FULL PAPER

Guanidinates as chelating anionic ligands for early, middle and late transition metals: syntheses and crystal structures of $[Ti{\eta^2-(NPh)_2CNEt_2}_2Cl_2]$, $[Ru{\eta^2-(NPh)_2CNHPh}_3]$ and $[Pt{\eta^2-(NPh)_2-CNHPh}_2]$

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Treatment of the dimeric ruthenium halide complex $[Ru(\eta-C_6H_6)Cl_2]_2$ with 1,2,3-triphenylguanidine provided the tris-chelate $[Ru\{\eta^2-(NPh)_2CNHPh\}_3]$ with loss of the aromatic ligand and metal oxidation. This product may also be prepared by treatment of the previously reported $[Ru(\eta-p-Pr^iC_6H_4Me)\{\eta^2-(NPh)_2CNHPh\}Cl]$ with bases (KOH, LiN^{*i*}Pr₂, NEt₃). Complexes containing chelating guanidinate ligands are also available by means of metathesis of the monolithiated ligands Li[C(NR)_2NR_2] with metal halide complexes, as exemplified by the synthesis of the square planar bis-chelate $[Pt\{\eta^2-(NPh)_2CNHPh\}_2]$ from $[Pt(PhCN)_2Cl_2]$ and $[Ti\{\eta^2-(NPh)_2CN(Et)_2\}_2Cl_2]$ from $[TiCl_4(THF)_2]$. The characterisation of these complexes allows a comparison of the co-ordination properties of chelating guanidinates with early, middle and late transition metals.

Since the first report in 1996 of the ability of the anions of 1,2,3-trisubstituted guanidines [(NR)₂CNHR]⁻ to act as chelating guanidinate ligands,1 a large number of such complexes of transition, main group and lanthanide metals have appeared in the literature.²⁻¹⁴ Guanidinate(1-) ligands are related to amidinates by substitution of the central carbon with an amino group and, as such, have available to them an iminium/diamide type resonance structure in which the lone pair of the unco-ordinated nitrogen atom is delocalised into the ligand π system (Fig. 1), a possibility clearly unavailable to the amidinates.¹ We have previously reported ruthenium and rhodium complexes containing chelating guanidinate ligands,¹ and the redox pair $[Mo_2{\mu-\eta^2-(NPh)_2CNHPh}_4]^{0/+}$ which gave the first indications of the flexible donor properties of these ligands,15 and in addition we have characterised a number of examples of complexes containing guanidines acting as neutral monodentate ligands¹⁶ and main group complexes containing both guanidinate-(1-) and -(2-) ligands.¹⁷ Here we report the synthesis and characterisation of three complexes of early, middle and late transition metals [Ti^{IV}, Ru^{III} and Pt^{II}] containing chelating guanidinate(1-) ligands and discuss the evidence available to support the involvement of the unco-ordinated nitrogen lone pair in the ligand π system.

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 complexes $[Pt(PhCN)_2Cl_2]_{18}$ [Ru(η -C₆H₆)Cl₂]₂ and [Ru{ η^2 -(NPh)₂CNHPh}(η -*p*-PrⁱC₆H₄Me)Cl]¹⁹ were prepared according to literature procedures, 1,2,3-triphenylguanidine and 1,1-diethyl-2,3-diphenylguanidine by condensation of aniline or diethylamine with diphenylcarbodiimide in THF under reflux. NMR spectra were recorded on a Bruker AC 250 spectrometer, and mass spectra on a Kratos MS50 TC instrument in positive ion FAB mode using 3-



Fig. 1 Alternative 1,3-diazaallyl (A) and iminium/diamide (B) resonance structures for a guanidinate(1-) anion.

nitrobenzyl alcohol as matrix and CsI as calibrant. Elemental analyses were conducted by the microanalytical service of this department.

Syntheses

[Ru{ η^{2} -(NPh)₂CNHPh}₃] 1. *Method a.* To a suspension of [Ru(η -C₆H₆)Cl₂]₂ (500 mg, 1.0 mmol) in toluene (30 cm³) was added 1,2,3-triphenylguanidine (3.44 g, 12.0 mmol). Over a period of 1 week the stirred solution became dark green and the brown [Ru(η -C₆H₆)Cl₂]₂ dissolved to be replaced by colourless 1,2,3-triphenylguanidinium chloride. The salt was removed by filtration and the filtrate reduced to dryness under vacuum. The residue was redissolved in pentane (50 cm³) and filtered through Celite. Reduction of the solution volume to 10 cm³ and storage at -20 °C for 2 weeks provided black crystals of complex 1 (0.45 g, 0.47 mmol, 47%).

Method b. To a solution of $[Ru{\eta^2-(NPh)_2CNHPh}(\eta-p-Pr^iC_6H_4Me)Cl]$ (250 mg, 0.449 mmol) in THF (20 cm³) cooled to -78 °C was added 4.40 cm³ of a 0.105 M solution (0.462 mmol) of lithium diisopropylamide in THF. The mixture was allowed to warm slowly to room temperature with stirring and after 1 h the green solution was reduced to dryness. The residue was extracted with pentane (3 × 10 cm³) and the extracts reduced in volume to 10 cm³. Cooling to -20 °C for 3 weeks provided black crystals of complex 1 in 16% yield. The isolation of pure 1 was hampered by its very high solubility in all organic solvents and a consistent set of microanalytical data could not be obtained. We attribute this problem to the presence of residual free 1,2,3-triphenylguanidine which was evident in the NMR spectrum of crystalline samples of 1 and which could not

J. Chem. Soc., Dalton Trans., 2000, 1887–1891 1887

be separated by chromatography, however the mass spectrum (+FAB) showed a molecular ion at m/z 960 (C₅₇H₄₈N₉Ru requires m/z 959). EPR (CH₂Cl₂-Toluene): v = 9.44 GHz, T = 293 K, axial spectrum, $g_{iso} = 2.29$; v = 9.44 GHz, T = 150 K, $g_{\parallel} = 1.809$, $g_{\perp} = 2.472$, $g_{av} = 2.251$.

 $[Pt{\eta^2-(NPh)_2CNHPh}_2]$ 2. To a solution of 1,2,3triphenylguanidine (600 mg, 2.08 mmol) in diethyl ether (40 cm³) at -78 °C was added 0.85 cm³ of a 2.5 M solution (2.12 mmol) of "BuLi in hexanes. The mixture was allowed to warm to room temperature and stirred for 30 min. The solution was recooled to -78 °C and then [Pt(PhCN)₂Cl₂] (440 mg, 1.02 mmol) solid was added. After 12 h stirring at room temperature the mixture was filtered providing a yellow solid and a brown filtrate. The solid was washed on the filter with CH₂Cl₂ and the washings were added to the filtrate. The evaporation of the resulting solution to dryness and recrystallisation of the residue from CH₂Cl₂-hexane provided [Pt{ η^2 -(NPh)₂CNHPh}₂] 2 in 53% yield as well formed very pale yellow crystals. ¹H NMR (250 MHz, CDCl₃): δ 7.2–6.8 (m, 30 H) and 5.9 (s, 2 H). ¹³C NMR (62.9 MHz, CDCl₃): δ 154.5 (CN₃), 153.5, 143.6, 137.1, 129.3, 128.6, 125.3, 124.4 and 121.8. MS (+FAB): m/z 768 (M⁺), 480 (M⁺ – L) and 288 (L). Found C, 58.9; H, 4.28; N, 10.8%. C₃₈H₃₂N₆Pt requires C, 59.5; H, 4.17; N, 11.0%.

 $[Ti{\eta^2-(NPh)_2CNEt_2}_2Cl_2]$ 3. 1,1-Diethyl-2,3-diphenylguanidine (705 mg, 2.64 mmol) was dissolved in diethyl ether (20 cm³) and cooled to -78 °C. n-Butyllithium (2.64 mmol, 1.05 cm³ of a 2.5 M solution) was added and the mixture stirred for 10 minutes then allowed to warm to room temperature. This solution was recooled to -78 °C, then added to a suspension of $[TiCl_4(THF)_2]$ (350 mg, 1.33 mmol) in diethyl ether (20 cm³) at -78 °C and an instant change to bright red was observed. The mixture was warmed to room temperature and stirred for 18 hours. The resulting red solution was reduced to dryness under vacuum leaving a red solid which was dissolved in toluene (10 cm³). Filtration of this solution through Celite yielded a clear red solution which, upon storage at -30 °C, produced red needles. These were found to be of insufficient quality for X-ray diffraction. The solution was re-filtered through Celite and the resulting solution stored at 5 °C. After 3 weeks the solution afforded a crop of red needles (170 mg, 0.26 mmol, 20%). ¹H NMR (250 MHz, CDCl₃): δ 0.84 (t, J = 7.2, 12 H, CH₂CH₃), 2.64 (q, J = 7.2 Hz, 8 H, CH_2CH_3) and 6.93–7.27 (cm, 20 H, aryl H). ¹³C NMR (62.9 MHz, CDCl₃): δ 12.8 (CH₂CH₃), 42.2 (CH₂CH₃), 121.7, 122.6, 124.8, 125.2 (aryl C) and 165.6 (CN₃). Found C, 61.9; H, 5.79; N, 13.3%. C₃₄H₄₀Cl₂N₆Ti requires C, 62.2; H, 6.19; N, 12.9%). The crystal structure shows the presence of a disordered toluene molecule in the unit cell, however the elemental analysis indicates that this is absent from the powder sample analysed, presumably removed by the vacuum drying to which it was subjected.

X-Ray crystallography

Crystal data for complexes 1, 2 and 3 are presented in Table 1. All data sets were collected on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device. The structures of 1 and 3 were solved by direct methods (SIR 92);²⁰ the structure of **2** was solved by placing a Pt atom at the unit cell origin. Hydrogen atoms were placed in calculated positions. Difference maps for 1 and 2 exhibited weak peaks suggesting that the H atoms attached to non-ligating N atoms lie in the C-N-C(Ph) plane. The structure of 1 contains a molecule of pentane exhibiting disorder in two carbon positions in the ratio 60:40; this ratio was fixed during refinement, with the part-weight atoms having a common isotropic displacement parameter. Similarity restraints were applied to chemically equivalent bond lengths and angles. Although 1 has molecular mirror symmetry, with the Ru atoms conforming to the centrosymmetric space group Pnam (non-standard setting

of *Pnma*), the orientation of the molecules is not consistent with a mirror plane perpendicular to the z axis of the unit cell setting given here. Complex 3 contains a molecule of toluene disordered over two crystallographically unique orientations both further disordered about an inversion centre; one partweight molecule was refined with explicit restraints on the bond lengths and angles, the other refined as a rigid body.

CCDC reference number 186/1949.

See http://www.rsc.org/suppdata/dt/b0/b001992p/ for crystallographic files in .cif format.

Results and discussion

Our previous observations of the reactivity of 1,2,3-triphenylguanidine with the metal halide complexes $[RhCp*Cl_2]_2$ and $[Ru(\eta-p-Pr^iC_6H_4Me)Cl_2]_2$ 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 (Scheme 1).¹ Indeed,



treatment of these dimers with four 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. Subsequent to these observations we have found that reaction of the insoluble dimer [Ru(n- C_6H_6 Cl₂ with 1,2,3-triphenylguanidine in toluene provides the dark green $[Ru{\eta^2-(NPh)_2CNHPh}_3]$ 1 in a slow reaction (1 week), the first example of such a tris-chelate guanidinate complex, and not the anticipated $[Ru(\eta-C_6H_6)\{\eta^2-(NPh)_2CN-$ HPh}Cl]. The difference in reactivity for the η -p-cymene and η-benzene complexes can only be explained by a stronger Ru-arene bond for the p-cymene ligand than for benzene and the consequent easier displacement of the latter. However, displacement of the *p*-cymene ligand from $[Ru(\eta-p-Pr^{i}C_{6}H_{4}-$ Me){ η^2 -(NPh)₂CNHPh}Cl] and formation of 1 can also be achieved by treatment of this species with base (NEt₃, KOH, LiNⁱPr₂), a reaction which was explored in an attempt to eliminate HCl from the complex and establish a η^3 coordination mode for the ligand by use of the third nitrogen atom. The unexpected formation of an oxidised species in these reactions is consistent with observations by others who have found on several occasions that treatment of metal complex precursors with lithium amidinates or triazinates provides an oxidised product in the form of the tris-chelate. Examples of this behaviour are the predominant formation of [Cr- $(\eta^2\text{-PhNNNPh})_3]$ when $[\text{Li}(\text{THF})_4]_2[\text{Cr}_2\text{Me}_8]$ is treated with [LiPhNNNPh],²¹ and the formation of $[Fe{\eta^2-(NPh)_2CH}_3]$ on reaction of Li(NPh)₂CH with an iron(II) precursor.²² However, such behaviour has never been reported for a reaction in which the metal precursor is treated with the neutral ligand as in the current example. One factor which favours the formation of such oxidised species is the donor characteristics of the ligands which, in the absence of additional π -acid ligands, are more compatible with M³⁺ than M²⁺ ions. On the basis of comparisons between the electrochemical behaviour of the



Fig. 2 Molecular structure of $[Ru{\eta^2-(NPh)_2CNHPh}_3]$ 1.

isostructural molybendum dimers $[Mo_2L_4]$ $[L = \mu - \eta^2 - (NPh)_2 - CNHPh$ or $\mu - \eta^2 - (p-MeC_6H_4N)_2CH]$ we have established that the guanidinate ligands are considerably stronger donors and therefore better at stabilising the higher oxidation states of Mo than the amidinates.¹⁵ We have attributed this to the involvement of a ligand resonance form unavailable to the amidinate in which the non-ligating nitrogen lone pair is delocalised into the ligand π system (Fig. 1). On the basis of the above observations, therefore, it is unsurprising that we observe the ready formation of the ruthenium(III) tris-chelate 1 from ruthenium(II) precursors, although the mechanism still remains obscure.

The frozen glass EPR spectrum of complex 1 at 150 K in a CH2Cl2-toluene solvent mixture displays an axial spectrum with $g_{\parallel} = 1.809$ and $g_{\perp} = 2.472$ ($g_{iso} = 2.29$ at 293 K) and no evidence for coupling of the unpaired electron to nitrogen. The molecular structure of 1 is shown in Fig. 2 and selected bond distances and angles given in Table 2. The co-ordination geometry may be described as severely distorted octahedral resulting from the very small bite angle of the chelating ligands (intraligand N-Ru-N ca. 63°). The co-ordination of the ligand to the metal results in a distortion of the angles around the ligand central carbon atom such that the N-C-N angle between the ligating nitrogens is considerably less than 120° [range 109.1(10)-109.7(9)°] whilst the remaining angles are greater than 120° [range 121.2(9)-128.9(10)°]. However, the sum of the angles around the central carbon for each ligand is 360° indicating no deviation from planarity.

For the Group 10 metals Ni, Pd and Pt the bis-amidinate and -triazinate complexes [M(L-X)₂] show an interesting balance between monomeric square planar and dimeric ligand-bridged tetragonal prismatic $\operatorname{Cu}_2(\operatorname{OAc})_4$ type structures, the structure adopted being dependent upon the identity of both the metal and ligand. Thus, both bis(diphenyltriazinate) complexes of Ni^{II} and Pd^{II} (L–X = PhNNNPh⁻) have been found to adopt the dimeric structure,²³ and the bis(formamidinate) palladium(II) complexes $[L-X = (RN)_2CH^-]$ are also reported to be dimeric.²⁴ In contrast, bis(acetamidinato)palladium(II) complexes $[L-X = (RN)_2CMe^{-}]$ are found to adopt the square planar structure.24 However, replacement of the ligand central CMe group by a CPh effects a structural transformation and the bis(benzamidinato)palladium(II) complexes [L-X =(RN)₂CPh⁻] are found to be dimeric in the vapour (by mass spectrometry) and solid phases but to exist as an equilibrium mixture of mono- and di-meric species in solution.²⁴ The benzamidinate ligand also favours a tetrabridged dimeric structure for the bis(benzamidinato)nickel(II) complex, although this species appears to be monomeric in solution.²⁵ The bis(benz-

Table 1Crystal data for complexes 1–3

	1 <i>a</i>	2 ^{<i>b</i>}	$3 \cdot C_6 H_5 Me^a$
Empirical formula	C ₆₂ H ₆₀ N ₉ Ru	$C_{38}H_{32}N_6Pt$	C ₄₁ H ₄₈ Cl ₂ N ₆ Ti
М	1032.26	767.80	743.65
T/K	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$Pna2_1$	$P\bar{1}$	C2/c
aĺÅ	22.248(3)	6.455(5)	9.813(4)
b/Å	20.648(4)	10.971(8)	17.821(7)
c/Å	11.784(2)	11.591(8)	23.802(8)
a/°	~ /	76.11(5)	
βl°		77.68(4)	94.95(3)
v/°		86.81(6)	
V/Å ³	5413(2)	778.49	4147
Ζ	4	1	4
μ (Mo-K α)/mm ⁻¹	2.710	4.59	0.370
Independent reflections	4193	3252	3675
Data with $I > 2\sigma(I)$	3237	2677	2332
<i>R</i> 1	0.0554	0.0388	0.0688
wR2	0.1286	0.0394	0.2242
^{<i>a</i>} Refined on F^2 . ^{<i>b</i>} R	efined on F.		

amidinato)platinum(II) complex is however monomeric in all phases.²⁵ The structure adopted by bis(guanidinato)platinum(II) complexes is therefore open to speculation.

The treatment of 1,2,3-triphenylguanidine with one molar equivalent of *n*-butyllithium in diethyl ether followed by $[Pt(PhCN)_2Cl_2]$ provides a yellow solution from which $[Pt{\eta^2} (NPh)_2CNHPh_2$] 2 may be isolated. A crystal structure determination shows 2 to have a monomeric, square planar structure with a crystallographically imposed twofold axis relating the two ligands. The structure is shown in Fig. 3 and selected bond distances and angles are given in Table 2. The structure is similar to that of bis(diphenylbenzamidinato)platinum(II),²⁵ but differs from that adopted by $[Pd{\eta^2} (PhN)_2CNHPh$ { μ - η^2 -(PhN)_2CNHPh]₂ which features both chelating and bridging triphenylguanidinate ligands, a structure intermediate between the square planar bis-chelate and the tetra-bridged tetragonal prismatic structures.9 Features similar to those we have previously observed for complexes with chelating guanidinate ligands are observed in the structure of 2. Thus, the C-N bonds to the ligand central carbon show a pattern indicating delocalised bonding within the co-ordinated RN····C····NR unit [C-N(1) 1.348(7), C-N(2) 1.323(8) Å] and a marginally longer bond to the unco-ordinated N(3) [1.373(7) Å].

Guanidinates have recently attracted attention as ligands for more electropositive transition, main group and lanthanide metals. Their potential high basicity conferred by the delocalisation of the unco-ordinated nitrogen lone pair into the ligand π system (Fig. 1) means that they are well suited to stabilisation of higher oxidation state metal ions with strong π -acceptor properties and other electron deficient metals. The steric flexibility available through variation of the nitrogen substituents allows for a high degree of steric shielding of the metal centre to be built into the ligand and preliminary investigations into the use of such bulky guanidinates as ancillary ligands in alkene polymerisation catalysts where such factors are significant have been reported.²⁶ Three synthetic routes to guanidinate complexes of these metals have been reported and involve either treatment of the metal dialkylamide complex $[M(NR_2)_n]$ with the required guanidine,⁶ in situ formation of the guanidinate ligand in the co-ordination sphere of the metal by insertion of a carbodiimide into a metal-dialkylamido ligand bond⁷ or metathesis of a metal halide complex with a lithium guanidinate.^{2,11} We have investigated the latter route for the synthesis of titanium complexes. Treatment of [TiCl₄(THF)₂] with two

Table 2Selected bond lengths (Å) and angles (°) for complexes 1–3

1		2		3	
Ru–N(11)	2.099(8)	Pt–N(1)	2.028(4)	Ti–N(1)	2.056(4)
Ru–N(21)	2.064(7)	Pt-N(2)	2.061(5)	Ti-N(2)	2.078(4)
Ru-N(12)	2.082(9)	C(1) - N(1)	1.348(7)	Ti-Cl(1)	2.2957(15)
Ru-N(22)	2.061(9)	C(1) - N(2)	1.323(8)	C(1) - N(1)	1.341(6)
Ru-N(13)	2.055(9)	C(1) - N(3)	1.373(7)	C(1) - N(2)	1.343(6)
Ru-N(23)	2.095(8)	N(1) - C(11)	1.399(7)	C(1) - N(3)	1.341(6)
C(1) - N(11)	1.309(13)	N(2) - C(12)	1.427(7)	N(1) - C(11)	1.427(6)
C(1) - N(21)	1.335(13)	N(3) - C(13)	1.430(7)	N(2) - C(21)	1.423(6)
C(1) - N(31)	1.387(8)	N(1) - C(11)	1.399(7)	N(3) - C(31)	1.474(6)
C(2) - N(12)	1.313(12)	N(2) - C(12)	1.427(7)	N(3) - C(33)	1.478(7)
C(2) - N(22)	1.347(13)	N(3) - C(13)	1.430(7)		
C(2) - N(32)	1.396(14)			N(1)–Ti–N(2)	63.39(15)
C(3) - N(13)	1.33(3)	N(1)– Pt – $N(2)$	64.0(2)	N(1) - Ti - N(1A)	146.9(2)
C(3) - N(23)	1.325(14)	N(1)-C(1)-N(2)	108.4(5)	N(1) - Ti - N(2A)	92.31(16)
C(3) - N(33)	1.394(14)	N(1)-C(1)-N(3)	128.0(5)	Cl(1) - Ti - Cl(1A)	94.20(8)
		N(2)-C(1)-N(3)	123.6(5)	C(1) = N(1) = C(11)	122.2(4)
N(11)-Ru-N(21)	62.6(3)	C(1)-N(1)-C(11)	128.8(5)	C(1) = N(2) = C(21)	127.5(4)
N(12) - Ru - N(22)	63.3(3)	C(1)-N(2)-C(12)	122.0(4)	C(1) = N(3) = C(31)	120.3(4)
N(12) - Ru - N(22)	62.9(3)	C(1) = N(3) = C(13)	124 9(5)	C(1) = N(3) = C(33)	121.3(4)
1.(12) 141 11(25)	02.5(0)		12(3)	C(31) = N(3) = C(33)	118 3(4)



Fig. 3 Molecular structure of $[Pt{\eta^2-(NPh)_2CNHPh}_2]$ 2.



Fig. 4 Molecular structure of $[Ti{\eta^2-(NPh)_2CNEt_2}_2Cl_2]$ 3.

molar equivalents of Li(NPh)₂CNEt₂ in diethyl ether provides $[Ti{\eta^2-(NPh)_2CNEt_2}_2Cl_2]$ **3** in 20% yield on crystallisation from toluene solution. The ¹H and ¹³C NMR spectra of **3** indicate the equivalence of the two guanidinate ligands and also the equivalence of the phenyl and ethyl groups within the ligands, containing only one set of signals for each. Single crystal X-ray diffraction shows that in the solid state the complex adopts a severely distorted octahedral co-ordination geometry as shown in Fig. 4. The guanidinate ligands are symmetry related by a twofold rotation axis passing through the Ti atom and bisecting the Cl–Ti–Cl angle and are thus crystallographically equivalent.

The restricted bite angle [63.39(15)°] of the chelating guanidinate ligands imposes a severe distortion upon the geometry although the interligand N(1)–Ti–N(2A) and N(1A)–Ti–N(2) [92.31(16)°] and the Cl-Ti-Cl [94.20(8)°] angles approach the ideal. The structure of 3 is very similar to those of the corresponding amidinate complexes [Ti{(NSiMe₃)₂CPh}₂Cl₂]²⁷ and $[Zr{(CyN)_2CMe}_2Cl_2]^{28}$ and the guanidinate complexes [M- $\{\eta^2 - (NR)_2 CN(SiMe_3)_2\}_2 Cl_2\} (R = {}^i Pr \text{ or } cyclo - C_6 H_{11}; M = Zr \text{ or }$ Hf).² In these latter complexes steric crowding between the SiMe₃ groups and the nitrogen alkyl substituents results in the dihedral angle formed between the planar NSi₂ unit and the CN₃ ligand plane falling in the region 86–88°, and it was therefore argued that the almost orthogonal arrangement negated the possibility of any conjugation of this nitrogen into the ligand π system. These guanidinate ligands may thus be regarded as electronically similar to amidinates. In 3 the dihedral angle between the NC₂ [N(Et)₂] and CN₃ planes is 30.4° indicating the less severe steric crowding in this system and, although not optimal, some π conjugation might be anticipated (see below).

A sufficient number of guanidinate complexes have now been structurally characterised to allow a comparison of the metrical parameters of this ligand system in a variety of metal environments, and in particular to address the question of the conjugation of the unco-ordinated nitrogen atom into the ligand π system, *i.e.* the relative contributions from the two resonance forms A and B in Fig. 1. The intraligand C-N bond distances within the CN₃ ligand core for a variety of guanidinate(1-)complexes are provided in Fig. 5. Unfortunately the nitrogen substituents in the ligands vary between the complexes and this cannot be ruled out as the origin of some of the variations observed, and furthermore some of the errors in the distances are rather large meaning that some of the apparent variations are not statistically significant. Nevertheless, taken together the data provide a picture in which the extent of conjugation of the unco-ordinated nitrogen lone pair into the ligand π system is consistent with the anticipated electronic requirements of the metal centre. As previously discussed, the steric bulk of the SiMe₃ and cyclohexyl groups in 7 dictate that the NSi₂ plane is almost orthogonal to the CN₃ plane. This complex can therefore be regarded as a system in which such π overlap is absent, and this fact is reflected in the pattern of C-N bond lengths, with the bond to the unco-ordinated nitrogen atom being longer than those to the other two by a significant margin. In the tantalum(v) complex 8 the SiMe₃ groups have been replaced by methyl groups although the other substituents remain unchanged. In this system it could be argued that the reduced bulk of the methyl groups would allow coplanarity of the NC₂



Fig. 5 Intraligand C–N bond distances for guanidinate ligands in a number of structurally characterised complexes. $[Ru{\eta^2-(NPh)_2-CNHPh}_3]$ 1; $[Pt{\eta^2-(NPh)_2CNHPh}_2]$ 2; $[Ti{\eta^2-(NPh)_2CNEt_2}_2Cl_2]$ 3; $[Ru(\eta-p-Pr^iC_6H_4Me){\eta^2-(NPh)_2CNHPh}Cl]$ 4; $[Mo_2{\mu-\eta^2-(NPh)_2CN+Ph}_4]$ 5; $[Mo_2{\mu-\eta^2-(NPh)_2CNHPh}_4]^+$ 6; $[Zr{\eta^2-(NCy)_2CN-(SiMe_3)_2}_2Cl_2]$ 7; $[Ta{\eta^2-(NCy)_2CNMe_2}(NMe_2)_4]$ 8.7 * Mean values for the number of crystallographically independent guanidinate ligands in the complex.

and CN3 planes to be achieved, however the angle between these planes is 80.7°, furthermore the unco-ordinated nitrogen is distinctly pyramidal with the sum of the C-N-C angles at this atom totalling to only 351°. Again the C-N bond to the unco-ordinated nitrogen is the longest, as would be anticipated from these observations. Inspection of the crystallographically determined structure suggests that these features are not sterically imposed and must therefore reflect the electronic requirements of the metal. Tantalum(v) would certainly be expected to exhibit very strong π -acceptor behaviour which would elicit a strong contribution from the B resonance form of the ligand (Fig. 1), however it is apparent that its electronic requirement is satisfied by the four dimethylamido ligands also co-ordinated to the metal, all of which are planar at nitrogen. These observations contrast with the data reported here for 3 in which the unco-ordinated nitrogen atoms in the two guanidinate ligands bear two ethyl groups. In this titanium(IV) complex all three C-N bond distances are statistically identical, and although the steric bulk of the ethyl groups forces the NC2 plane out of the CN₃ ligand plane by 30.4°, it is planar with the three C-N-C angles totalling to 360°. Since the evident sp² hybridisation of this nitrogen atom cannot be a result of conjugation with the ethyl substituents, a circumstance which cannot be ruled out for ligands bearing aromatic or silicon groups at this position, it is clear that in this complex a significant contribution from **B** is present. This is, to our knowledge, the first example of a chelating guanidinate where this may conclusively be stated. A comparison of the C-N distances in the ligand CN_3 core in complexes 2 and 4 shows that they are very similar, and reflect the low oxidation state of the ruthenium(II) and platinum(II) metal ions which would not be expected to require a significant contribution from resonance form **B**. It might be anticipated that the higher oxidation state in the ruthenium(III) complex 1 would be reflected in a relative shortening of the unco-ordinated C-N bonds in the guanidinate ligands, however there is no evidence for this. The dimeric molybdenum complexes 5 and 6 do however illustrate the effect upon the guanidinate ligand of changing the metal oxidation state. In the dimolybdenum(II) system 5 the ligand C-N distances are very similar to those in 1, 2 and 4, however the one electron oxidation of this complex results in significant changes within the guanidinate ligands such that the C-N bond to the unco-ordinated nitrogen is now the shortest of the three indicating a significantly greater contribution from B (Fig. 1). The mean values of the Mo-N bond distances of 2.166(5) for 5 and 2.133(7) Å for 6 also suggest a shortening of the Mo-N bond

distances thus supporting a greater contribution from **B**. It is therefore evident that bridging guanidinates are also capable of considerable electronic flexibility.

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