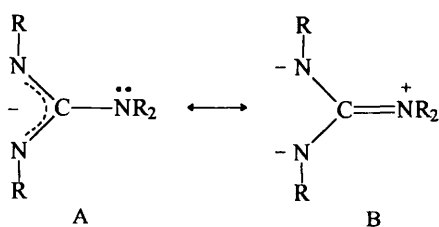


Fig. 3 Alternative resonance structures of the guanidine anion ligand

angle between this ligand plane and the N(1B)–Rh–N(1C) plane is 6.1(4)° suggesting a possible interaction between the central carbon and the metal as would be contributed by a diazaallyl form of the ligand. This is consistent with the observation of coupling between the central carbon and rhodium in the ^{13}C NMR spectrum [$J(^{13}\text{C}\text{--}^{103}\text{Rh}) = 4 \text{ Hz}$]. In the ruthenium complex this puckering of the four-membered chelate ring is slightly less at 4.2(2)°.

The question of whether the lone pair of the unco-ordinated nitrogen is indeed located on this nitrogen or delocalised into the ligand should be addressed (Fig. 3). Such a contribution is often implied in the isoelectronic dialkyldithiocarbamates (S_2CNR_2^-) where it may be associated with the stabilisation of unusually high formal oxidation states.⁷ For the ruthenium complex **2** the bonds between the metal-co-ordinated nitrogens and the central carbon of the ligand [1.326(5) and 1.330(5) Å] are indistinguishable, however the bond to the unco-ordinated nitrogen [N(1A)] is significantly longer at 1.374(5) Å, strongly suggesting a predominant contribution from **A** (Fig. 3) to the ligand bonding. A similar conclusion may be drawn from a consideration of the data for the rhodium complex structure. It is also significant in this context that the equivalence of the two co-ordinated NPh groups, as evidenced by the ^1H and ^{13}C NMR spectra, indicates sp^2 hybridisation at N(1A) with the phenyl positioned perpendicular to the CN_3 plane to generate local C_s symmetry and/or relatively unrestricted rotation about the C–N(1A) bond. A tendency towards sp^2 hybridisation at such NPh nitrogens may of course be associated with delocalisation of the nitrogen lone pair into the phenyl ring. Although the NH hydrogens were located in the X-ray study the errors associated with their positions are too large for the geometry at this nitrogen to be distinguished. The only angle at this centre which is defined with any precision is that to the phenyl [C–N(1A)–C(1A) 123.8(6)° in **1** and 125.0(4)° in **2**]. This indeed suggests approximate sp^2 hybridisation at the nitrogen and compares with a value of 126° for a similar angle at an HNPh nitrogen in the free triphenylguanidine.⁸

These complexes contain the first examples of chelating guanidine ligands. Work is underway to investigate further the

Table 2 Selected bond distances (Å), angles and torsion angles (°) for $[\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr}^i\text{-p})\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}] \mathbf{2}$

Ru–N(1B)	2.087(3)	C–N(1A)	1.374(5)
Ru–N(1C)	2.103(3)	N(1A)–H(1A)	0.75(4)
Ru–Cl	2.4339(12)	N(1A)–C(1A)	1.421(5)
C(1)–C(6)	1.405(6)	N(1B)–C(1B)	1.399(5)
C–N(1B)	1.326(5)	N(1C)–C(1C)	1.398(5)
C–N(1C)	1.330(5)		
N(1B)–Ru–N(1C)	61.75(13)	C–N(1A)–C(1A)	125.0(4)
N(1B)–Ru–C(1)	125.3(2)	C–N(1B)–C(1B)	131.7(4)
N(1B)–Ru–Cl	85.86(9)	C–N(1B)–Ru	95.2(2)
N(1B)–C–N(1C)	108.1(3)	C(1B)–N(1B)–Ru	132.8(3)
N(1B)–C–N(1A)	126.9(4)	C–N(1C)–C(1C)	128.8(3)
N(1C)–C–N(1A)	125.0(4)	C–N(1C)–Ru	94.4(2)
H(1A)–N(1A)–C	120(4)	C(1C)–N(1C)–Ru	133.7(3)
H(1A)–N(1A)–C(1A)	110(4)		

N(1B)–Ru–N(1C)–C 4.2(2)

characteristics and preferences of guanidine anions as ligands, and to establish whether a contribution from resonance form **B** (Fig. 3) can be induced by co-ordination to d-electron-poor metal centres and/or replacement of the unco-ordinated NPh group with NR_2 groups ($\text{R} = \text{alkyl}$). Our objective in this research, as described in a previous publication,⁶ is the formation of systems in which the guanidine dianion is co-ordinated to a single metal through all three nitrogens with the expectation of generating chiral C_3 symmetric ligands.⁹ The ability of such ligands to co-ordinate facially an octahedral complex would be complementary to the well established chiral C_2 -symmetric chelating diphosphines which can only co-ordinate two *cis* positions.¹⁰ The complexes reported here may be regarded as intermediates en route to this objective and we are currently investigating the elimination of HCl from such chelating guanidine anion complexes.

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 compounds $[\{\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2]$ ¹¹ and $[\{\text{Ru}(\text{MeC}_6\text{H}_4\text{Pr}^i\text{-p})\text{Cl}_2\}_2]$ ¹² were prepared by the literature procedures whilst 1,2,3-triphenylguanidine was prepared by condensation of aniline with diphenylcarbodiimide in tetrahydrofuran under reflux. The NMR spectra were recorded on a Bruker AC 250 spectrometer, infrared spectra on a Perkin-Elmer Paragon 1000 spectrometer from samples as KBr discs 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

$[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\{\eta^2\text{-(NPh)}_2\text{CNHPh}\}\text{Cl}] \mathbf{1}$. To a suspension of $[\{\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2]$ (0.480 g, 1 mmol) in toluene (20 cm³) was added 1,2,3-triphenylguanidine (1.150 g, 4 mmol). The mixture was stirred for 1 h at room temperature and then the precipitated guanidinium hydrochloride was filtered off to leave an orange solution. Removal of the solvent under vacuum and crystallisation of the resulting solid from dichloromethane–hexane gave orange crystals of the product (0.14 g, 12.7% unoptimised yield) [Found: C, 63.9; H, 5.65; N, 7.90%; m/z 559 (M^+). $\text{C}_{29}\text{H}_{31}\text{ClN}_3\text{Rh}$ requires C, 62.2; H, 5.55; N, 7.5%; M 559]. NMR (CDCl_3): ^1H (250 MHz), δ 1.24 (s, 15 H), 6.04 (s, 1 H) and 6.9–7.3 (m, 15 H); ^{13}C (62.9 MHz), δ 9.0 (CH_3), 91.3 [d, $J(^{13}\text{C}\text{--}^{103}\text{Rh}) = 8$, C_5Me_5], 120.7, 122.1, 122.4, 124.0, 128.0,

128.4, 138.1, 144.7 and 154.4 [$d, J(^{13}\text{C}-^{103}\text{Rh}) = 4 \text{ Hz}$, N_3C]. IR (KBr disc): 3320w (NH), 1593m, 1537m and 1485m cm^{-1} .

Ru($\eta\text{-MeC}_6\text{H}_4\text{Pr}^i\text{-p}$){ $\eta^2\text{-(NPh)}_2\text{CNHPh}$ }Cl] **2.** To a suspension of [$\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr}^i\text{-p})\text{Cl}_2$] $_2$ (1.350 g, 2.2 mmol) in toluene (20 cm^3) was added 1,2,3-triphenylguanidine (2.70 g, 9.4 mmol). The mixture was stirred for 1 h at room temperature and then the precipitated guanidinium hydrochloride was filtered off to leave an orange solution. Removal of the solvent under vacuum and crystallisation of the resulting solid from dichloromethane–hexane gave orange crystals of the product (1.00 g, 41% unoptimised yield) [Found: C, 62.5; H, 6.15; N, 7.60%; m/z 557 (M^+). $\text{C}_{29}\text{H}_{30}\text{ClN}_3\text{Ru}$ requires C, 62.5; H, 5.40; N, 7.55%; M 556]. NMR (CDCl_3): ^1H (250 MHz), δ 1.21 (d, $J = 8.5$, 6 H), 2.23 (s, 3 H), 2.71 (spt, $J = 8.5 \text{ Hz}$, 1 H), 5.11–5.36 [m, (AB) $_2$, 4 H], 6.07 (s, 1 H) and 6.66–7.25 (m, 15 H); ^{13}C (62.9 MHz), δ 18.6, 22.0, 30.8, 78.3, 80.3, 97.2, 98.1, 119.8, 121.8, 122.1, 122.9, 127.8, 128.1, 137.3, 146.2 and 152.9 (N_3C). IR (KBr disc): 3299w (NH), 1595m, 1534m and 1490m. Positive-ion FAB mass spectrum: m/z 557 (M^+).

X-Ray crystallography

Crystals of both complexes **1** and **2** were grown from saturated dichloromethane–hexane solutions at 4 $^\circ\text{C}$.

Crystal data. For **1**, $\text{C}_{29}\text{H}_{31}\text{ClN}_3\text{Rh}$, $M = 559.93$, monoclinic, space group Cc , $a = 8.4636(11)$, $b = 20.845(3)$, $c = 15.037(2)$ Å, $\beta = 104.49(2)^\circ$, $U = 2568.5(6)$ Å 3 (from 41 reflections, $30 < 2\theta < 32^\circ$, measured at $\pm\omega$, $\lambda = 0.71073$ Å), $Z = 4$, $D_c = 1.448 \text{ g cm}^{-3}$, $F(000) = 1152$, orange plate, $0.54 \times 0.19 \times 0.08$ mm, $\mu(\text{Mo-K}\alpha) = 0.791 \text{ mm}^{-1}$. For **2**, $\text{C}_{29}\text{H}_{30}\text{ClN}_3\text{Ru}$, $M = 557.08$, orthorhombic, space group $Pbca$, $a = 16.381(5)$, $b = 14.319(8)$, $c = 21.580(6)$ Å, $U = 5062(4)$ Å 3 (from 49 reflections, $30 < 2\theta < 35^\circ$, measured at $\pm\omega$, $\lambda = 0.71073$ Å), $Z = 8$, $D_c = 1.462 \text{ g cm}^{-3}$, $F(000) = 2288$, orange tablet, $0.58 \times 0.47 \times 0.16$ mm, $\mu(\text{Mo-K}\alpha) = 0.747 \text{ mm}^{-1}$.

Data collection and processing. Diffraction data were collected on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems Cryostream low-temperature device.¹³ Data for complex **1** were collected at 150 K, $-10 \leq h \leq 9$, $0 \leq k \leq 24$, $0 \leq l \leq 17$, using ω – θ scans. Data for **2** were collected at 220 K (crystal quality deteriorated seriously on cooling to 150 K), $0 \leq h \leq 21$, $0 \leq k \leq 18$, $-28 \leq l \leq 0$, using ω scans. For **1** the data were corrected for absorption using DIFABS¹⁴ during refinement (maximum and minimum corrections 1.94 and 0.750 respectively). Absorption effects for **2** were corrected using psi-scan data ($T_{\min} = 0.519$, $T_{\max} = 0.579$).

Structure analysis and refinement. Both structures were solved by direct methods (SIR92 for complex **1** and SHELX 86 for **2**).¹⁵ The H atoms attached to N(1A) (the non-ligating nitrogen) in both structures were located in ΔF maps and their positions refined freely with $U_{\text{iso}} = 1.2_{\text{eq}} U(\text{N})$. Other hydrogen atoms were placed in calculated positions and treated as riding on the atoms to which they are attached. During the final cycles

of least squares against F^2 (SHELXL 93¹⁶) all non-hydrogen atoms were refined anisotropically, and at convergence, for **1**, $R1 = 0.0365$ [based on 2031 data with $F > 4\sigma(F)$], $wR2 = 0.0837$ (based on all 2268 unique data) and for **2**, $R1 = 0.0468$ [based on 3367 data with $F > 4\sigma(F)$], $wR2 = 0.0990$ (based on all 5824 data). For **1** the absolute structure parameter refined to $-0.01(5)$. The weighting schemes for both refinements took the form $w = 1/[\sigma^2(F_o^2) + aP]$ where $P = (F_o^2 + 2F_c^2)/3$; for **1** $a = 0.0500$, for **2** $a = 0.0391$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/108.

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