ELSEVIER

Coordination Chemistry Reviews
214 (2001) 91–141

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

The coordination chemistry of guanidines and guanidinates

Philip J. Bailey *, Stuart Pace

Department of Chemistry, The University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, UK

Received 19 May 2000; accepted 25 September 2000

Contents

Abstract

Species containing the Y-shaped CN_3 unit have recently attracted increasing attention as electronically and sterically flexible ligands. Neutral guanidines $[(R_2N)_2C{=}NR]$, guanidinates(-1) $[(RN)_2CNR_2]^-$ and guanidinates(2–) $[(RN)_2C{=}NR]^{2-}$ are capable of exhibiting a variety of coordination modes and a range of donor properties leading to compatibility with a remarkably wide range of metal ions from all parts of the periodic table. The coordination chemistry of these species is reviewed up to July 2000, and aspects of their electronic structures and metal-ligand bonding characteristics discussed.

Keywords: Nitrogen ligands; Guanidines; Coordination chemistry

---

* Corresponding author.
E-mail address: philip.bailey@ed.ac.uk (P.J. Bailey).

PII: S0010-8545(00)00389-1

1. Introduction

In comparison to other nitrogen analogues of carbonic and carboxylic acids (ureas, amidines, amides etc.) the coordination chemistry of guanidines has been slow to develop. The reasons for this are unclear, but may be associated with the high basicity of guanidine and its substituted derivatives and their consequent ready formation of guanidinium cations in aqueous media. Such guanidinium species $[C(NR_2)_3]^+$ show a negligible ability to behave as Lewis bases, and therefore as ligands, towards metals due to the involvement of the nitrogen lone pairs in intramolecular π-bonding and the lowering of the energy of this π-system by the positive charge. That the latter factor is significant is reflected in the fact that $B(NMe_2)_3$, an isoelectronic, but neutral, analogue of $[C(NMe_2)_3]^+$, is capable of tridentate metal coordination [1], whilst a similar ability has never been demonstrated for a guanidinium system. It has long been speculated that the exceptionally high basicity of guanidine ($pK_a = 13.6$) is associated with a form of aromaticity associated with the delocalisation of the six π-electrons across the symmetric Y-shaped CN_3 unit in the guanidinium cation, and the term Y-aromaticity has been coined to describe this [2]. However, this remains an area of controversy, which is outside the scope of the present review. Similar arguments have been put forward to explain the stability of what might be considered the carbon analogue of carbonate, the trimethylenemethane dianion $[C(CH_2)_3]^{2-}$ [3]. Over recent years however, the exploration of the ligand properties of guanidine, and in particular substituted guanidines, and their anions has intensified and a rich variety of coordination modes have been characterised in complexes of metals from all parts of the periodic table. The steric and electronic flexibility of guanidinates, the variety of possible coordination modes, the availability of both monoanionic $[(RN)_2CNR_2]^-$ [guanidinate(1–)] and dianionic $[(RN)_3C]^{2-}$ [guanidinate(2–)] forms, coupled with the ease with which guanidines bearing virtually any combination of substituents may be synthesised by a number of routes from readily available starting materials [4], means that guanidinates have the potential to develop into valuable ancillary ligands in coordination and organometallic chemistry.

A short review of guanidine ligand chemistry by Mehrota was published in *Comprehensive Coordination Chemistry* [5]. This gave an introduction to the various aspects of the field, which at the time of writing was dominated by reports of guanidinium cations (binding to anions) and neutral guanidines forming adducts through the imine nitrogen. However, in the past decade, the coordination of deprotonated guanidines (guanidinates) to metals has received more attention and the volume of work reported in this area has blossomed. A variety of complexes formed by ligands containing the guanidine moiety are reported in the chemical literature. A vast number of these reports detail complexes in which guanidinium cations are present, but these are not contained within the coordination sphere of the metal ion and consequently merely represent counterions [6]. Cyanoguanidines have also received a great deal of attention but in the main they are coordinated to the metal through the cyano nitrogen alone and the guanidine moiety plays no part in metal binding [7]. The bioligands creatine and creatinine, which contain guanidine moieties, have a rich and varied coordination chemistry, which was reviewed recently by Mitewa [8]. Furthermore, a discussion of the synthesis and chemistry of guanidine derivatives was published by Yamamoto and Kojima [4]. This also contains some information on the coordination of guanidines to anions and crown ethers. This review is primarily concerned with the ability of guanidine molecules and their deprotonated anions to coordinate to metal centres. As a consequence only complexes in which the guanidine moiety is directly bound to the metal (i.e. through one or more of the nitrogen atoms of the central CN_3 core) are considered.

2. Neutral guanidines

There are a large number of complexes reported which contain a neutral guanidine ligand and these can be classified into two main groups:

1. substituted guanidines containing no additional donor atoms and;
2. substituted guanidines containing additional donor atoms.

The major difference in the coordination chemistry of these classes is that when no additional donor atoms are present, the guanidines act exclusively as monodentate ligands binding through the lone pair located on the imine nitrogen. However, when additional donor atoms are present there is a tendency for the molecules to behave as bidentate ligands. For this reason, and also to emphasise the coordination of the guanidine moiety, these two classes will be reviewed separately.

2.1. Guanidines with no additional donor atoms

The early reports of complexes of this type focused on the formation of adducts with 1,1,2,(2–)tetramethylguanidine [tmg; $HNC\{N(CH_3)_2\}_2$] and to date the majority of known complexes containing a neutral guanidine contain this ligand. The first report of complexes containing this ligand (indeed the first report of a guanidine coordinating to a metal) was published by Drago and co-workers in 1965 [9]. Complexes of Co(II), Cu(II), Zn(II), Pd(II), Ni(II) and Cr(III) were prepared with the tetracoordinate cobalt, copper, and zinc perchlorate complexes characterised by spectroscopy, magnetic measurements and X-ray powder diffraction. Elemental analyses confirmed that these complexes had the composition $[M(tmg)_4](ClO_4)_2$. A shift of the $\nu(C=N)$ stretch in the IR spectrum towards lower wavenumbers {e.g. from 1609 to 1548 cm^{-1} in $[Co(tmg)_4](ClO_4)_2$} confirmed coordination through the imine nitrogen. The cobalt complex was suggested to have a tetrahedral geometry based on spectral and magnetic measurements although this could not be confirmed from X-ray powder diffraction data. The copper and zinc complexes were also found to have tetrahedral geometries and their X-ray powder patterns were very similar suggesting that they showed little distortion from true tetrahedral symmetry.

As part of their study of the interaction of imines with aluminium Lewis acids, Wade et al. examined adduct formation of tetramethylguanidine with AlX_3 (X =

Me, Et, Cl) [10]. The 1:1 reaction of these produced the adducts $[(Me_2N)_2CNH{\cdot}AlX_3]$ which were found to be monomeric in benzene. IR and ^{1}H-NMR spectroscopy of the adducts confirmed that the guanidine binds through the imine nitrogen (Fig. 1(a)). Thermal decomposition of the alkyl aluminium adducts led to evolution of alkane (RH) leaving dialkyl(diaminomethyleneamino)aluminium which contains a guanidinate(1–) ligand. These were found to exist as dimers in benzene (by cryoscopy) and ^{1}H-NMR data suggests that the guanidinate ligands are bridged by dialkylaluminium groups (Fig. 1(b)). The analogous dichloro complexes were prepared from the reaction of the monolithiated guanidine $[(Me_2N)_2C{=}NLi]$ and $AlCl_3$.

The reaction of guanidines with $[Pt(trpy)Cl]^+$ (trpy = 2,2′:6′,2″-terpyridine) was reported by Kostic and co-workers as part of their efforts to model the metal binding sites in metallo-proteins [11]. The product complex, characterised by UV–vis and IR spectroscopy, contains a square planar Pt(II) centre coordinated by a tridentate trpy ligand and a monodentate guanidine, binding through its imine nitrogen (Fig. 2). A range of monosubstituted guanidines were studied from methylguanidine to the biomolecules arginine, *N*-acetylarginine and canavanine (where $R = (CH_2)_3CH(NH_3)(COO)$, $(CH_2)_3CH[CH_3C(O)NH](COO)^-$ and $O(CH_2)_2CH(NH_3)(COO)$, respectively). This communication was followed by a report describing the first crystallographic study of a guanidine binding to a transition metal [12]. The synthesis of bimetallic complexes, where the guanidine bridges the metals, was achieved by the 2:1 reaction of the appropriate guanidine hydrochloride with the Pt(trpy) fragment in aqueous solution. A similar range of substituted guanidines were studied and the structure of the bimetallic complex $[\{Pt(trpy)\}_2(can)]^{3+}$ (where can = canavanine) was determined by X-ray diffraction (Fig. 3). In this case the canavanine ligand is anionic, although the negative charge resides solely on the carboxylate which plays no part in metal binding. Hence, no

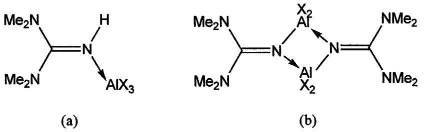


Fig. 1.

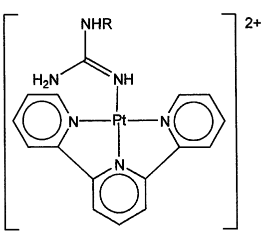


Fig. 2.

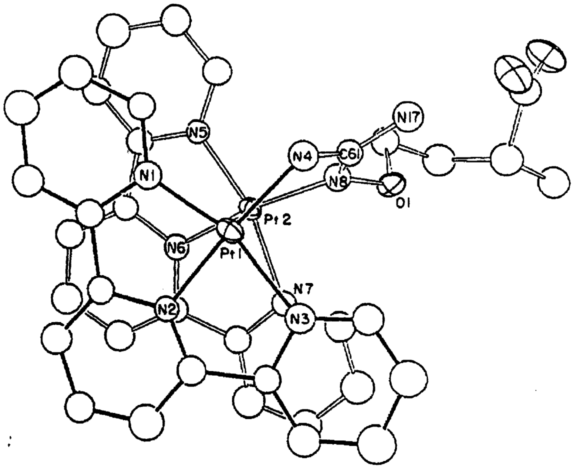


Fig. 3. The molecular structure of $[\{Pt(trpy)\}_2(\mu\text{-}\eta^2\text{-canavanine})]^{3+}$. Reproduced from Ref. [12] with permission of The American Chemical Society.

charge resides on the guanidine moiety and it can be considered as a neutral bidentate donor. In the crystal structure the two Pt(trpy) fragments are bridged by the guanidine ligand giving a Pt–Pt distance of 2.9884(7) Å. The trpy groups are almost parallel (angle between the planes is ca. 9°) and are ca. eclipsed with each other. The Pt–N distances are similar [Pt(1)–N(4) 2.06(1) Å and Pt(2)–N(8) 2.07(1) Å] and the CN_3 core of the guanidine remains planar. One C–N distance remains considerably shorter than the other two [1.26(2) Å versus 1.34(2) and 1.36(2) Å] confirming the presence of a C=N double bond and the neutrality of the guanidine function.

Davison and co-workers, reported the formation of a monodentate 1,1,2,(2–)tetramethylguanidine complex upon reaction of 2,3,5,6-tetramethylbenzenethiolate (tmbt) with the technetium nitridotetrachloride anion $[TcNCl_4]^-$ in the presence of tetramethylguanidine [13]. The formation of a guanidine complex was somewhat fortuitous as the anticipated product was $[TcN(tmbt)_4]^-$ and tetramethylguanidine was only present in the reaction mixture as a 'noncoordinating' base. The isolated product $[TcN(tmbt)_2(tmg)_2]$ has equivalent ^{1}H-NMR signals for the tmbt and tmg ligands, which suggests that the ligands are bound in a transoid fashion across the base of a square pyramid. This was confirmed by an X-ray crystal structure study (Fig. 4). The nitrido group is in the apical position with the other ligands alternating around the square base. The guanidine ligands are symmetrically bound to the technetium through their imine nitrogens [Tc(1)–N(3) 2.130(6) Å and Tc(1)–N(4) 2.128(6) Å] with the dimethylamino nitrogens uncoordinated. The guanidines are indeed neutral ligands as hydrogens were located on both the imine nitrogens from Fourier difference maps and further evidence was supplied from the ^{1}H-NMR spectrum which shows a signal for 2H at 3.87 ppm.

Another complex containing a monodentate, tetrasubstituted guanidine ligand was obtained from the reaction of diiodobis(*N*-isocyanodialkylamine)platinum(II) with excess dialkylamine [14]. The products, $[PtI_2(HNR_2)\{HN{=}C(NR_2)_2\}]$ (where R = Et, 2R = $-(CH_2)_5-$, $-(CH_2)_2O(CH_2)(2-)$), were spectroscopically characterised and, where R = Et, by X-ray diffraction. From the IR spectra, ν(C–N) was found at 1512 cm^{-1}, ca. 100 cm^{-1} lower than would be expected for the free guanidine and indicative of the guanidine binding through the imine nitrogen. The ^{1}H-NMR spectrum shows two signals for N–H protons confirming that the guanidine is indeed neutral. In the crystal structure of $[PtI_2(HNEt_2)\{HN{=}C(NEt_2)_2\}]$ (Fig. 5), the platinum has square planar geometry [I–Pt–N 89–93°] with the nitrogen ligands coordinated *trans* to each other. The iodine atoms are coordinated symmetrically [Pt–I(1) = Pt–I(2) = 2.597(2) Å], although the Pt–N bond lengths are slightly different. The guanidine coordinate bond is shorter than that for the amine [Pt–N(1) 2.006(9) Å and Pt–N(2) 2.095(9) Å] which would be expected as the guanidine is bound via a sp^2 hybridised imine nitrogen. The central CN_3 core of the guanidine is planar, although as a result of coordination the imine bond is slightly lengthened (C(1)–N(1) 1.32(1) Å; c.f. 1.36(1) and 1.35(2) Å for C(1)–N(3) and C(1)–N(4), respectively). It was suggested that this may also be as a result of resonance within the CN_3 core.

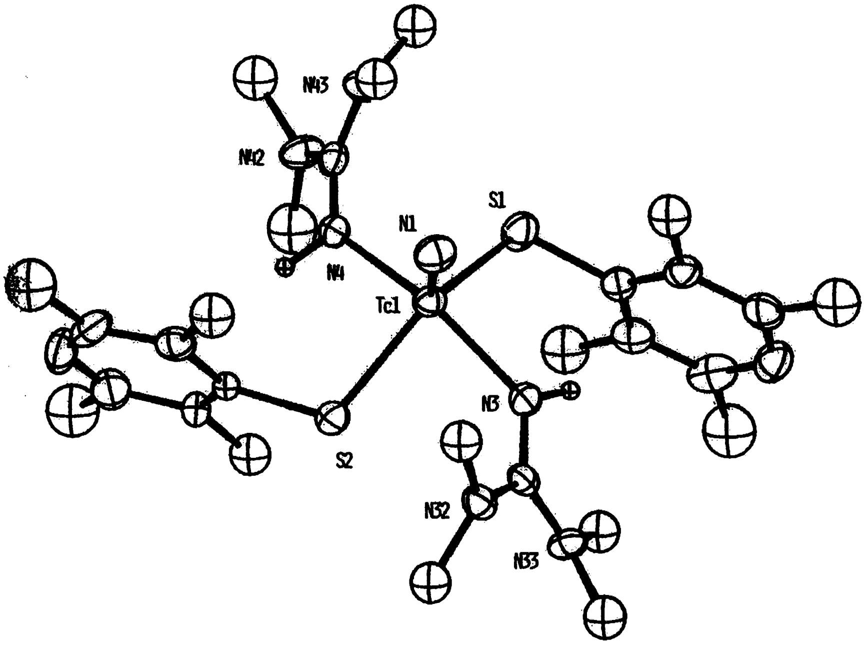


Fig. 4. The molecular structure of $[TcN(tmbt)_2(tmg)_2]$ (tmbt = 2,3,5,6-tetramethylbenzenethiolate, tmg = 1,1,2,2,tetramethylguanidine). Reproduced from Ref. [13] with permission of The American Chemical Society.

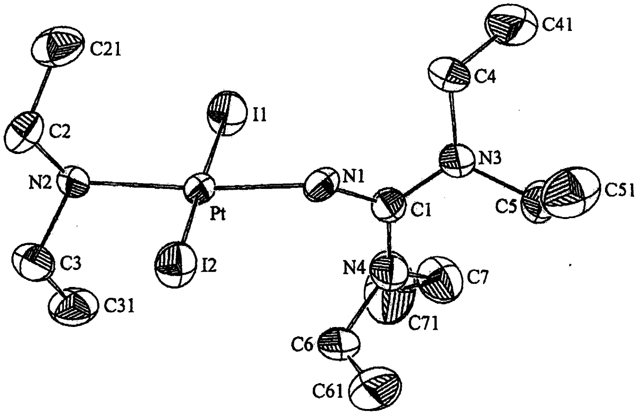


Fig. 5. The molecular structure of [$PtI_2(NEt_2)\{HN{=}C(NEt_2)_2\}$]. Reproduced from Ref. [14] with permission of Wiley–VCH.

Evidence of an unsubstituted guanidine complex with Cu^+ was obtained from FAB mass spectrometry of solutions containing guanidine hydrochloride and copper(II) chloride [15]. A small peak at m/z 122 [guanidine, Cu^+] was obtained and a monodentate coordination mode postulated, although no other evidence of complex formation was reported. Of interest though, are the DFT calculations which show that for this system coordination of the imine nitrogen is 26 kcal mol^{-1} more favourable than coordination through the amine nitrogen.

A recent report by Schmidbaur and co-workers detailed the first guanidine complexes of gold(I) [16]. The high yielding, stoichiometric reactions between 1,1,2,(2–)tetramethylguanidine and [$AuCl(SMe_2)$] or [AuBr(tht)] (tht = tetrahydrothiophene) gave [(tmg)AuCl] and [(tmg)AuBr], respectively. In solution these were found to disproportionate into an equilibrium mixture of neutral [$AuX\{HN{=}C(NMe_2)_2\}$] and ionic [$Au\{HN{=}C(NMe_2)_2\}_2$][AuX_2]. However, the crystalline precipitates of these mixtures show single ν(NH) and ν(C=N) bands in their IR spectra indicating that they are of uniform composition. X-ray crystallography confirmed that they exist in the ionic form (Fig. 6(a)). The [$Au\{NH{=}C(NMe_2)_2\}_2$]$^+$ cations and $AuBr_2^-$ anions form ion pairs via Au···Au contacts [3.1413(8) Å]. Both the axes N(1)–Au(1)–N(4) and Br(1)–Au(2)–Br(2) are virtually linear [178.8(5)° and 176.89(6)°, respectively]. These units enclose a dihedral angle of 41.5° and this precludes any hydrogen bonding between the NH and Br groups. In the cation, the two coordinate bonds are equal within one standard deviation [Au(1)–N(1) 2.006(9) Å, Au(1)–N(1) 1.993(9) Å]. The guanidine is bound to the metal through its imine nitrogen with the amine (NMe_2) groups not involved in coordination. The other guanidine complex reported in the paper was formed by the reaction of tetramethylguanidine with [$(Ph_3P)Au(OTf)$] to yield [$Au\{NH{=}C(NMe_2)_2\}(PPh_3)$]$^+$($CF_3SO_3$)$^-$, the structure of which was also determined (Fig. 6b). The P(1)–Au(1)–N(1) axis is slightly distorted from linear [177.1(3)°] and the guanidine is again coordinated through its imine nitrogen, although the coordinate bond is slightly longer than the

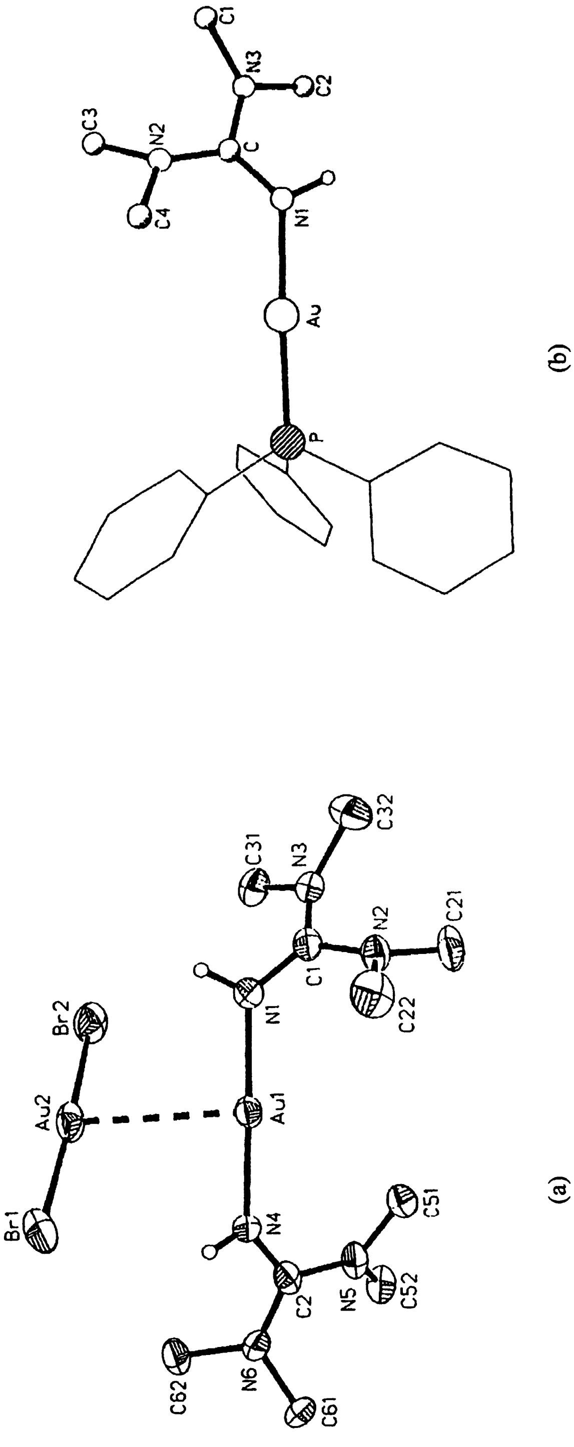


Fig. 6. The molecular structures of [Au{HN=C(NMe$_2$)$_2$}$_2$][AuBr$_2$] (a) and [(PPh$_3$)Au{HN=C(NMe$_2$)$_2$}] (b). Reproduced from Ref. [16] with permission of Wiley–VCH.

previous example [Au(1)–N(1) 2.044(9) Å]. Of the three C–N distances the imine bond is shorter than the others [C(1)–N(1) 1.27(1) Å c.f. C(1)–N(2) 1.32(1) Å and C(1)–N(3) 1.38(1) Å] although all three are intermediate between single and double bonds. This, allied to the fact that the central CN_3 unit is planar (sum of angles total 360°), would indicate that there is extensive delocalisation over the guanidine ligand.

The first complexes containing a neutral trisubstituted guanidine ligand were published by Bailey and co-workers [17]. Reaction of anhydrous $CoCl_2$ with two molar equivalents of 1,2,3-triphenylguanidine in refluxing THF provided the bright blue $[Co\{PhN{=}C(NHPh)_2\}_2Cl_2]$. The IR spectrum of this indicated a lowering of the $\nu(C{=}N)$ band energy which is consistent with binding through the imine nitrogen. The X-ray crystal structure was determined and the tetrahedral complex was found to contain two chlorides and two neutral monodentate guanidine ligands (Fig. 7(a)). The guanidine ligands bind symmetrically to the cobalt centre [Co(1)–N(11) 2.014(6) Å and Co(1)–N(12) 2.013(5) Å]. Fourier difference maps located the NH hydrogens on the non-ligating nitrogens proving coordination via the imine nitrogens. Further confirmation of this was obtained by considering the bond lengths within the central CN_3 core of the guanidines. The bonds between the central guanidine carbon and the ligating nitrogens [1.312(8) and 1.295(8) Å] are significantly shorter than the remaining C–N bonds [range 1.342(8)–1.384(8) Å]. The second complex described in this paper, the product of the reaction between 1,2,3-triphenylguanidine and silver triflate, also showed a reduction in its $\nu(C{=}N)$ stretching frequency from the free ligand. The complex was found to be $[Ag\{(PhN)C(NHPh)_2\}_2][SO_3CF_3]$ (Fig. 7(b)) and is similar to the first gold(I) complex described previously. The [N–Ag–N] axis is perfectly linear since the complex contains a crystallographic inversion centre at silver. The coordinate bonds [Ag(1)–N(11) 2.135(8) Å] are slightly longer than for the gold complex, although typical of linear Ag–N coordinate bonds. Although the hydrogens were not located, the C–N bond lengths again show that the imine nitrogen is the one coordinated [C(11)–N(11) 1.32(1) Å, C(11)–N(21) and C(11)–N(31) both 1.36(1) Å]. Unlike the gold(I) complex, the triflate anion is hydrogen bonded via two S=O oxygen atoms to the non-coordinated amine NH protons. The N–O distances in these N–H···O systems range in length from 2.912(12) to 3.109(13) Å.

A final example of neutral guanidine coordination was described by Mitewa and co-workers [18]. Reaction of two or four molar equivalents of triphenylguanidine with $(NH_4)_2[PdCl_4]$ in aqueous methanol yields the complexes $[Pd\{PhN{=}C(NHPh)_2\}_2Cl_2]$ and $[Pd\{PhN{=}C(NHPh)_2\}_4](ClO_4)_2$. In their IR spectra these both exhibit a reduction in $\nu(C{=}N)$ from the free ligand, indicative of coordination through the imine nitrogen. A crystal structure determination was performed on the bis-guanidine complex (Fig. 8). The complex has distorted square planar geometry around the Pd [angles in the range 88.77(20)–91.63(20)°] with the ligands *trans* around the Pd centre. The guanidines are symmetrically bound to the metal [Pd–N(11) 2.036(7) Å and Pd–N(21) 2.023(7) Å] and coordination through the imine nitrogen is confirmed by analysis of the C–N distances within the central CN_3 unit [C(11)–N(11) 1.309(11) Å and C(21)–N(21) 1.312(11) Å; c.f. range

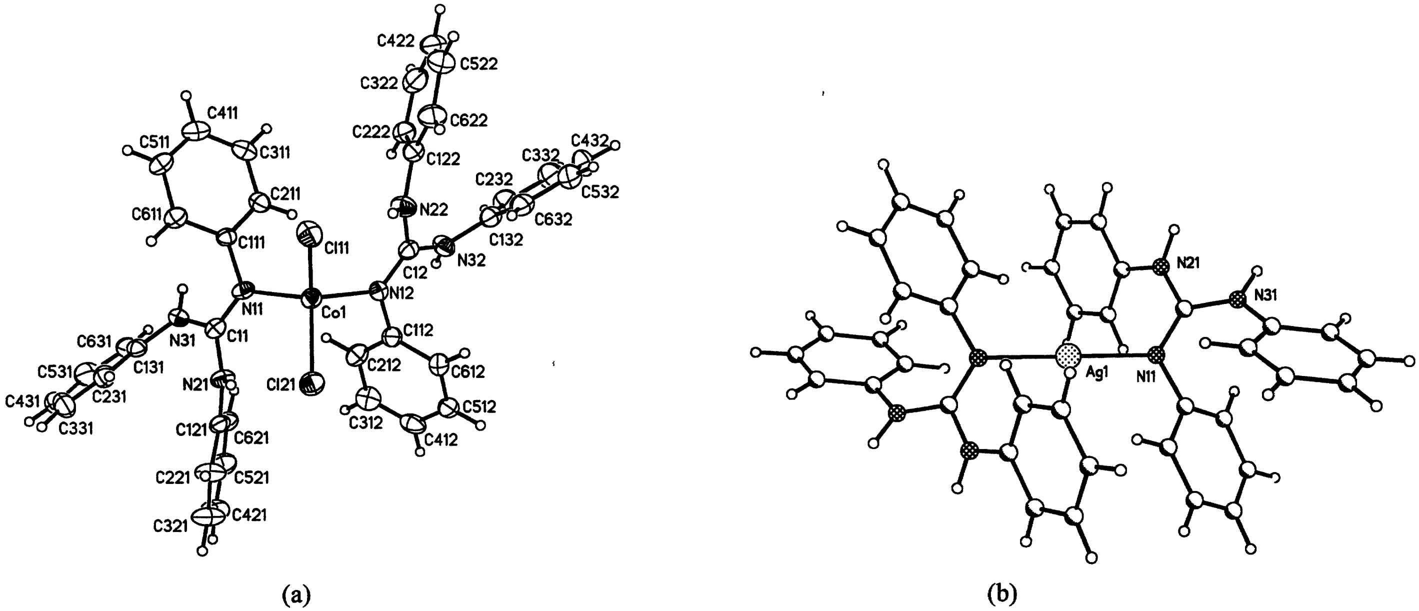


Fig. 7. The structures of $[CoCl_2\{PhN{=}C(NHPh)_2\}_2]$ (a) and $[Ag\{PhN{=}C(NHPh)_2\}_2]^+$ (b). Reproduced from Ref. [17] with permission of The Royal Society of Chemistry.

1.348(11)–1.364(11) Å for the non-coordinating nitrogens]. Two of the amine hydrogens [H(13) and H(23)] form hydrogen bonds of the type N–H···Cl to the chloride ligands. These bonds range from 3.409(8) to 3.317(7) Å and the N–H–Cl angles from 139(1) to 144(1)°.

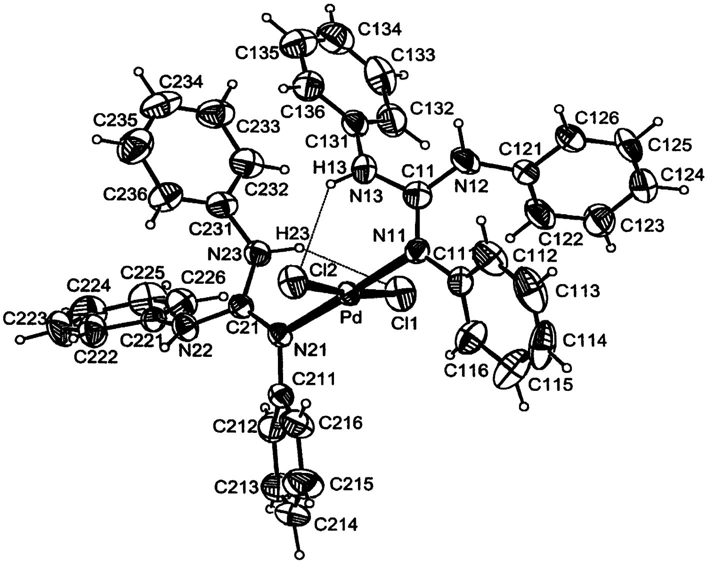


Fig. 8. The molecular structure of [$PdCl_2\{PhN{=}C(NHPh)_2\}_2$]. Reproduced from Ref. [18] with permission of Elsevier.

All of these complexes show that a neutral guanidine, with no additional donor atoms, will coordinate as a monodentate ligand through the imine nitrogen alone. A feature of these ligands is that, upon coordination, the central CN_3 core remains planar and the C–N distances become intermediate between single and double bonds. This is indicative of the extensive delocalisation that exists within the guanidine ligand and the delocalisation may also enhance the inherent stability of these complexes.

2.2. Guanidines with additional donor atoms

There is large scope for the introduction of different substituents (which may contain additional donor atoms) onto a guanidine moiety, as their stepwise synthesis readily permits the incorporation and variation of substituent groups. The most commonly encountered example which contains an additional donor atom is cyanoguanidine. In addition to this, complexes of guanidine substituted azo and phosphorous compounds are known. All of these ligand types will be reviewed herein.

Complexes containing cyanoguanidine [cnge; $(NH_2)_2CNCN$] ligands are fairly common in the literature, although in the majority of cases it acts as a monodentate ligand, binding to the metal through the cyano nitrogen alone. However, examples in which any of the guanidine nitrogens are actually involved in metal coordination are scarce. In these few examples the cyanoguanidine is invariably found to act as a bidentate, bridging ligand coordinated to two separate metal centres via the nitrile nitrogen and the imine nitrogen to which the nitrile is bonded. The major differences between these complexes arise in the way the metal–guanidine units interact with each other to form either dimers or oligomeric structures. This in turn, is normally due to the steric effects imposed on the complexes by the coordination geometry at the metal centre or by the other ligands which are bound to the metal, rather than any steric or electronic influence exerted by the cyanoguanidine ligand.

The first structurally characterised cyanoguanidine complex was obtained from the reaction of ethylenediamine hydrochloride, cyanoguanidine and copper(II) sulphate [19]. The isolated crystals analysed as the anticipated product ethylenebisbiguanidecopper(II) sulphate except for the presence of a C≡N stretch in the IR spectrum. The structure was determined as (1–)((2–)aminoethyl)biguanidecyanoguanidinecopper(II) sulphate monohydrate by an X-ray diffraction study (Fig. 9). The coordination sphere of the copper consists of three nitrogens from the (1–)((2–)aminoethyl)biguanide ligand with the fourth equatorial position occupied by the cyano nitrogen of cyanoguanidine. The axial positions are occupied by a further cyano nitrogen and an imine nitrogen from the guanidine moiety with the amino nitrogens of the guanidine not involved in coordination. The two copper units are linked via a common coordination to form a pair of coordination bipyramids in which the copper atoms are separated by a distance of 3.44 Å. These are linked in turn by two bridges and the pairs of bipyramids form chains.

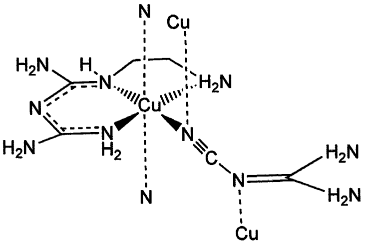


Fig. 9. The structure adopted by (2-aminoethyl)biguanidecyanoguanidinecopper(II) sulphate monohydrate.

Of the large number of complexes containing cyanoguanidine ligands synthesised by Hubberstey and co-workers only four show direct coordination of the imino nitrogen of the guanidine moiety. In [di-μ-sulphato-tetraaquo-bis-(μ-cyanoguanidine)dicadmium(II)] the two cadmium atoms are bridged by the two cyanoguanidine ligands; one cadmium bound to the cyano nitrogen, the other to the imino nitrogen [20]. The remaining amino nitrogens of the guanidine play no part in coordination to the cadmium. The two water molecules are *trans*-to these Cd–N bonds with the sulphato groups occupying the axial positions. The

$Cd_2(cnge)_2$ units are essentially planar and these planes are linked together by bridging sulphate anions to form infinite chain structures. Reduction of copper(II) chloride in the presence of cyanoguanidine yields $[Cu_2(cnge)_4]^{2+}$ where the cyanoguanidine again acts as a bidentate bridging ligand (Fig. 10(a)) [21]. The copper(I) centres are bridged by two cyanoguanidine ligands to form an eight membered metallacycle [Cu–N≡C–N–Cu–N≡C–N]. The coordination mode of the cyanoguanidine is similar to the previous example in that the nitrilic nitrogen N(11) and the imino nitrogen N(12) form coordinate bonds to the metals with the amino nitrogens [N(13) and N(14)] uncoordinated. The distorted trigonal planar geometry of the copper(I) centres is completed by a second molecule of cyanoguanidine which binds, in a monodentate manner, through its nitrilic nitrogen N(21). In contrast to the previous example, no other ligands are bound to the metal leaving the copper(I) centres coordinatively unsaturated. In the solid phase, the dimeric units stack in a lattice such that the nitrile function of a monodentate cyanoguanidine ligand is in the axial position of a neighbouring Cu(I) atom.

Further examples of cyanoguanidine acting as a bridging ligand were reported by Hubberstey and co-workers in 1994 [22]. This report again describes the reduction of copper(II) halides in the presence of cyanoguanidine to yield the complexes $[Cu_2X_2{\cdot}cnge]$ (X = Cl or Br) and $[CuBr{\cdot}cnge{\cdot}H_2O]$. However in this case, due to the coordination of residual halides, the Cu(I) centres are more sterically hindered so dimers are not able to form. Instead the [XCu(cnge)] units form chains in the solid state (Fig. 10(b)). Once again the cyanoguanidine is bound through its nitrilic N(1) and imino N(2) nitrogens with the amino nitrogens [N(3) and N(4)] uncoordinated. A further example of a bridging cyanoguanidine ligand is found in the complex $[Hg(cnge)Cl_2]$ reported by Pickardt and co-workers [23]. The mercury atoms have an octahedral geometry with four chlorine atoms in equatorial positions and two cyanoguanidine nitrogens in the axial sites. The Hg atoms are bridged by two chlorine atoms and these $HgCl_2$ units form polymeric chains. These chains are

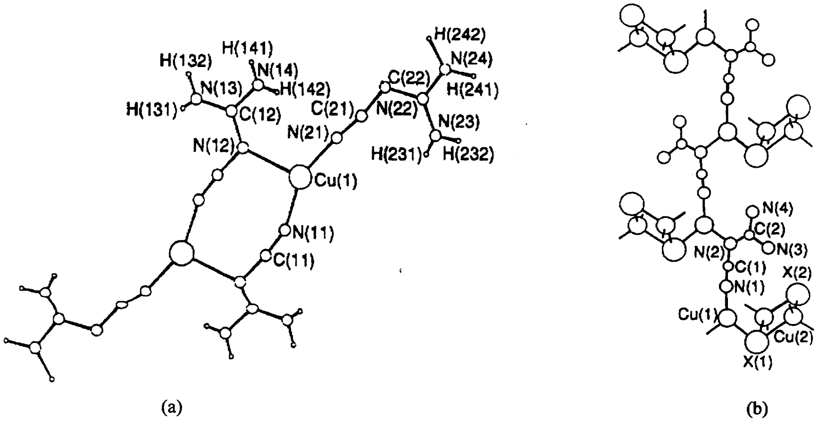


Fig. 10. The structures of $[Cu_2(cnge)_4]^{2+}$ (a) and $[Cu_2X_2(cnge)]$ (b) (cnge = cyanoguanidine, X = Cl, Br). Reproduced from Refs. [21b,22] with permission of The Royal Society of Chemistry.

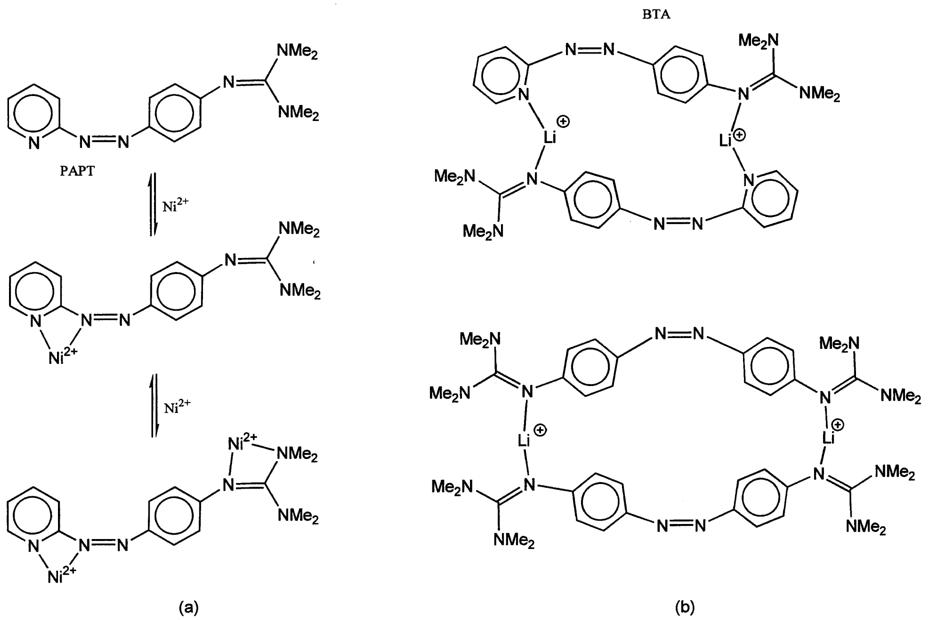


Fig. 11.

cross-linked by bidentate bridging cyanoguanidine ligands to form a net-like array. The cyanoguanidine is again bound to the metal through the cyano and imino nitrogen atoms.

Incorporation into the guanidine of donor atoms/groups other than nitrile also usually results in the guanidine acting as a bidentate ligand. The ligand normally binds through one of the guanidine nitrogens and the other donor atom, although it is also known for the metal to be bound by two of the guanidine nitrogens. The ligand pyridine-(2–)azo-*p*-phenyltetramethylguanidine (PAPT) was synthesised and its interactions with Ni^{2+}, Co^{2+} and Zn^{2+} were studied [24] These reactions were followed by UV–vis spectroscopy and the ligand was found to chelate to the metals. Complexation of the first equivalent of metal occurred through the azo and pyridine nitrogens and the second equivalent through the imine and amine nitrogens of the guanidine moiety (Fig. 11(a)). A further report of the PAPT ligand detailed its complexation of lithium cations [25]. The paper also reports the reactions of 4,4′-bis(tetramethylguanidine)azobenzene (BTA). For both ligands, dimers were formed with the Li$^+$ bridging between either a pyridine nitrogen and an imine nitrogen (PAPT) or between two imine nitrogens (Fig. 11(b)). A different type of substituted guanidine, guanidinopyrimidine, which contains an additional donor nitrogen, was studied by Zawadski and co-workers [26]. 2,6-Dihloro-4-guanidinopyrimidine and 4,6-dihloro-4-guanidinopyrimidine were utilised as potential chelating ligands in reactions with Pd(II) salts. Upon chelation, shifts in the stretching frequencies in the guanidine and pyrimidine moieties were observed in the IR spectrum, suggesting coordination through both groups. UV–vis spectroscopic analysis agreed with this postulation and a proposed structure of the complexes has the Pd coordinated by the imine nitrogen from the guanidine and one of the pyrimidine nitrogens (Fig. 12).

The reaction of methanol with the cyanoguanidine complex $[Pt(cnge)_2(PPh_3)_2][BPh_4]_2$ (in which the cyanoguanidine is bound through its cyano nitrogen alone) in acetone solution provided the unusual azametallacyclic species *cis*-$[(Ph_3P)_2Pt\{NHC(OMe)=NC(NH_2)=NH\}][BPh_4]$ [27]. The structure of the azametallacycle was confirmed by X-ray crystallography and was shown to contain a bidentate ligand binding through guanidine and cyano nitrogen atoms (Fig. 13). This ligand forms as a result of activation, by the Pt(II) centre, of a cyanoguanidine ligand towards nucleophilic addition of MeOH at the cyano group and deprotonation of the guanidine group. In the crystal structure itself, the platinum ion exhibits square planar geometry, bound by two phosphines and the azametallacycle. The six-membered chelate ring is planar indicating a delocalised π-electron system and the two coordinate bonds are essentially identical [Pt–N(1) 2.048(6) Å and Pt–N(2) 2.032(7) Å]. Complexes of phosphorylguanidines, where the ligand binds through a guanidine nitrogen and the phosphoryl oxygen, were reported by Lin and co-workers [28]. The reaction of dialkylphosphorylguanidines with metal ions was followed by UV titration and conductivity measurements and evidence for complex formation was obtained with Cu^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+} and Al^{3+}. It was found that the free ligands undergo an intramolecular rearrangement to yield, in the solid state, a six-membered structure containing an intramolecular hydrogen bonding bridge (Fig. 14). It was suggested that when a metal ion is introduced the hydrogen bond bridge is readily cleaved by simple rotation of the C–N bond, creating a complexation site for the metal ion.

Complexes of phosphorus substituted tetramethylguanidine have recently been reported by Schmutzler's group. The first of these papers discusses the reactions of dialkylphosphinous-*N*-(1,1,2,(2–)tetramethyl)guanidine and alkylphosphonous-bis-*N*-(1,1,2,(2–)tetramethyl)guanidine with zero valent transition metals [29]. Mostly the ligands are bound through the phosphorus alone, although reaction with tetracarbonyl molybdenum fragments produced complexes containing P,N- and P,*N*,*N*′-donor ligands which were characterised by IR and NMR spectroscopy (Fig.

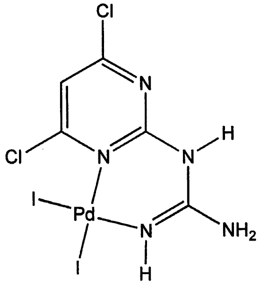


Fig. 12.

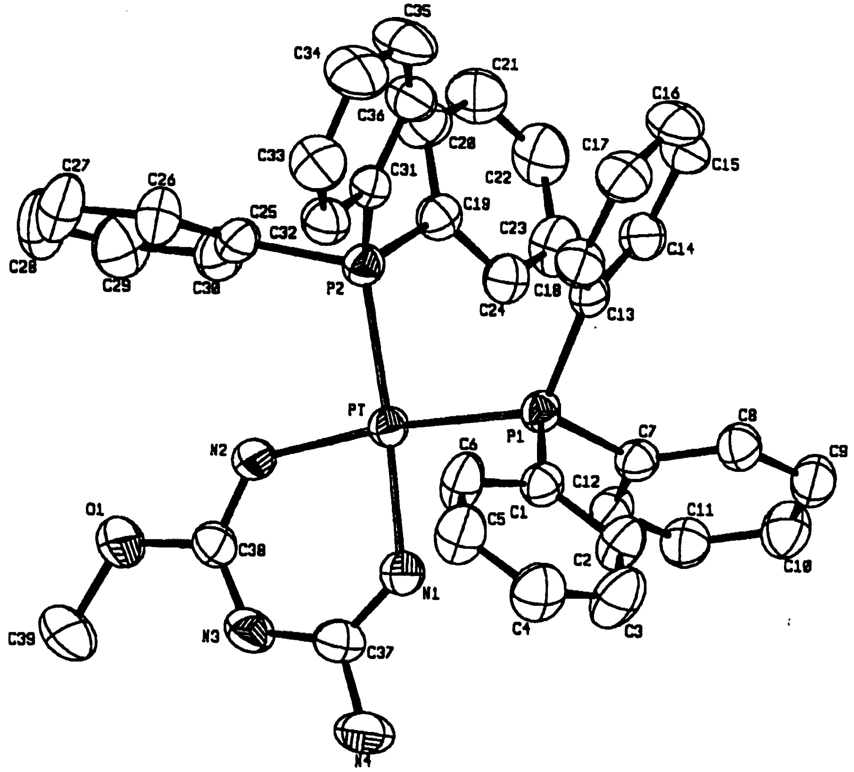


Fig. 13. The structure of the cation in [(Ph$_3$P)$_2$Pt{NHC(OMe)=NC(NH$_2$)=NH}][BPh$_4$]. Reproduced from Ref. [27] with permission of Elsevier.

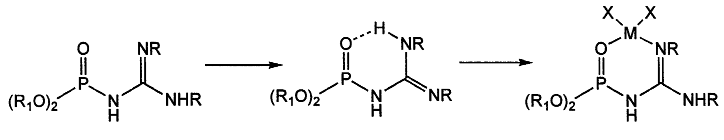


Fig. 14.

15). A second paper from this group reported the reaction of alkylphosphonic-bis-*N*-(1,1,2,(2–)tetramethyl)guanidine with a variety of first row transition metals [30]. Again coordination through the P=O bond alone is observed, although coordination through guanidine nitrogens is also observed. In fact for the complex $[(^t\mathrm{BuP{=}O})(\mathrm{tmg})_2\cdot\mathrm{CuCl_2}]$ the ligand chelates the metal, binding through guanidine imine nitrogens alone (Fig. 16). Chelation of the metal forms a four-membered Cu–N–P–N metallacycle which is slightly puckered [7.9° along N(1)–N(4) axis]. The copper atom has distorted square planar geometry, the largest deviation occurring for the endocyclic angle N(1)–Cu–N(4) 72.68(9)°, due to the restricted bite of the ligand. The ligand symmetrically binds the copper [Cu–N(1) 2.006(3), Cu–N(4)

2.004(2) Å] through its imine nitrogens, the amine (NMe_2) groups remaining uncoordinated.

The attachment of additional donor atoms onto the guanidine moiety can have a marked effect on its ligand capabilities. Although at present there are only a

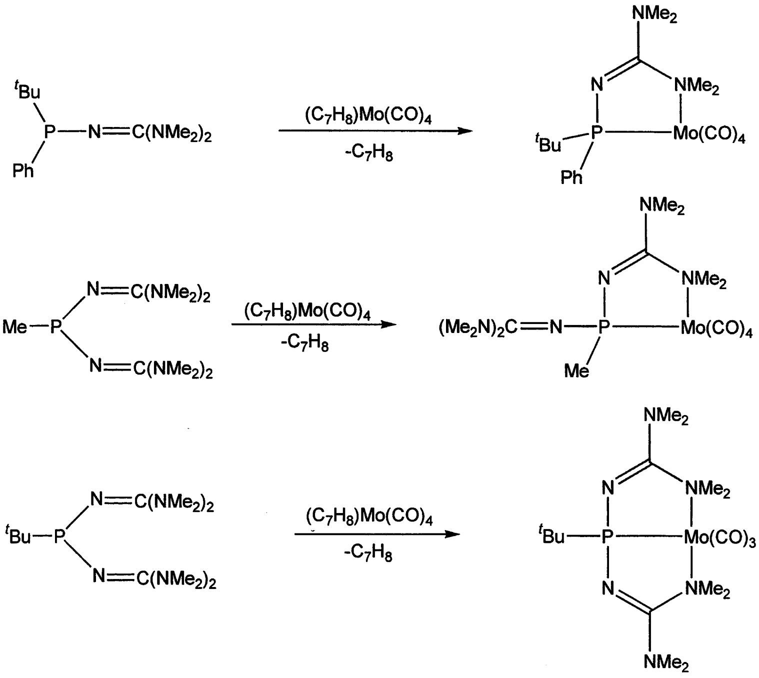


Fig. 15.

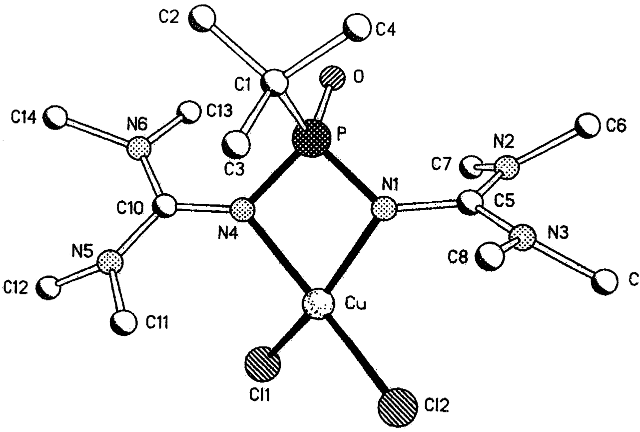


Fig. 16. The molecular structure of [(ᵗBuP=O)$CuCl_2$(tmg)$_2$] (tmg = 1,1,2,(2–)tetramethylguanidine). Reproduced from Ref. [27] with permission of Wiley–VCH.

handful of reports of ligands of this type, diversity in the binding mode of the ligands already exists. From these few reports it seems clear that a large, and as yet unexplored, area of coordination chemistry exists and that many novel ligand systems, based on substituted guanidines, show promise for future research in this field.

3. Monoanionic guanidinates [guanidinates(1–)]

3.1. Ligand electronic structure

As will become clear in the following sections, guanidinates(1–) display compatibility with a remarkable range of metals in a variety of oxidation states from metal carbonyl species to early transition and lanthanide metals. This must be attributed to the electronic flexibility of this system due to the variable contributions of the two possible resonance forms of the coordinated ligand determined by the electronic requirements of the metal (Fig. 17). Thus, in resonance form (A) the ligand is effectively an amidinate bearing an amino-substituent on the central carbon atom. Amidinates are themselves an electronically flexible ligand system displaying compatibility with transition metals in a range of oxidation states [31]. However, the potential for a contribution from the iminium/diamide type resonance form (B) means that this flexibility is exceeded by guanidinates whose π-donor ability, and hence compatibility with electron deficient metal ions, is augmented by any contribution from this resonance form. Guanidinates(1–) are therefore stronger donors (more basic) than amidinates and, for a given metal, replacement of an amidinate by a guanidinate would be expected to increase the electron density on the metal and reduce its oxidation potential. This has effectively been illustrated by a comparison between the quadruply bonded molybdenum dimers $[Mo_2(\mu\text{-}\eta^2\text{-L-X})_4]$ ($L\text{–}X^- =$ formamidinate $[(p\text{-tolyl})_2NCH]^-$; $[(PhN)_2CNHPh]^-$ guanidinate) [32]. Cyclovoltametric studies show the first redox potential for the formamidinate complex to occur at +0.21 V versus Ag/AgCl while the second oxidation to the dication is an irreversible process at ca. +1.3 V. By contrast, the guanidinate complex displays two reversible redox processes at −0.05 and +0.85 V versus Ag/AgCl thus clearly indicating the superior donor properties of the guanidinate ligand system and its ability to stabilise metals in higher oxidation states. The structural features of this system will be discussed further below.

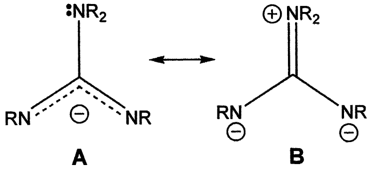


Fig. 17. The 1,3-diazaallyl (A) and iminium/diamide (B) resonance forms of a guanidinate(1–) ligand.

An indication of the relative contributions which resonance forms A and B make to a coordinated guanidinate ligand can in principle be provided by a comparison of the C–N bond lengths within the CN_3 core of the coordinated ligand. Clearly the larger the contribution made by form B the shorter the C–N bond to the uncoordinated nitrogen atom and the longer those to the coordinated nitrogen atoms will be. However, in most cases it is found that the C–N bond lengths indicate a predominant contribution from form A. Even for complexes containing d-electron deficient metal ions, where a higher contribution from form B would be predicted, the C–N bond lengths to the coordinated nitrogen atoms are often significantly shorter than those to the uncoordinated nitrogen, and it is only very recently that an example of a complex containing a guanidinate(1–) ligand in which there is clear, crystallographically significant, evidence for a contribution from form B has been reported [33]. The complex $[Ti\{\eta^2\text{-}(NPh)_2CNEt_2\}_2Cl_2]$ contains crystallographically equivalent guanidinate(1–) ligands in which the C–N bond to the uncoordinated nitrogen atom is 1.341(6) Å while those to the coordinated nitrogen atoms are 1.343(6) and 1.341(6) Å. The three bonds are therefore indistinguishable indicating considerable delocalisation of the uncoordinated nitrogen lone pair into the ligand π-system. These data contrast with that for all previously reported guanidinate(1–) ligands where the C–N bond to the uncoordinated nitrogen atom is significantly longer than those involving the coordinated nitrogen atoms. This situation should be compared with complexes containing guanidinate(2–) ligands such as $[Pt\{\eta^2\text{-}(PhN)_2C{=}NPh\}(COD)]$, which may be viewed as effectively 100% resonance form B, in which the two different C–N bonds differ by 0.1 Å [1.30(1) and 1.40(1) Å] [34]. A second structural parameter which may be used to assess the involvement of resonance form B in the ligand, although not its extent, is the planarity, or otherwise, of the uncoordinated nitrogen atom. In the absence of potentially π-conjugating substituents such as aromatic or silicon groups on this nitrogen, its planarity must indicate a contribution from form B, and in this Ti complex the NEt_2 group is indeed planar. For comparison, the guanidinate(1–) ligand in the complex $[Ta\{\eta^2\text{-}(CyN)_2CNMe_2\}(NMe_2)_4]$ may be regarded as 100% form A [35]. The π-donor properties of the guanidinate B form is not called upon by the metal in this complex since the electron deficiency of the d^0 metal ion is apparently satisfied by the four strongly π-donating dimethylamido ligands. This situation is evidenced by the fact that the C–N–C plane of the NMe_2 group in the guanidinate is effectively orthogonal (80.7°) to the CN_3 plane of the ligand core, and furthermore, this uncoordinated nitrogen atom is distinctly pyramidal with the sum of the angles around N totalling only to 351°. The lone pair of the uncoordinated nitrogen atom is thus clearly not involved in the ligand π-system and this is reflected in the pattern of C–N bond lengths in the ligand core; those to the coordinated nitrogen atoms are 1.318(6) and 1.331(6) Å, whilst that to the uncoordinated N is significantly longer at 1.426(6) Å.

3.2. Survey of complexes

Reports of complexes containing guanidinate(1–) ligands were very scarce until the early 1990s. Since then however, interest in these ligands has surged and a number of accounts of novel complexes have been published. The guanidinate(1–) ligand is found to adopt a number of different coordination modes; monodentate, chelating or doubly/triply bridging modes being observed dependant on the metal system to which it is bound. The first report of a guanidinate(1–) complex was published by Wade et al. in 1968 [36]. Reaction of 1,1,2,(2–)tetramethylguanidine with MeLi in ether at −40°C smoothly evolved methane and provided the complex $[(Me_2N)_2C{=}NLi]$, which existed as a dimer in benzene (by cryoscopy). The ^1H-NMR spectrum of this is very similar to that of the free ligand confirming that the guanidinate is bound via the imine nitrogen alone. This is very similar to the aluminium compounds discussed in the earlier section on neutral guanidines.

The crystal structure of the product obtained from the reaction between tetramethylguanidine and BuLi in ether was reported somewhat later [37]. The crystalline product isolated from this reaction was found to exist as a hexamer $[Li\{N{=}C(NMe_2)_2\}]_6$ (Fig. 18). The Li_6 rings form a chair-shaped structure with the lithium atoms held together by triply bridging $N{=}C(NMe_2)_2$ groups. These bridging nitrogens are ca. equidistant from the three Li atoms it binds to [Li–N distances 1.98, 2.00 and 2.02 Å]. Within the hexameric unit, 24 valence electrons are available for the 18 Li–N contacts resulting in a formal Li–N bond order of 0.66. Therefore, locally each ligand nitrogen has two electron pairs to bond to three Li atoms so one two-centre bond and one three-centre bond must exist. As the nitrogen is symmetrically bound to the lithium atoms, these bonding systems must be delocalised.

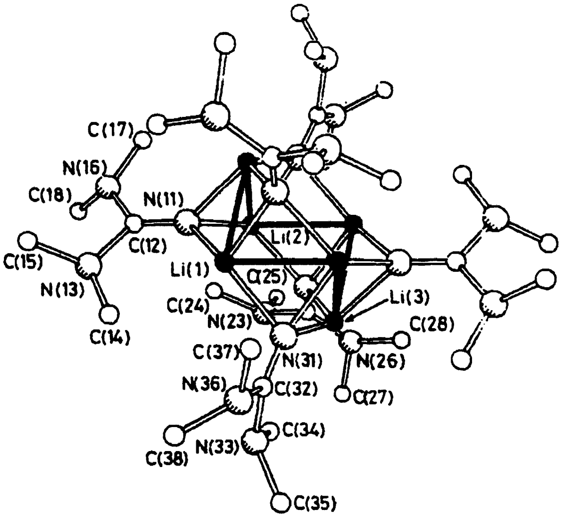


Fig. 18. The molecular structure of $[Li\{N{=}C(NMe_2)_2]_6$. Reproduced from Ref. [37] with permission of The Royal Society of Chemistry.

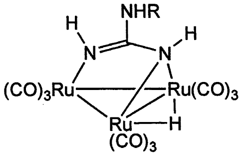


Fig. 19.

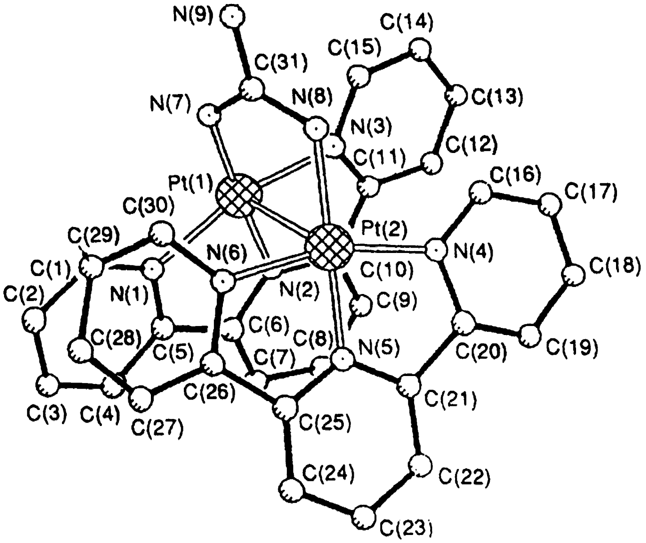


Fig. 20. The structure of the trication $[\{Pt(trpy)\}_2\{\mu\text{-}\eta^2\text{-}(NH)_2CNH_2\}]^{3+}$. Reproduced from Ref. [40] with permission of The Royal Society of Chemistry.

Jackson et al. reported the amination of the cyanamide complex $[(NH_3)_5CoN{\equiv}CN(CH_3)_2]^{2+}$ in liquid ammonia, forming the guanidinate complex tentatively assigned as $[(NH_3)_5CoN{=}C(NH_2)N(CH_3)_2]^{2+}$ [38]. Upon evaporation of the ammonia gleaming purple crystals were reported to form, although little spectroscopic or structural evidence was provided.

Thermolysis of guanidine and methylguanidine with $Ru_3(CO)_{12}$ in THF produced interesting complexes in which the guanidinate is bound to all three Ru atoms on one face of the cluster (Fig. 19) [39]. The mechanism of the reaction is thought to proceed via a hydrogen atom transfer to form a μ(2–)hydride on the Ru_3 skeleton. The guanidinate(1–) ligand then binds to the cluster with the Ru–Ru edge bridged by the μ(2–)hydride also bridged by the guanidine, and the third Ru atom coordinated by the third nitrogen atom.

The reaction of [Pt(trpy)Cl]Cl with guanidinium carbonate in aqueous solution yielded $[\{Pt(trpy)\}_2\{\mu\text{-}(NH)_2CNH_2\}]^{3+}$, which has a similar structure to the dimer discussed in the earlier section on neutral guanidines (Fig. 20) [40]. In contrast to the first example however, the guanidinate in this complex is truly monoanionic with the negative charge present on the guanidine framework. This does not have a dramatic effect on the geometry of the complex in the solid state, which is closely related to the example where the guanidine is neutral. The Pt–Pt separation is 3.071(1) Å and the trpy ligands are nearly parallel to each other [angle between planes 9°]. They adopt a slightly staggered conformation in the solid state, although they only show one set of signals in the ^{13}C-NMR spectrum indicating they are equivalent in solution. The guanidinate is symmetrically coordinated to the metals [Pt(1)–N(7) and Pt(2)–N(8) both 2.00(1) Å] which is slightly more tightly bound than for the neutral example, as would be expected for this anionic ligand.

As part of their study of the reaction of cyclopentadienyl complexes of heavy p-block metals with nucleophiles Wright et al. examined the 1:1 molar reaction of Cp_2Sn with lithiated tetramethylguanidine $[LiN{=}C(NMe_2)_2]$ [41]. The product of the reaction was found to be that of nucleophilic substitution of one Cp ligand to form the dimeric complex $[CpSn\{\mu\text{-}N{=}C(NMe_2)_2\}]_2$ (Fig. 21). The X-ray crystal structure of the product showed the dimer to be centrosymmetric with a planar Sn_2N_2 ring. The imino groups bridge the Sn centres almost symmetrically [Sn(1)–N(1) 2.196(3) Å and Sn(1)–N(1a) 2.185(3) Å] and there is considerable distortion within the ring [N–Sn–N 75.36(12)° and Sn–N–Sn 104.64(12)°]. Comparison of the C–N bond lengths within the central CN_3 ring of the guanidinate moiety shows there to be no delocalisation of electronic charge, with the imino bond retaining its double bond character [C(6)–N(1) 1.294(5) Å, C(6)–N(2) and C(6)–N(3) 1.371(5) Å]. In the solid state the complex adopts a *trans*-configuration, although ^{1}H-NMR studies in THF also showed the presence of a *cis* isomer (1:1 at +25°C).

The first report of chelating guanidinate(1–) complexes was published by Bailey and co-workers [42]. Treatment of the chloro-bridged dimers, $[Cp^*RhCl_2]_2$ and $[(p\text{-cymene})RuCl_2]_2$, with four molar equivalents of 1,2,3-triphenylguanidine in

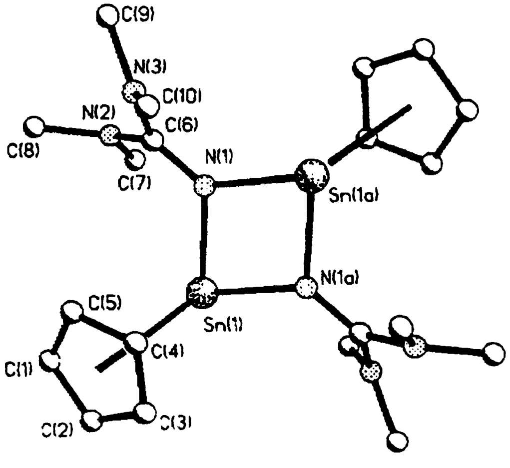
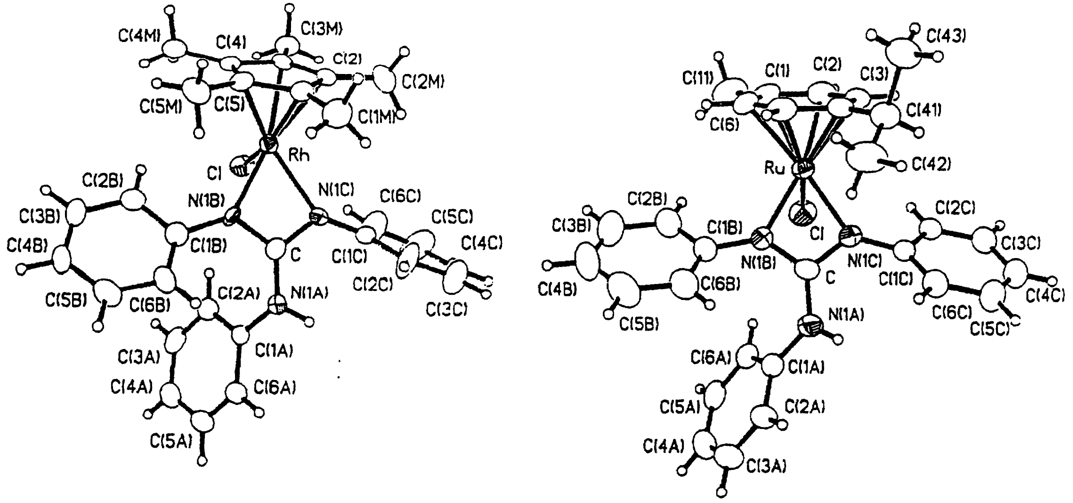


Fig. 21. The structure of the trication $[CpSn\{\mu(2\text{-})N{=}C(NMe_2)_2\}]_2$. Reproduced from Ref. [41] with permission of Wiley–VCH.



(a) (b)

Fig. 22. The molecular structures of [Cp*Rh{η^2-$(PhN)_2$CNHPh}Cl] (a) and [(*p*-cymene)Ru{η^2-$(PhN)_2$CNHPh}Cl] (b). Reproduced from Ref. [42] with permission of The Royal Society of Chemistry.

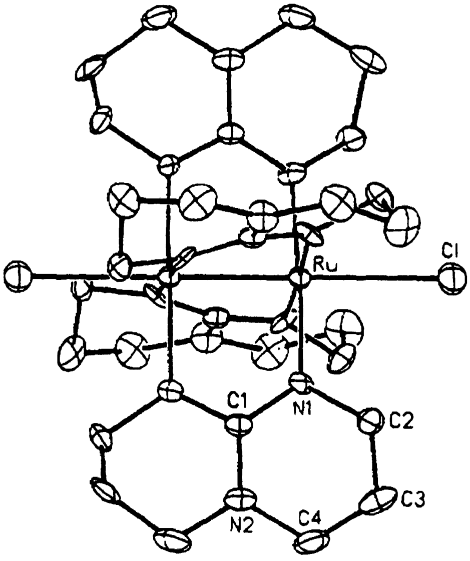


Fig. 23. The molecular structure of $[Ru_2(hpp)_4Cl_2]$ (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimidino[1,(2–)a]pyrimidinate) Reproduced from Ref. [43] with permission of The American Chemical Society.

toluene solution led to precipitation of two equivalents of the guanidinium chloride salt leaving the chelate complexes $[Cp^*Rh\{\eta^2\text{-}(PhN)_2CNHPh\}Cl]$ and $[(p\text{-cymene})Ru\{\eta^2\text{-}(PhN)_2CNHPh\}Cl]$ in solution. In this case two equivalents of the guanidine act as a base and also a halide abstractor, removing a proton from the other guanidine equivalents and a halide from the metal. The structure of the complexes were determined by X-ray diffraction and were found to be very similar with the metal ligated by a η-bonded aromatic, a terminal chloride and a chelating triphenylguanidinate (Fig. 22). In the rhodium complex the coordinate bonds are slightly different [Rh–N(1B) 2.085(6) Å, Rh–N(1C) 2.136(8) Å], although this may be due to steric repulsion between the phenyl substituents on N(1B) and N(1C) rather than an actual difference in their donor strengths. Within the guanidinate ligand the central CN_3 unit is planar and the C–N distances are intermediate between those typical for single and double bonds, indicating a delocalisation of charge within this group. Although the amine hydrogen was not located in the structure, ^1H- and ^{13}C-NMR showed the phenyls to be in a 2:1 ratio, consistent with the N–H being on the uncoordinated nitrogen (as shown in Fig. 22).

Recently, there has been a number of reports describing the formation of tetrabridged dimers which adopt the paddlewheel structure $[M_2L_4X_2]$ (where L = bridging ligand, X = axial ligand). The first of these described a paramagnetic diruthenium(III) complex bridged by 1,3,4,6,7,8-hexahydro-2*H*-pyrimidino[1,(2–)*a*]pyrimidinate ions (hpp), a hetero-bicyclic system which contains a guanidine moiety [43]. The X-ray crystal structure was determined and the complex was found to be [$Ru_2(hpp)_4Cl_2$] (Fig. 23). The geometry around the ruthenium centres is essentially octahedral with four hpp nitrogens in the equatorial sites [Ru–N(1) 2.045(5) Å, Ru–N(1′) 2.063(5) Å] and a chloride in an axial position [Ru–Cl 2.705(2) Å]. The Ru–Ru bond distance of 2.321(1) Å was not considered unusual with regard to the theoretical bond order of 3 for a Ru_2^{6+} system. The three C–N bond lengths within the guanidinate ligand are similar [C(1)–N(1) 1.332(6) Å, C(1)–N(1′) 1.352(5) Å, C(1)–N(2) 1.363(7) Å] and intermediate between single and double bonds indicating some delocalisation over these bonds. The cyclic voltammogram of the complex showed two reversible one-electron processes: reduction at $E_{1/2} = -0.60$ V and oxidation at $E_{1/2} = 0.55$ V. The magnetic susceptibility of the complex 2.78 μ_B is consistent with a system containing two unpaired electrons. From these data the ground state electronic configuration was determined to be either $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$ or $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^1(\delta^*)^1$.

Another example of a monoanionic bridging guanidinate was formed in the reaction of 1,2,3-triphenylguanidine with $Mo(CO)_6$ under reflux in diglyme solution [32a]. The isolated product [$Mo_2\{\mu\text{-}\eta^2\text{-}(PhN)_2CNHPh\}_4$] was structurally characterised as the quadruply bonded Mo_2 dimer with a Mo–Mo separation of 2.0839(9) Å (Fig. 24). The dimer is bridged by four guanidinate ligands in a paddlewheel arrangement with two crystallographically independent ligands. The four Mo–N distances do not vary significantly [range 2.156(5) to 2.179(4) Å] and the CN_3 units of the guanidines are essentially planar. Hydrogen atoms were located on the noncoordinating nitrogens in Fourier difference maps, confirming the monoanionic

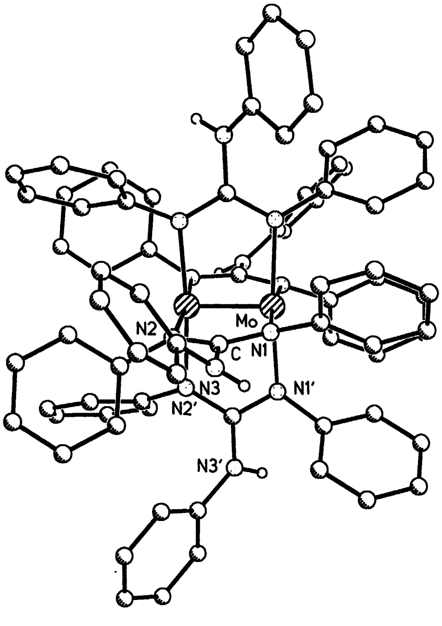


Fig. 24. The molecular structure of [$Mo_2\{\mu\text{-}\eta^2\text{-}(NPh)_2CNHPh\}_4$]. Reproduced from Ref. [32a] with permission of The American Chemical Society.

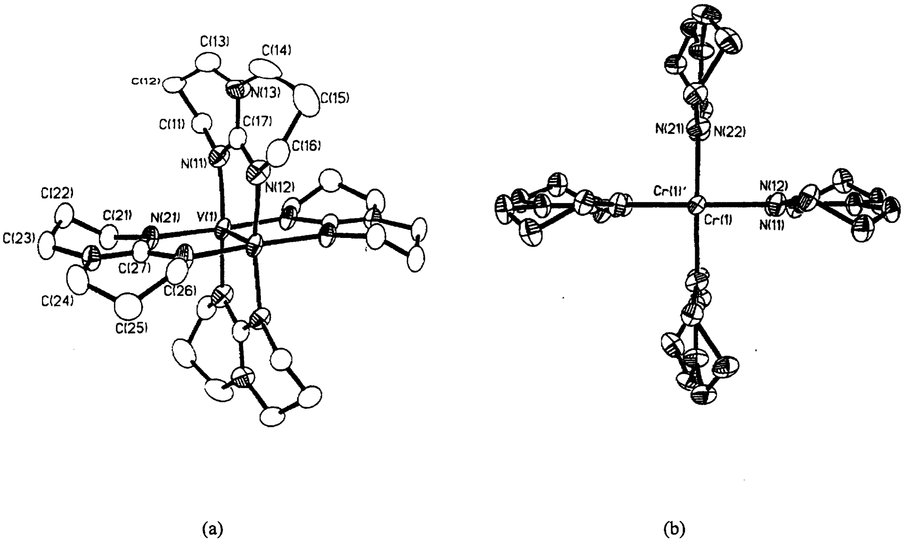


Fig. 25. The molecular structures of $[V_2(hpp)_4]$ (a) and $[Cr_2(hpp)_2]$ (b) (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimidino[1,(2–)a]pyrimidinate). Reproduced from refs. [44] with permission of Elsevier.

character of the ligands. The yellow product was found to be very air sensitive and cyclic voltammetry in CH_2Cl_2 solution showed two reversible one-electron oxidation waves at -0.05 and $+0.85$ V versus Ag/AgCl waves corresponding to the $[Mo_2]^{4+/5+}$ and $[Mo_2]^{5+/6+}$ couples. The deep red monocation $[Mo_2\{\mu\text{-}\eta^2\text{-}(PhN)_2CNHPh\}_4]^+$ and the dark blue dication $[Mo_2\{\mu\text{-}\eta^2\text{-}(PhN)_2CNHPh\}_4]^{2+}$ could also be prepared by chemical oxidation using silver tetrafluoroborate or ammonium cerium(IV) nitrate, respectively. The crystal structure of the monocationic species was obtained as its tetrafluoroborate salt, $[Mo_2\{\mu\text{-}\eta^2\text{-}(PhN)_2CNHPh\}_4][BF_4]$, although attempts to crystallise the dication failed due to reduction of the species to the monocation during crystallisation. The monocation has a similar structure to the neutral species with a Mo–Mo separation of 2.1194(12) Å [32b]. As with the neutral species, there is no axial ligation of the Mo centres as substituent phenyl groups block these sites [shortest Mo–F (BF_4^-) 6.035 Å]. The fact that the neutral complex is readily oxidised indicates that the guanidinate ligand is effective at stabilising the oxidised species, i.e. the ligands are able to donate more electron density to the metal centres (vide supra). This was rationalised by involvement of a resonance form of the ligand in which the uncoordinated nitrogen lone pair is delocalised into the ligand π-system thus increasing the π-basicity of the coordinated nitrogen atoms (Fig. 17). Indeed, there is some evidence from the crystal structure of the monocation that there is a greater contribution from resonance form B than is observed for the neutral complex.

Cotton and co-workers have recently published a series of papers in which they describe the formation and structure of various hpp^- bridged metal dimers. Their interest in this bicyclic ligand resulted from the desire to synthesise dimeric compounds containing ligands with similar properties to amidinates, but with greater resistance to cleavage. The first of these publications detailed the synthesis of V_2^{4+}, Cr_2^{4+} and Mo_2^{4+} compounds which are all tetrabridged by the monoanionic hpp ligand [44]. Reduction of $VCl_3(THF)_3$ at -78°C, followed by addition of two molar equivalents of Li[hpp] produced a toluene soluble brown powder from which crystals were obtained. X-ray structural analysis of this complex confirmed that the complex adopts a paddlewheel structure with a very short V–V bond [1.932(1) Å] (Fig. 25(a)). The molecule lies on an inversion centre and the five-membered chelate rings [M–M–N–C–N] are essentially planar The hpp is symmetrically coordinated to the metal centres [e.g. V(1)–N(11) 2.061(4) Å] and within the guanidinate ligand framework the C–N distances are consistent with partial bond character [av. C(17)–N 1.35(2) Å]. Synthesis of the dimolybdenum complex was achieved by the reaction of $Mo_2(O_2CCF_3)_4$ with Li[hpp] in toluene solution. Crystals obtained from this solution were found to be crystallographically similar to the divanadium complex. The Mo–Mo distance of 2.067(1) Å is very short in comparison to other molybdenum paddlewheels with nitrogen donor atom bridges while the coordinate bonds are crystallographically equivalent [Mo(1)–N(11) 2.159(6) Å, Mo(1)–N(12)′ 2.167(6) Å]. Reaction of Li[hpp] with anhydrous $CrCl_2$ at -78°C provided a yellow solution from which a highly air and water sensitive product was obtained. X-ray structural analysis of the product confirmed that it was $Cr_2(hpp)_4$, but the crystal packing differed slightly from the previous examples (Fig. 25(b)). Again, the molecule has an inversion centre and the coordinate bonds are crystallographically equivalent [e.g. Cr(1)–N(11) 2.041(2) Å]. The central CN_3 core of the guanidinate ligands are again planar with C–N bonds averaging 1.35(2) Å and the Cr–Cr distance [1.8517(7) Å] is short in comparison to other nitrogen bridged systems. A communication discussing the bond lengths in dimolybdenum complexes was also published by this group [45]. The synthesis of $[Mo_2(hpp)_4(BF_4)_2]$ by the oxidation of $Mo_2(hpp)_4$ was described and its X-ray crystal structure presented (Fig. 26). The paddlewheel structure of the starting material is maintained, the only major difference being the weak coordination of the BF_4^- anions in axial sites [Mo(1)···F(3) 2.768(6) Å]. The central Mo_2^{6+} unit has a formal triple bond with a Mo–Mo distance of 2.142(2) Å, an increase of 0.075 Å from the quadruply bonded Mo_2^{4+} described previously. The Mo–N distances are shorter than observed for the neutral system [av. 2.08(7) Å]. The communication highlights the error in Mo–Mo bond length given for the monocationic $[Mo_2\{\mu\text{-}\eta^2\text{-}(PhN)_2CNHPh\}_4]^+$ system in the original publication (vide supra), although this had previously been corrected [32b].

A further publication by this group detailed the synthesis of a dimeric, triply bonded niobium complex $[Nb_2(hpp)_4]$ in which the Nb–Nb distance 2.2035(9) Å, is the shortest known [46]. The complex was formed by the reaction of $NbCl_3(DME)$ and Li[hpp] in the presence of KC_8 at room temperature in THF and produced green crystals of the diamagnetic product. An X-ray crystal study confirmed the complex to exist in a paddlewheel arrangement, similar to the vanadium, chromium and molybdenum complexes previously described, with the Nb_2^{4+} unit bridged by four monoanionic hpp ligands (Fig. 27(a)). The dimer is centrosymmetric with

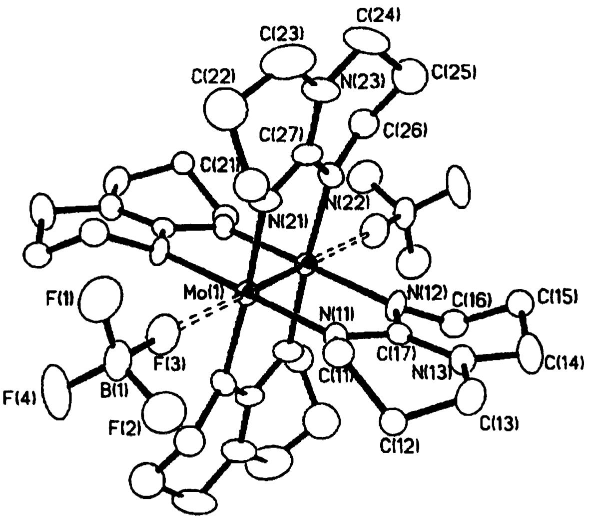
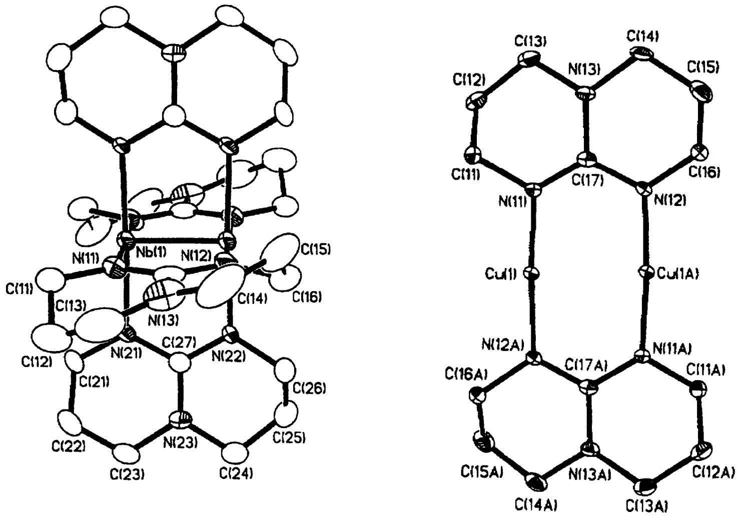


Fig. 26. The molecular structure of $[Mo_2(hpp)_4][BF_4]_2$ (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimidino[1,(2–)a]pyrimidinate). Reproduced from Ref. [45] with permission of The Royal Society of Chemistry.



(a) (b)

Fig. 27. The molecular structures of $[Nb_2(hpp)_4]$ (a) and $[Cu_2(hpp)_2]$ (b) (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimidino[1,(2–)a]pyrimidinate). Reproduced from Refs. [46,47] with permission of The American Chemical Society.

crystallographically symmetrical coordinate bonds [Nb(1)–N(11) 2.201(4) Å, Nb(1a)–N(12) 2.198(4) Å]. The guanidinate ligand has a planar CN_3 core [angles at C(17) total 360°], while the coordinated nitrogens have shorter bonds to the central carbon [C(17)–N(11) 1.347(7) Å, C(17)–N(12) 1.332(7) Å] indicating partial double bond character of these bonds. Of added interest is the Nb–Nb triple bond in this complex is very short, indeed it is considerably shorter than the Nb–Nb distance in the metal itself (2.85 Å). The most recent paper from this research group outlined the formation of a copper(I) dimer containing a very short non-bonded contact [47]. The reaction of CuCl with Li[hpp] in THF at −78°C yielded a white precipitate from which colourless crystal were readily obtained. X-ray structural analysis of these revealed that the Cu(I) centres are bridged by two monoanionic hpp ligands (Fig. 27(b)). The ligands are symmetrically coordinated [Cu(1)–N(11) 1.862 Å, Cu(1)–N(12a) 1.863 Å] while the Cu–Cu separation of 2.4527(10) is somewhat shorter than previously observed for complexes of this type. For the guanidinate ligands themselves, the central CN_3 unit is planar while there is some variation of the bonds within this unit [C(17)–N(11) 1.339(5) Å, C(17)–N(12) 1.346(5) Å, C(17)–N(13) 1.371(5) Å] indicating partial double bond character within the guanidinate ligand. DFT calculations indicate that there is no bonding interaction between the two copper centres. The close contact between the two metals was thought to be due to a combination of strong Cu–N bonding and very short bite distances for the ligands.

A rare example of a complex which contains both monoanionic and dianionic guanidinate ligands was formed in the reaction of 1,2,3-triisopropylguanidine with antimony tris(dimethylamide) [$Sb(NMe_2)_3$] [48]. The isolated product [$Sb\{\eta^2\text{-}(Pr^iN)_2CNHPr^i\}\{\eta^2\text{-}(Pr^iN)_2CNPr^i\}$] contains two chelating guanidinate ligands which, although crystallographically indistinguishable, must formally be mono- and dianionic in order to balance the +3 charge of the antimony. The X-ray crystal structure shows that the coordination geometry of the SbN_4 unit is best described as a heavily distorted trigonal bipyramid, the fifth coordination site being occupied by the antimony lone pair in an equatorial position (Fig. 28). A two-fold rotational axis relates the guanidinate ligands which were found to coordinate the Sb centre asymmetrically [Sb–N(11) 2.227(6) Å, Sb–N(13) 2.069(6) Å]. This difference in the bond lengths is consistent with the trigonal bipyramid description of the geometry as these nitrogens occupy axial and equatorial sites, respectively. The large distortion in bond angles from an ideal trigonal bipyramid can be attributed to the rigidity of the guanidinate ligands and the geometric constraints that they impose. The chelating angle [N(11)–Sb–N(13) 62.0(2)°] is dramatically reduced from the ideal of 90° and as a result the N–Sb–N angle between the axial nitrogens is distorted from 180° [N(11)–Sb–N(11a) 140.3(3)°] and similarly for the equatorial centres [N(13)–Sb–N(13a) 104.5(3)°] from 120°, although the presence of the Sb lone pair in this equatorial plane might also be anticipated to lead to some reduction in this angle. In the crystal structure the ligands cannot be distinguished as the uncoordinated NPr^i groups (one of which has a residual hydrogen bound to it) are involved in hydrogen bonding to an adjacent molecule with a N···N distance of 3.184(12) Å and N–H···N angle of 160°. As a result of the distorted nature of the

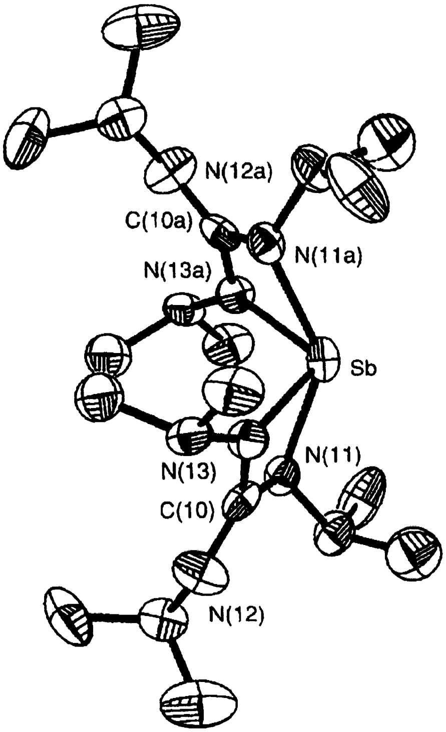


Fig. 28. The molecular structure of [Sb{η^2-($Pr^iN)_2CNHPr^i$}{η^2-($Pr^iN)_2CNPr^i$}]. Reproduced from Ref. [48] with permission of The Royal Society of Chemistry.

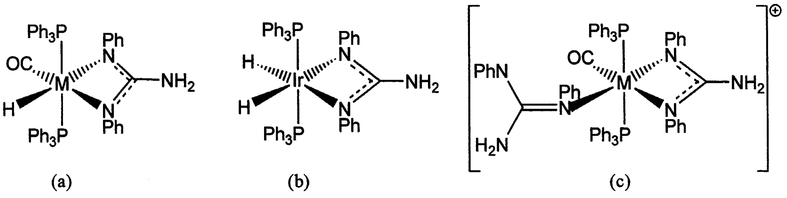


Fig. 29.

individual molecules, the molecular chains formed by these bonds form left-handed helices in the crystal studied with three molecules per 360° turn. This helical hydrogen-bonded network is unprecedented for any metallo-organic complex.

1,2-dipenylguanidine was found to react with the transition metal hydrides [$MH_2(CO)(PPh_3)_3$] (M = Ru, Os) yielding complexes containing chelating guanidinate(1–) ligands [49]. The products of these reactions, [MH{η^2-$(NPh)_2CNH_2$}(CO)$(PPh_3)_2$], characterised by IR and NMR spectroscopy, were found to contain mutually *trans*-phosphine ligands with the guanidinate ligand coordinated symmetrically to the metal centre (Fig. 29(a)). In an analogous reaction

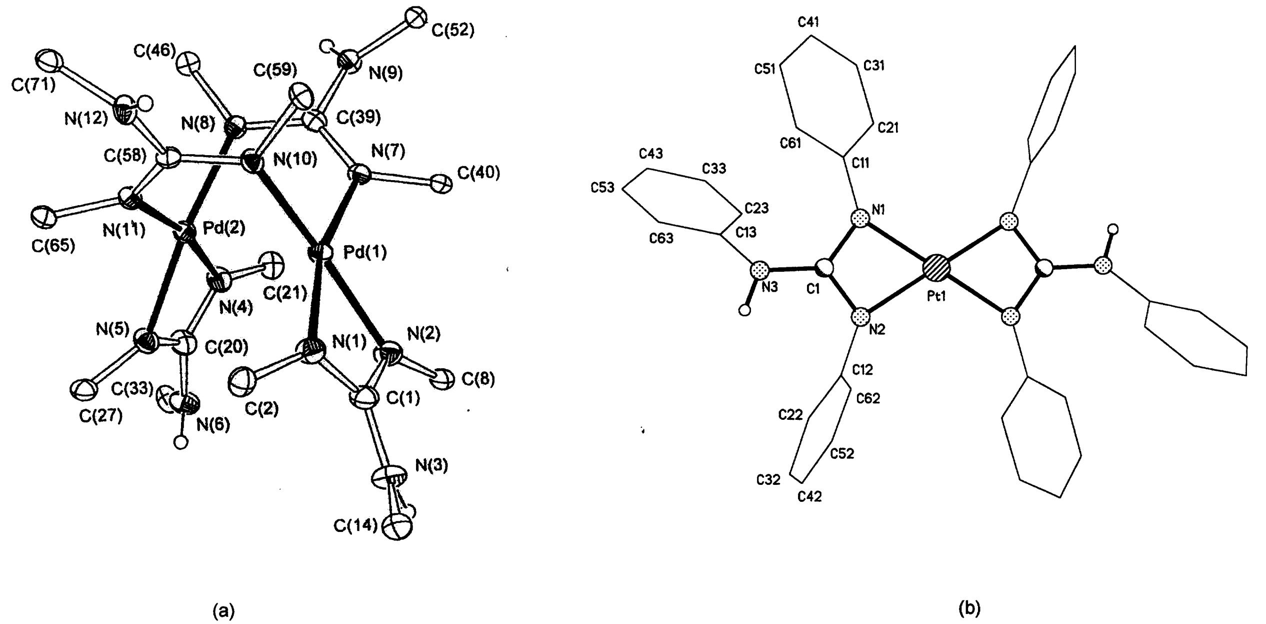


Fig. 30. The molecular structures of [Pd{η^2-(PhN)$_2$CNHPh}{μ-η^2-(PhN)$_2$CNHPh}]$_2$ (a) and [Pt{η^2-(PhN)$_2$CNHPh}$_2$] (b). Reproduced from Refs. [50,33] with permission of The Royal Society of Chemistry.

$[IrH_2\{\eta^2\text{-}PhNC(NH_2)NPh\}(PPh_3)_2]$ was obtained from $[IrH_3(PPh_3)_3]$ and *N*,*N*′-diphenylguanidine (Fig. 29(b)). Also reported was the formation of complexes containing both monoanionic and neutral guanidines in which the guanidinate(1–) ligand chelates the metal and the neutral guanidine acts as a monodentate ligand (Fig. 29(c)). These were synthesised in the reaction of the trifluoroacetate complexes $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$ (M = Ru, Os) with *N*,*N*′-diphenylguanidine. The tentative formulation of these complexes as the salts $[M\{\eta^2\text{-}PhNC(NH_2)NPh\}\{\eta^1\text{-}PhNC(NH_2)NHPh\}(CO)(PPh_3)_2][O_2CCF_3]$ was consistent with elemental analysis and spectroscopic data. However, in a subsequent report [50], an X-ray structure determination of the corresponding ruthenium product formed with 1,2,3-triphenylguanidine showed the structure to be $[Ru(CO)PPh_3\{\eta^2\text{-}(PhN)_2CNHPh\}_2]$ containing two chelating guanidinate(1–) ligands. Also in this paper the treatment of palladium(II)acetate with 1,2,3-triphenylguanidine was shown to provide the dimer $[Pd\{\eta^2\text{-}(PhN)_2CNHPh\}\{\mu\text{-}\eta^2\text{-}(PhN)_2CNHPh\}]_2$ containing both bridging and chelating guanidinate(1–) ligands (Fig. 30(a)). The structure of this product contrasts with the platinum analogue with the same empirical formula, obtained from the treatment of $[PtCl_2(NCPh)_2]$ with $Li[(PhN)_2CNHPh]$, which adopts the $[Pt\{\eta^2\text{-}(PhN)_2CNHPh\}_2]$ bis-chelating square planar structure (Fig. 30(b)) [33].

The only example of a tris-chelate guanidinate(1–) complex currently in the literature is the Ru(III) species $[Ru\{\eta^2\text{-}(PhN)_2CNHPh\}_3]$ (Fig. 31) [33]. This complex is formed in a mechanistically obscure reaction on treatment of $[(\eta\text{-}C_6H_6)RuCl_2]_2$ with a large excess of 1,2,3-triphenylguanidine. The reaction involves

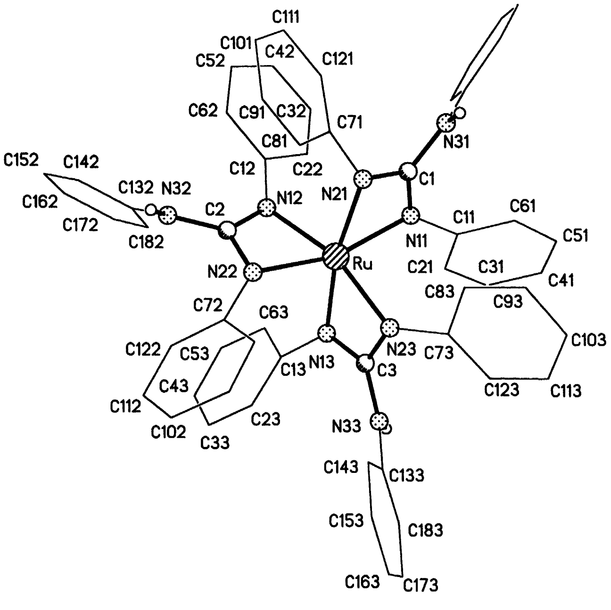


Fig. 31. The molecular structure of $[Ru\{\eta^2\text{-}(Pr^iN)_2CNHPr^i\}_3]$. Reproduced from Ref. [33] with permission of The Royal Society of Chemistry.

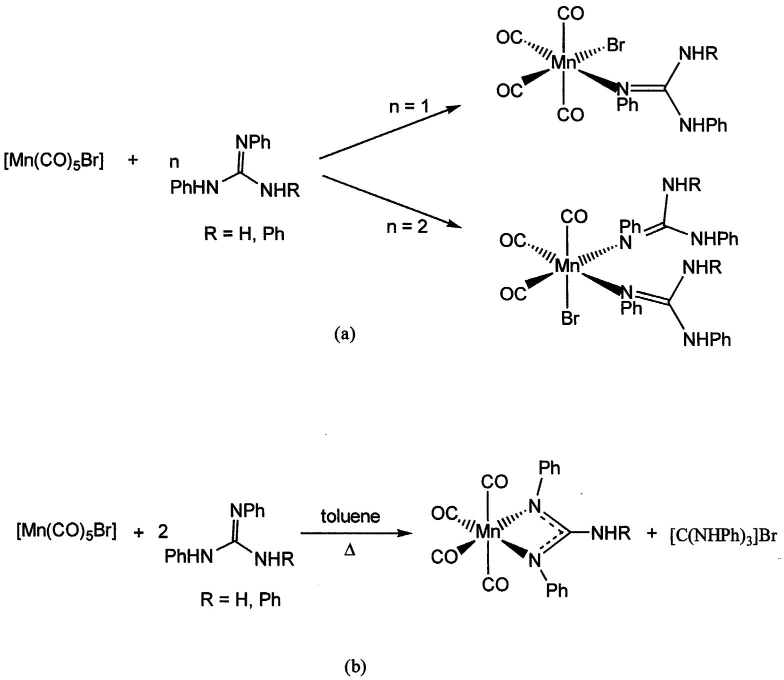


Fig. 32.

displacement of the aromatic ligand and oxidation of the ruthenium. The other surprising feature of this reaction is that it produces this product at all since the corresponding reaction with $[(\eta\text{-}p\text{-cymene})RuCl_2]_2$ had been previously shown to produce the more understandable product $[[(\eta\text{-}p\text{-cymene})Ru\{\eta^2\text{-}(PhN)_2\text{-}CNHPh\}Cl]$ [42]. The difference between these two reactions was rationalised by the slightly weaker donor of the benzene being more readily displaced, and the presence of the three guanidinate(1–) ligands favouring stabilisation of Ru(III) over Ru(II).

In a recent article a number of reactions of 1,(2–)di- and 1,2,3-triphenylguanidine with $[Mn(CO)_5Br]$ and $[CpMo(CO)_3Cl]$ are described [51]. In the reaction with $[Mn(CO)_5Br]$, guanidines acted as neutral monodentate imine donors (as described in Section 2) substituting one or two carbonyl groups (Fig. 32(a)). The stereochemistry of these complexes was assigned from the CO bands in their IR spectra. Reaction of two equivalents of a guanidine with $[Mn(CO)_5Br]$ in toluene provided a white precipitate (guanidinium bromide) leaving the mononuclear guanidinate(1–) complex $[Mn\{\eta^2\text{-}(NPh)_2CNHR\}(CO)_4]$ (R = H, Ph) in solution (Fig. 32(b)). In this case the guanidine acts as a Brönsted base in a similar manner as described in the formation of the rhodium and ruthenium chelate complexes previously. This product was also obtained in the reaction of $[Mn(CO)_5Br]$ with monolithiated triphenylguanidine in THF. The ability of guanidine to act as a base and a halide abstractor was also observed in the reaction between $[CpMo(CO)_3Cl]$ and 1,(2–)di-or 1,2,3-triphenylguanidine. Displacement of a carbonyl group by the guanidine, followed by elimination of HCl (which is removed by the second guanidine to form guanidinium chloride) results in the complex $[\mathrm{CpMo}\{\eta^2\text{-}(\mathrm{NPh})_2\mathrm{CNHR}\}(\mathrm{CO})_2]$ (R = H, Ph), the structure of which was determined by X-ray diffraction (Fig. 33). Both complexes have very similar structures, the presence of the additional phenyl group having only a limited effect on the complex as a whole. In the diphenylguanidinate complex the ligand chelates the Mo centre symmetrically [Mo–N(1) 2.187(3) Å] and with the triphenyl ligand the Mo–N distances are crystallographically equivalent [Mo–N(1) 2.172(4) Å, Mo–N(2) 2.191(4) Å]. In both complexes the central CN_3 units of the guanidinates are planar and the bond lengths in the chelating NCN moiety are all similar [range 1.327(6)–1.336(6) Å]. One difference the introduction of the phenyl ring makes is to lengthen the bond between the uncoordinated nitrogen and the central carbon [from 1.357(6) Å to 1.387(6) Å]. This is due to the bulky phenyl group causing a twist around the C–N bond which disrupts the π-delocalisation in the guanidinate ligand. Hydrogen bonds form in the solid state between NH groups on the uncoordinated nitrogen and the chelating nitrogens (diphenyl ligand) or the carbonyl oxygen (triphenyl ligand).

The insertion reactions of carbodiimides into the M–N bonds of metal amides, followed by migration of the amide from the metal to the central carbon of the carbodiimide to form chelating guanidinate anions have been reported recently by Chang and co-workers. In the first of these reports the reaction of bis(diisopropylamido)magnesium with one and two molar equivalents of 1,3-diisopropylcarbodiimide was described [52]. The product of the equimolar reaction was characterised spectroscopically and found to be the unsolvated dinuclear complex $[\mathrm{Mg}_2(\mu\text{-}\mathrm{NPr}^i_2)_2\{\eta^2\text{-}(\mathrm{Pr}^i\mathrm{N})_2\mathrm{CNPr}^i_2\}_2]$ which contains 1,1,2,3-tetraisopropylguanidinate lig-

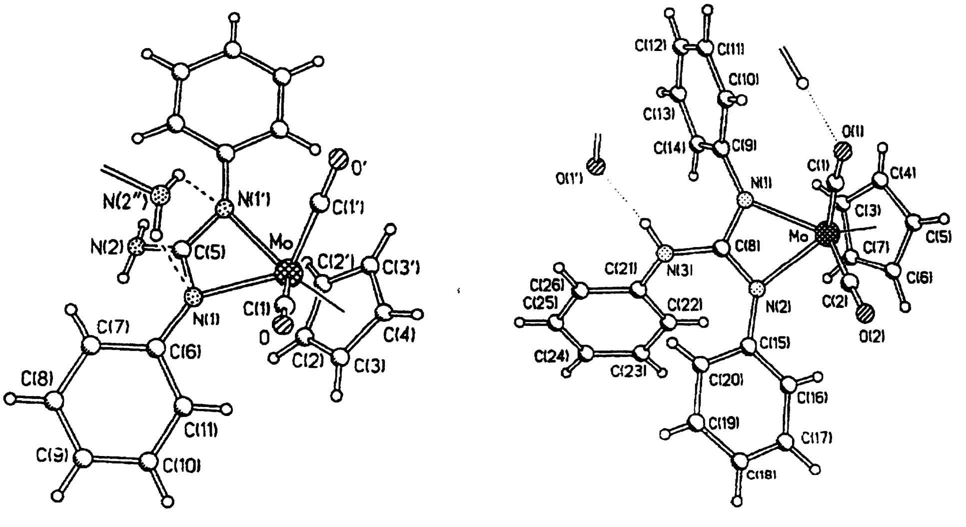


Fig. 33. The molecular structures of $[\mathrm{CpMo}\{(\mathrm{NPh})_2\mathrm{CNHR}\}(\mathrm{CO})_2]$ [R = H (a), Ph (b)]. Reproduced from Ref. [51] with permission of The Royal Society of Chemistry.

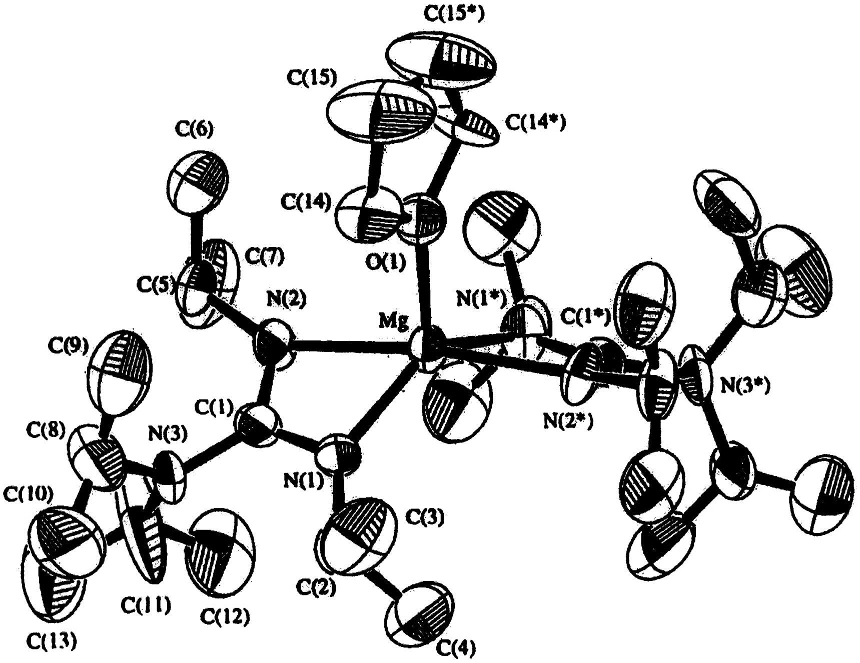


Fig. 34. The molecular structure of [Mg{η^2-($Pr^iN)_2CNPr^i_2\}_2$(THF)]. Reproduced from Ref. [52] with permission of The Royal Society of Chemistry.

ands. The 2:1 (carbodiimide to metal) reaction yielded the solvated monomer [Mg{η^2-($Pr^iN)_2CNPr^i_2\}_2$(THF)], the structure of which was determined by X-ray crystallography (Fig. 34). The complex is square-pyramidal at Mg with the chelating tetraisopropylguanidinate ligands forming the basal plane and THF in the axial position. A crystallographic C_2 axis exists through the Mg–O bond making the guanidinate ligands equivalent. The metal–ligand bonds [Mg–N(1) 2.066(7) Å, Mg–N(2) 2.183(6) Å] are typical for σ-bonding distances. Examination of the C–N bond lengths within the CN_3 core of the guanidinate [C(1)–N(1) 1.364(10) Å, C(1)–N(2) 1.306(9) Å, C(1)–N(3) 1.431(9) Å] indicates some delocalisation across the N(1)–C(1)–N(2) skeleton. However, with the much longer distance to the non-ligating nitrogen a more localised picture of bonding would appear appropriate.

The reactions of the amidoaluminium complexes AlX_2Y ($X = Cl$, R; $Y = NR'_2$) with 1,3-diisopropyl- and 1,3-di-*tert*-butylcarbodiimides were also reported by this group [53]. Pyrolysis of 1,3-diisopropylcarbodiimide with (diisopropylamido)aluminium chloride at 150°C in a sealed tube under vacuum yielded colourless crystals of the compound [Cl_2Al\{η^2-(NPr^i_2)$CNPr^i_2$\}], the structure of which was determined by X-ray crystallography (Fig. 35). The structure confirms the migration of the diisopropylamido ligand to the central carbodiimide carbon, producing the monoanionic tetraisopropylguanidinate ligand. In the complex the distorted tetrahedral coordination geometry of the aluminium comprises the bidentate guanidinate ligand and two chlorides. The guanidinate ligand is symmetrically bound to the metal centre [Al–N(1) and Al–N(2) 1.868(4) Å] as are the two chlorides [Al–Cl(1) 2.113(2) Å and Al–Cl(2) 2.117(2) Å]. In this complex the three C–N bond lengths in the guanidinate moiety are similar [C(1)–N(1) and C(1)–N(2) 1.355(5) Å, C(1)–N(3) 1.366(5) Å] and are shorter than single bonds indicating partial double bond character for these bonds and charge delocalisation within this system. Analogous reactions with diethylamidoaluminium chloride, dialkylamidoaluminium and 1,3-di-*tert*-butylcarbodiimide were also reported and these were all characterised spectroscopically.

Alternative routes to dichloro and dialkyl aluminium guanidinate(1–) complexes have also been reported [54]. The reaction of the aluminium complexes [AlX_2Cl, X = Cl. Me] with lithiated guanidines (formed in situ by the reaction of 1,3-diisopropylcarbodiimide with lithium amides) resulted in the formation of tetrasubstituted chelating guanidinate(1–) ligand complexes. Specifically, reaction of 1,3-diisopropylcarbodiimide with lithium dimethylamide [$LiNMe_2$] provided the monolithiated 1,1-dimethyl-2,3-diisopropyl-guanidinate species. A crystalline product was isolated from the reaction of this species with $AlCl_3$ and the X-ray crystal structure determined (Fig. 36(a)). The complex [$Al\{\eta^2\text{-}(NPr^i)_2CNMe_2\}Cl_2$] which exhibits distorted tetrahedral geometry has the aluminium ligated by two

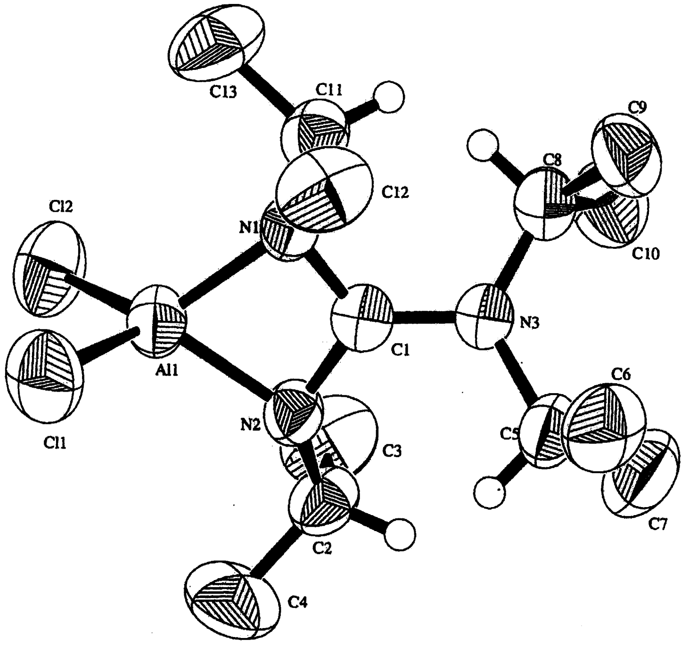
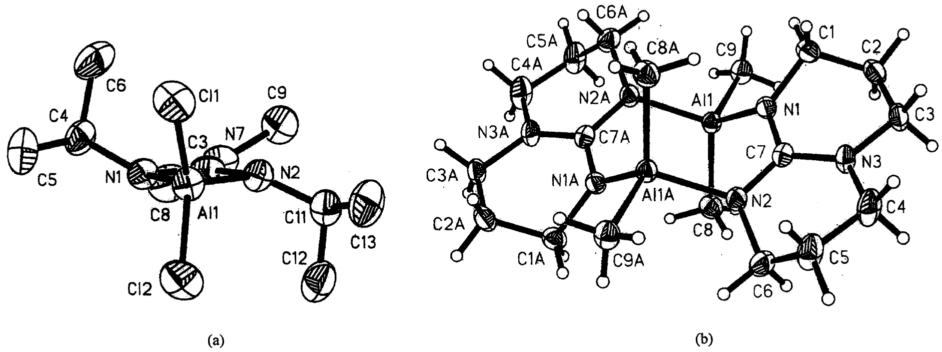


Fig. 35. The molecular structure of [$AlCl_2\{\eta^2\text{-}(Pr^i\}N)_2CNPr^i_2$]. Reproduced from Ref. [53] with permission of The American Chemical Society.



(a) (b)

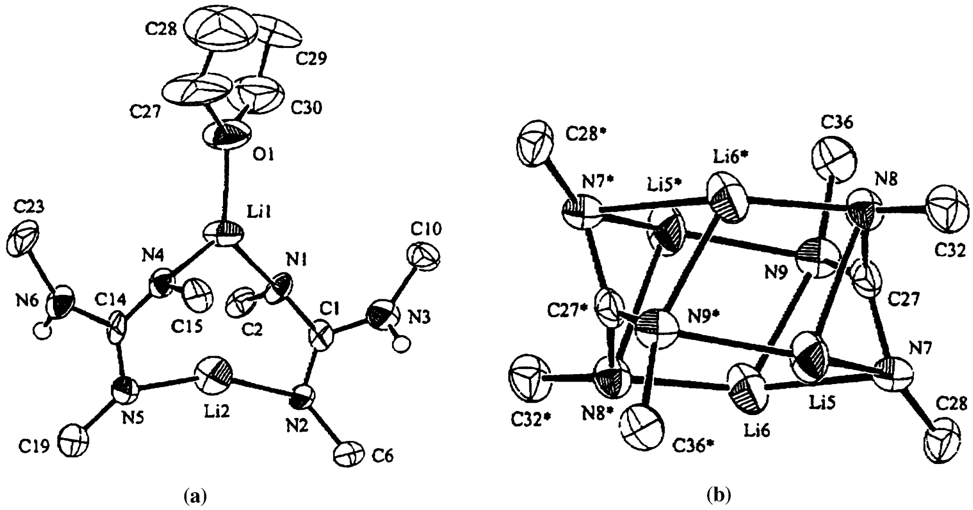
Fig. 36. The molecular structures of $[AlCl_2\{\eta^2\text{-}(Pr^iN)_2CNMe_2]$ (a) and $[AlMe_2(\mu\text{-}\eta^2\text{-hpp})]_2$ (b) (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimidino[1,(2–)a]pyrimidinate). Reproduced from Ref. [54] with permission of The American Chemical Society.

chlorides and a chelating guanidinate(1–), similar to the structures reported by Chang et al. (see above). The guanidinate is symmetrically bound [Al–N(1) 1.873(4) Å, Al–N(2) 1.870(4) Å] and the four membered Al–N–C–N chelate rings are essentially planar. The C–N bonds of the guanidinate ligand are intermediate in length between single and double bonds [C(3)–N(1) 1.356(6) Å, C(3)–N(2) 1.360(5) Å, C(3)–N(3) 1.343(5) Å] indicating that the negative charge is delocalised over the ligand. The reaction of $AlMe_3$ with Hhpp was also reported in this paper. Methane was evolved during the reaction and the product was crystallised from THF. An X-ray crystal structure determination confirmed the product to be $[(\mu\text{-}\eta^2\text{-hpp})AlMe_2]_2$, a dimer in which the hpp ligands link the two $AlMe_2$ units forming an eight-membered ring with a chair conformation (Fig. 36(b)). The geometry at the aluminium centres is tetrahedral with an average Al–N distance of 1.918 Å. The CN_3 core of the hpp^- ligand is planar with intermediate C–N distances [C(7)–N(1) 1.348(3) Å, C(7)–N(2) 1.346(3) Å, C(7)–N(3) 1.357(3) Å] again indicative of charge delocalisation, although comparison with the previous example is complicated by the bicyclic nature of this ligand.

Chivers and co-workers recently reported the crystal structures of mono- and dilithiated tri-*tert*-butylguanidine [55]. The monolithiate was synthesised in the low temperature reaction between 1,3-di-*tert*-butylcarbodiimide and lithium *tert*-butylamine and crystallised from THF. The X-ray crystal structure was determined and was found to have the composition $[Li(THF)\{\mu\text{-}\eta^2\text{-}(N^tBu)_2C(HN^tBu)\}_2Li]$ which forms an eight-membered $Li_2N_4C_2$ ring in the solid state (Fig. 37a). The two guanidinate monoanions are bridged by the lithium atoms, one of which is solvated by THF. The C–N bond distances of 1.32(1) Å and 1.37(1) Å within the ring suggest a tendency towards single and double bonds and only limited delocalisation of negative charge. The exocyclic C–N bonds [1.39(1) Å] are consistent with a single bond and the presence of a hydrogen on these nitrogens. The CN_3 moieties are planar with the sum of angles around the central carbon totalling 360°. Deprotonation of the monoanion with *n*-BuLi yielded the dilithioguanidinate(2–) which was crystallised from pentane to give the unsolvated $[Li_2\{C(N^tBu)_3\}]_2$. In the X-ray crystal structure this was found to exist as $C_2N_6Li_4$ cages which incorporate two planar guanidinate dianions linked by four three coordinate lithium atoms (Fig. 37(b)). Within the CN_3 core of the guanidinates the C–N bond distances average 1.379(7) Å which is consistent with single bonds. The overall structure of the cage can be viewed as a distorted cyclic ladder or alternatively as a highly distorted hexagonal prism. This is in marked contrast to the structure of the dilithio-1,2,3-triphenylguanidinate(2–) which will be described in Section 4 on dianionic guanidinates.

Unsolvated alkali metal guanidinates(1–) $[M\{CyNC(N(SiMe_3)_2)NCy\}]_n$ ($M = Li$, $n = 2$; $M = Na$, $n = 3$; $M = K$, $n = 2$) have been prepared by treatment of dicyclohexylcarbodiimide with $MN(SiMe_3)_2$ and all three species were characterised by X-ray crystallography (Fig. 38) [56]. The differing sizes of the metal ions result in the adoption of three different structures. In the dimeric lithium complex the two metals are bridged by the two ligands in different coordination modes allowing an orthogonal arrangement of the CN_3 planes of the ligands and the relief of steric clashing of the bulky nitrogen substituents. This contrasts with the structure of the potassium complex, which is also dimeric, in which the larger size of the metal allows the two ligands to adopt a symmetrical arrangement with the CN_3 units coplanar. The intermediate size of sodium results in the formation of a symmetrical trimeric structure in which all of the guanidinates are equivalent.

A number of guanidinate(1–) complexes of early transition metals have appeared recently. In these reports the guanidinate ligands are introduced into the complexes in a variety of ways. Treatment of carbodiimides RN=C=NR ($R = Cy$, Pr^i) with



(a) (b)

Fig. 37. The molecular structures of $[Li(THF)\{\mu\text{-}\eta^2\text{-}(N^tBu)_2C(HN^tBu)\}_2Li]$ (a) and $[Li_2\{C(N^tBu)_3\}]_2$ (b). Reproduced from Ref. [55] with permission of Elsevier.

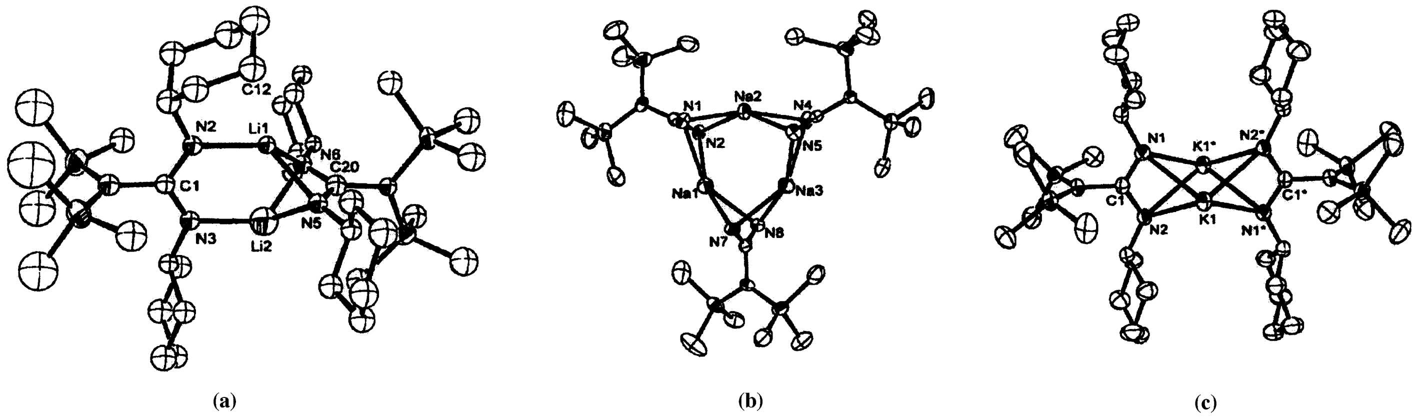


Fig. 38. The molecular structures of [Li{CyNC(N(SiMe$_3$)$_2$)NCy}]$_2$ (a), [Na{CyNC(N(SiMe$_3$)$_2$)NCy}]$_3$ (b) and [K{CyNC(N(SiMe$_3$)$_2$)NCy}]$_2$ (c). Reproduced from Ref. [56] with permission of The Royal Society of Chemistry.

Li[N(SiMe$_3$)$_2$] provides the lithium guanidinates Li[(RN)$_2$CN(SiMe$_3$)$_2$] which provided a number of mono- and bis-guanidinate(1–) complexes of zirconium and hafniuim on treatment with the metal tetrachlorides depending upon the ratio of ligand to MCl$_4$ employed [57]. Four of these complexes were structurally characterised and representative examples are shown in Fig. 39(a,b). Treatment of [Zr{η^2-(NCy)$_2$CN(SiMe$_3$)$_2$}Cl$_4$]$^-$ with three equivalents of PhCH$_2$MgCl provided the tribenzyl complex [Zr{η^2-(NCy)$_2$CN(SiMe$_3$)$_2$}(CH$_2$Ph)$_3$] (Fig. 39(c)). The steric bulk of the donor nitrogen substituents and the SiMe$_3$ groups preclude the uncoordinated nitrogen from adopting a coplanar orientation with the CN$_3$ ligand core, and in each of these structures the Si–N–Si plane is effectively orthogonal to the CN$_3$ plane. The lithiation of 1,1-diethyl-2,3-diphenylguanidine followed by treatment with TiCl$_4$(THF)$_2$ provides the bis-chelate complex [TiCl$_2${η^2-(NPh)$_2$CNEt$_2$}$_2$] (Fig. 40(a)) in which the C–N bond lengths within the CN$_3$ ligand cores of the guanidinate(1–) ligands are crystallographically indistinguishable, thus indicating considerable delocalisation of the uncoordinated nitrogen lone pair into the ligand π-system (Fig. 17, vide supra) [33]. Homleptic Group 5 amido complexes [M(NMe$_2$)$_5$] ($M = Nb$, Ta) provide the guanidinate(1–) complexes [M{η^2-(RN)$_2$CNMe$_2$}(NMe$_2$)$_4$] with carbodiimides RN=C=NR ($R = Cy$, Pr^i) in a reaction in which the guanidinate ligand is assembled within the coordination sphere of the metal [35]. The electronic structure of these complexes was discussed above, a significant feature being that, although the C–N–C plane of the uncoordinated NMe$_2$ group is almost orthogonal to the ligand CN$_3$ plane as was observed for the Group 4 complexes above, the lack of π-conjugating substituents on this nitrogen means that it is distinctly pyramidal, which contrasts with the planarity of the N(SiMe$_3$)$_2$ groups in the complexes above, and this is evident from the X-ray crystal structure of the tantalum complex shown in Fig. 40b. An illustration of a third route to early transition metal guanidinate(1–) complexes involves treatment of [Ta(NMe$_2$)$_4$Cl] with 1,2,3-triisopropylguanidine which provides [Ta{η^2-(Pr^{i}N)$_2$CNNPr^i}(NMe$_2$)$_3$Cl] with elimination of dimethylamine [58]. With the homoleptic dimethylamides [M(NMe$_2$)$_5$] ($M = Nb$, Ta) this route provides access to guanidinate(2–) complexes which are discussed below. Finally, the bis-guanidinate(1–) complex of niobium(IV) [Nb{η^2-(NCy)$_2$CN(SiMe$_3$)$_2$}$_2$Cl$_2$] has been prepared by treatment of [NbCl$_4$(THF)$_2$] with the preformed lithium guanidinate Li[(CyN)$_2$CN(SiMe$_3$)$_2$] and adopts the *trans*-structure [59].

To date there has only been one paper reporting guanidinate complexes of lanthanide metals [60]. The reaction of Li[(NCy)$_2$CN(SiMe$_3$)$_2$}$_2$Cl$_2$] with MCl$_3$ ($M = Sm$, Yb) in THF provides species with the formula [M{η^2-(NCy)$_2$CN(SiMe$_3$)$_2$}$_2$(μ-Cl)$_2$Li(Et$_2$O)$_2$] after crystallisation from Et$_2$O. The remaining chloro-ligands in these complexes may be substituted by reaction with either Li[CH(SiMe$_3$)$_2$] or Li[N(SiMe$_3$)$_2$] and the X-ray crystal structures of the two complexes [Sm{η^2-(NCy)$_2$CN(SiMe$_3$)$_2$}$_2${CH(SiMe$_3$)$_2$}] and [Yb{η^2-(NCy)$_2$CN-(SiMe$_3$)$_2$}$_2${N(SiMe$_3$)$_2$}] are reported (Fig. 41(a,b).

The articles discussed in this section show that monoanionic guanidinates are highly versatile ligands which are able to bind in a variety of coordination modes to alkali, transition, lanthanide and main group metals. Another facet of their

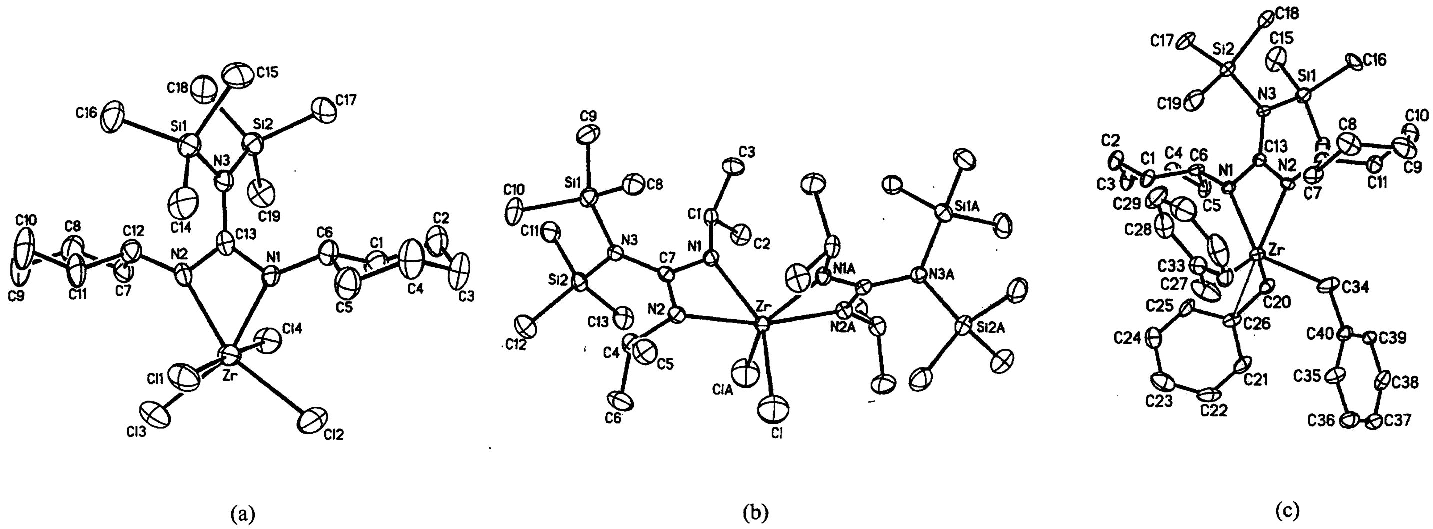
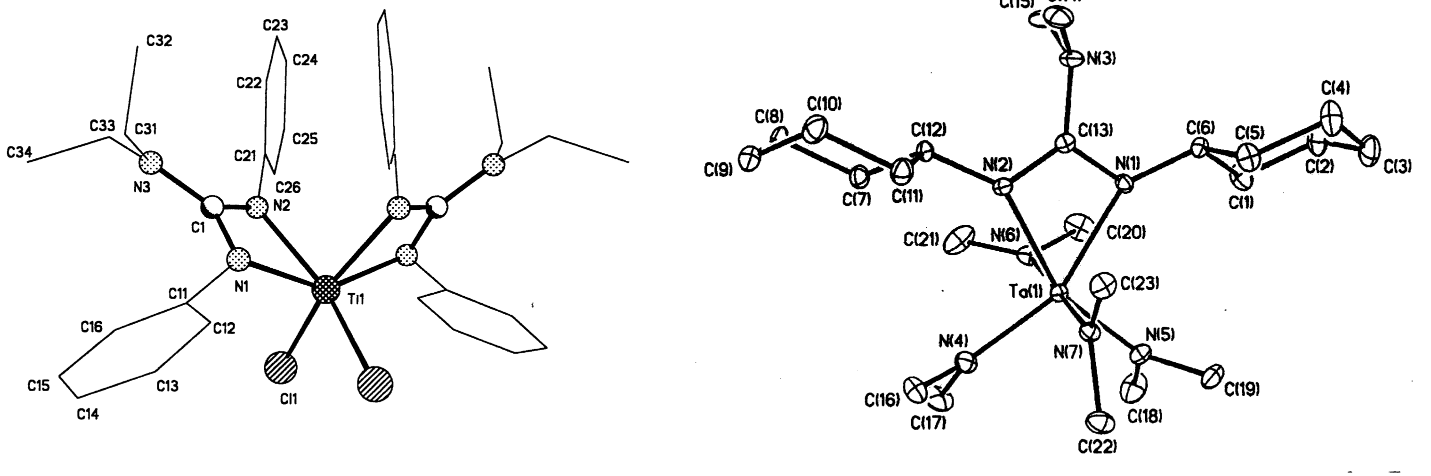


Fig. 39. The structures of $[Zr\{\eta^2\text{-}(NCy)_2CN(SiMe_3)_2\}Cl_4]^-$ (a), $[Zr\{\eta^2\text{-}(NPr^i)_2CN(SiMe_3)_2\}_2Cl_2]$ (b) and $[Zr\{\eta^2\text{-}(NCy)_2CN(SiMe_3)_2\}(CH_2Ph)_3]$ (c). Reproduced from Ref. [57] with permission of The American Chemical Society.



(a) (b)

Fig. 40. The molecular structures of [Ti{η^2-$(NPh)_2CNEt_2\}_2Cl_2$] (a) and [Ta{η^2-$(NCy)_2CNMe_2\}(NMe_2)_4$] (b). Reproduced from Refs. [33,35] with permission of The Royal Society of Chemistry and The American Chemical Society, respectively.

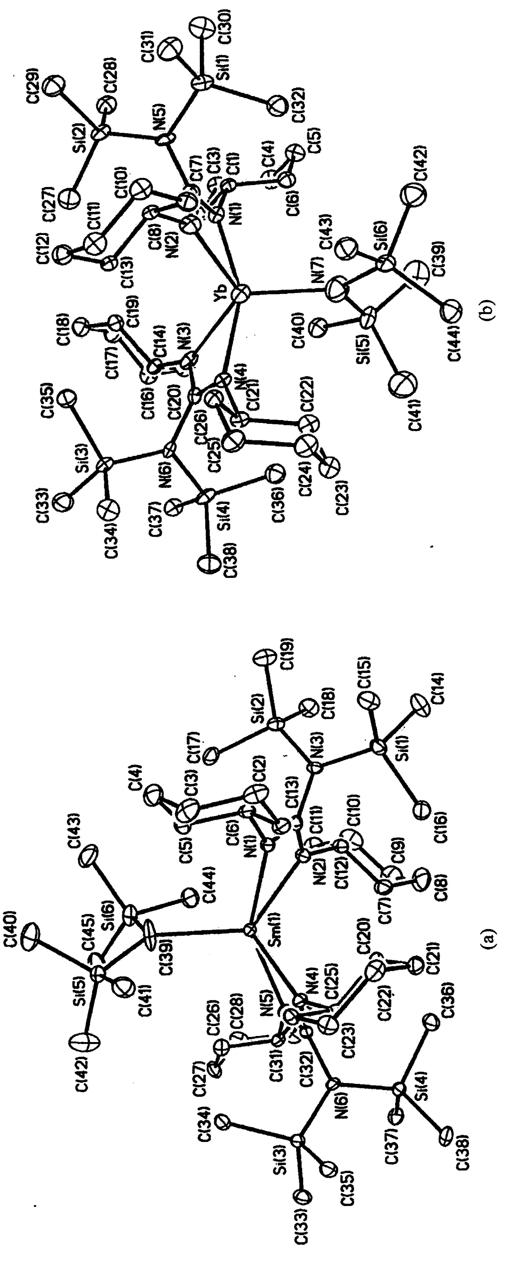


Fig. 41. The molecular structures of [Sm{η^2-$(NCy)_2CN(SiMe_3)_2$}$_2${$C(SiMe_3)_2$}] (a), and [Yb{η^2-$(NCy)_2CN(SiMe_3)_2$}$_2${$N(SiMe_3)_2$}] (b). Reproduced from Ref. [60] with permission of The American Chemical Society.

versatility is the opportunity to vary substituent groups which, while not greatly affecting their coordination mode, will have an effect on the properties of the complexes that form.

4. Dianionic guanidinates [guanidinate(2–) ligands]

There are considerably fewer examples of complexes containing a guanidinate(2–) ligand than for the previously discussed monoanionic or neutral ligands. Indeed, to date, there are only five reports of ligands of this type and in these the guanidinates are found to exhibit a variety of coordination geometries. Of further note is that all the guanidinates described in this section are 1,2,3-trisubstituted.

The first example, published by Farona and co-workers [61], describes the product of the mechanistically obscure reaction between $Fe(CO)_5$ and dialkylcarbodiimides in refluxing heptane. Spectroscopic analysis of the resultant orange crystalline product pointed to the product containing a dianionic guanidinate bound across a $Fe_2(CO)_6$ unit (Fig. 42). This was reported to have been confirmed by an X-ray diffraction study although the data and resulting structure have apparently never been published.

The first crystallographically characterised guanidinate(2–) complex, the THF solvated dimer $[Li_2\{C(NPh)_3\}]_2$ (Fig. 43), was reported by Bailey and co-workers [62]. In this centrosymmetric structure the trisubstituted guanidinate units are bridged by two lithium atoms, each coordinated by three nitrogens and a THF molecule. The two remaining lithium atoms are coordinated to the third nitrogen on each guanidinate, an *ipso*-*ortho* C–C bond of an adjacent phenyl ring and two THF molecules. Within the CN_3 central core the C–N bond lengths show no significant variation (average 1.36 Å) so there is no evidence for a localised double bond. Also, the sum of angles around the central C totals 360°, indicating a strict planarity of the CN_3 core and therefore significant π-delocalisation (Y-conjugation) around this carbon. In agreement with this is the sp^2 hybridisation of the nitrogens (mean C–N–C 121.6°) as would be required for such an electronic distribution.

The reaction of 1,2,3-triphenylguanidine with $[PtCl_2(COD)]$ in dichloromethane, mediated by silver(I) oxide, yielded the first mononuclear guanidinate(2–) complex $[Pt\{\eta^2\text{-}(NPh)_2C{=}NPh\}(COD)]$ [34]. An X-ray crystal structure determination of this complex confirmed that the guanidinate chelates the Pt centre, forming a planar,

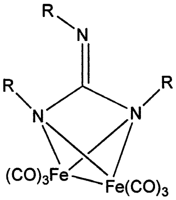


Fig. 42.

four-membered Pt–N–C–N metallacycle (Fig. 44). In contrast to the previous example the C–N bond lengths in the guanidinate unit differ considerably [C(1)–N(1) and C(1)–N(2) are 1.40(1) Å; C(1)–N(3) is 1.30(1) Å] indicating localised double and single bonds. In agreement with the dilithio-dimer is the planarity of the central CN_3 unit, with the angles around the central carbon again totalling 360°. The Pt–N coordinate bonds show a slight difference [Pt–N(1) is 2.034(8) Å and Pt–N(2) is 2.002(7) Å], although this is thought to be as a result of steric interactions between phenyl substituents on N(1) and N(3) and not indicative of a difference in the donor ability of the nitrogens.

An interesting product was obtained in the reaction between dilithio-triphenylguanidine $[\{(PhN)_3C\}Li_2]$ and cadmium bis(trimethylsilylamide) $[Cd\{N(SiMe_3)_2\}_2]$, as described by Bailey and co-workers [63]. The expected product of this reaction would be that of nucleophilic substitution of $\{N(SiMe_3)_2\}$ by $\{(PhN)_3C\}$. This however, does not occur and the isolated product was the co-complex of the two reaction components $[\{(Me_3Si)_2N\}_2Cd\{(PhN)_3C\}Li_2(THF)_3]$ (Fig. 45). The guanidinate unit is bound to the Cd via one nitrogen only [Cd(1)–N(11) 2.213(4) Å] and this nitrogen is also bound to one lithium. The other two nitrogen atoms of the guanidinate are coordinated to two independent THF solvated lithium atoms. There are a number of similarities between this structure and that obtained for the dilithio-1,2,3-triphenylguanidine. The average C–N bond length in the CN_3 core is again 1.36 Å although as a result of coordination to the Cd the C(10)–N(11) bond is slightly lengthened in comparison with the C(10)–N(12) and C(10)–N(13) bonds

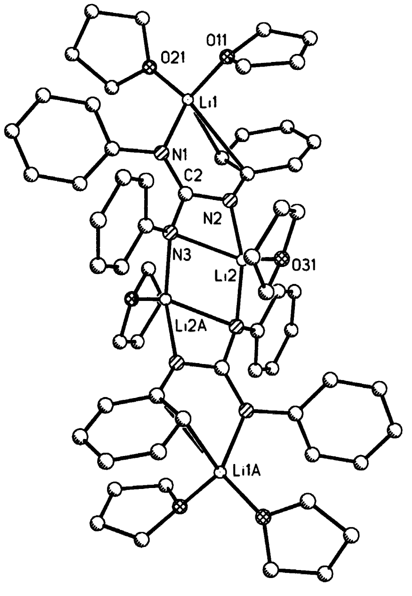


Fig. 43. The molecular structure of $[Li_2\{C(NPh)_3\}]_2$. Reproduced from Ref. [62] with permission of The Royal Society of Chemistry.

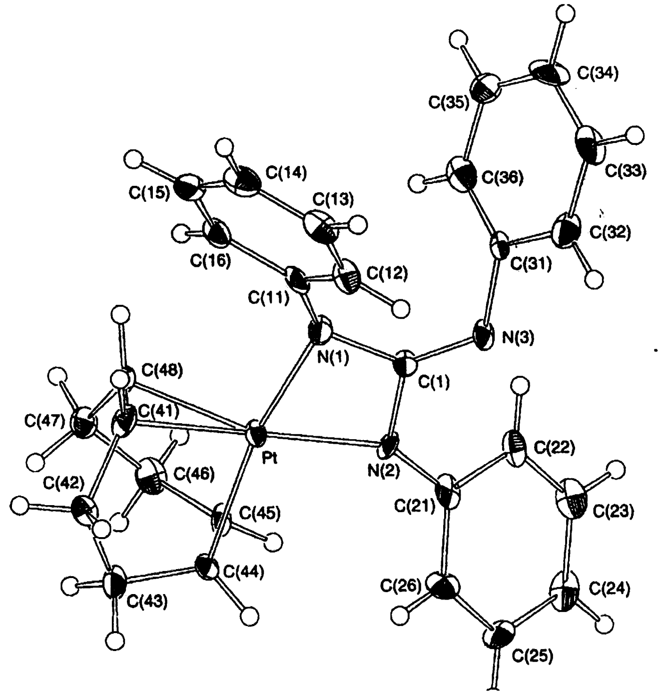


Fig. 44. The molecular structure of [Pt(COD){η^2-$(NPh)_2CNPh$}]. Reproduced from Ref. [34] with permission of The Royal Society of Chemistry.

[1.376(7) versus 1.350(7) and 1.358(7) Å, respectively]. The sum of angles around the central carbon of the CN_3 core again totals 360° indicating some delocalisation in the guanidinate moiety. The fact that the adduct is stable to [Li{$N(SiMe_3)_2$}] elimination may also give an indication of the extensive resonance stabilisation exhibited by the guanidinate(2–) ligand upon the adduct as a whole. A final similarity between the two structures is in the arrangement of the substituent phenyl groups which again adopt a *trans*, *trans*, *cis* conformation about the central carbon. This can be rationalised by the fact that in this arrangement the nitrogen lone pairs can point towards the Li^+ cations.

The reactivity of [{$(PhN)_3C$}Li_2] with transition metals has also been investigated. Treatment of this system with [Cp^*ZrCl_3] in THF followed by crystallisation from Et_2O provided the zwitterionic species [Cp^*Zr{$C(NPh_3)$}$Cl_2Li(Et_2O)(THF)$] [64]. In the presence of an excess of methylaluminoxane this species provides a modestly active ethene polymerisation catalyst. Substitution of one of the chlorides with $LiNPh_2$ provides [Cp^*Zr{$C(NPh_3)$}$(NPh_2)ClLi(THF)_2$] which was characterised crystallographically showing that the guanidinate ligand is chelating. Addition of [{$(PhN)_3C$}Li_2] to [$Cp^*TaMe_2Cl(OSO_3CF_3)$] provided [Cp^*Ta{$C(NPh)_3$}Me_2] in which the guanidinate is again acting in chelating coordination mode.

A report of transition metal complexes containing dianionic guanidinate ions as ligands was recently published by Henderson and co-workers [65]. The paper describes the synthesis of Ru(II), Os(II), Rh(III), Ir(III) and Pt(II) complexes containing chelating guanidinate ligands, formed in the reaction of trisubstituted guanidines (phenyl or acetyl) with metal halides mediated by silver(I) oxide. This procedure was first outlined in an earlier communication in which the structure of $[(COD)Pt\{\eta^2\text{-}(NPh)_2C{=}NPh\}]$ was described [34]. The synthesis and characterisation of this complex and of the novel complexes $[Cp^*M\{\eta^2\text{-}(NAc)_2C{=}NAc\}(PPh_3)]$ (M = Rh, Ir) and $[(p\text{-cymene})M\{\eta^2\text{-}(NAc)_2C{=}NAc\}(PPh_3)]$ (M = Ru, Os) were provided in detail. The X-ray crystal structure of $[(p\text{-cymene})Ru\{\eta^2\text{-}(NAc)_2C{=}NAc\}(PPh_3)]$ was described although due to problems in structure refinement, no discussion of its metrical parameters could be undertaken and the structure served only to confirm that the guanidinate ligand does indeed act as a chelating ligand to the ruthenium centre. Therefore, characterisation of the complexes was achieved by the unambiguous assignment of a series of NMR experiments including NOE, ^1H-^{13}C COSY and long range BIRDTRAP (^1J suppression) ^1H-^{13}C COSY. Electrospray mass spectrometry was also employed very successfully in this study, very strong peaks from parent ions being observed. Interestingly, when the complexes which contained a triphenylphosphine ligand were analysed using acetonitrile solutions, ions of the

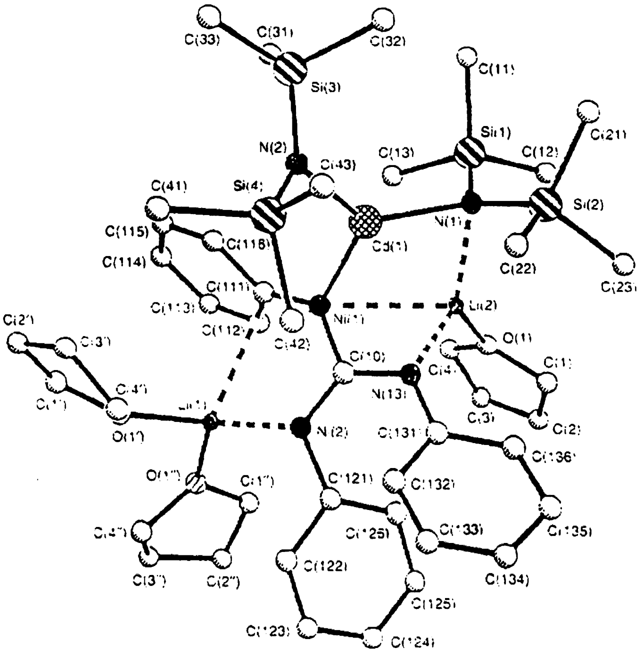


Fig. 45. The molecular structure of $[\{(Me_3Si)_2N\}_2Cd\{(PhN)_3C\}Li_2(THF)_3]$. Reproduced from Ref. [63] with permission of The Royal Society of Chemistry.

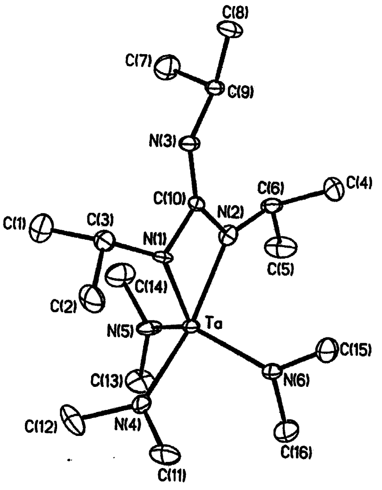


Fig. 46. The molecular structure [Ta{η^2-(NPr^i)$_2$CNPr^i}(NMe$_2$)$_3$]. Reproduced from Ref. [58] with permission of The Royal Society of Chemistry.

type $[M - PPh_3 + MeCN]^+$ were commonly found, the lability of the phosphine ligand being a direct result of steric crowding at the metal centre.

Treatment of the Group 5 homoleptic dimethylamides [M(NMe$_2$)$_5$] (M = Nb, Ta) with 1,2,3-trialkylguanidines RN=C(NHR)$_2$ (R = Cy, Pr^i) provides a further route to guanidinate(2–) complexes. Elimination of two molecules of dimethylamine in these reactions gives the complexes [M{η^2-(NR)$_2$C=NR}(NMe$_2$)$_3$] whose structures were confirmed by X-ray crystallography of a Ta complex (Fig. 46) [58]. A titanium complex [Ti{η^2-(N-*p*-Tolyl)$_2$C=N-*p*-Tolyl}(Me$_4$Taa)] (H$_2$Me$_4$Taa = tetramethyldibenzotetraaza[14]anulene) has been reported, although not structurally characterised, from the reaction of the corresponding imido complex [Ti(N-*p*-Tolyl)(Me$_4$Taa)] with di(*p*-tolyl)carbodiimide [66].

The only other species currently known to contain a guanidinate(2–) ligand is the Sb complex [Sb{(Pr^{i}N)$_2$CNHPr^i}{(Pr^{i}N)$_2$CNPr^i}] which was described in the earlier section dealing with guanidinate(1–) ligands [48], as was the dilithiate of 1,2,3-tri-*tert*-butylguanidine [55].

During early investigations of guanidinate(2–) ligands the isoelectronic relationship between the $[C(NR)_3]^{2-}$ system and the trimethylenemethane (TMM) dianion $[C(CH_2)_3]^{2-}$ was recognised [42,62]. The trimethylenemethane ligand and its substituted derivatives almost always coordinate in a trihapto-coordination mode via all three of the methylene arms [67], and it was anticipated that guanidinate(2–) ligands might also display such a coordination mode. However, there are now sufficient examples of guanidinate(2–) complexes to indicate that a chelating mode of coordination is strongly preferred, and despite specific attempts at the formation of complexes containing η^3-(NR)$_3$C ligands, none has yet been identified. This contrasting behaviour of the TMM and guanidinate(2–) ligands has been rationalised in terms of the relative energies of the in-plane π-orbitals in the two systems [68].

On metal coordination the TMM Y-shaped C_4 framework undergoes a so called 'umbrella' distortion in which the three methylene carbon atoms distort towards the metal atom while the methylene hydrogens distort away from the metal (Fig. 47), and as such the in-plane π-bonding present in the TMM dianion is substantially disrupted, an energy term compensated by the formation of the metal–ligand bond. This distortion may simplistically be viewed as a partial rehybridisation of the methylene carbon atoms from sp^2 to sp^3 such that lone pairs are located on these atoms and directed towards the metal ion. For the guanidinate(2–) system, the greater electronegativity of nitrogen results in a significant lowering in energy of the orbitals involved in in-plane π-bonding and consequently the type of distortion observed in the TMM system on metal coordination is a higher energy process which is insufficiently compensated by the energy released by metal–ligand bond formation. It is interesting to note that there is one example of the η^2-coordination of a TMM ligand, but this is driven by the unavailability of a suitable arrangement of metal orbitals on the zirconocene metal unit involved to allow η^3-coordination (Fig. 48) [69].

To summarise, although as yet there are only a few examples of dianionic guanidinate ligands, a diversity exists in the range of metals to which they have been shown to coordinate (both transition and main group) and also in the mode in which these ligands coordinate. There is also evidence for there being two distinct electronic distributions which the ligand can adopt, either localised or delocalised, which seems dependant upon whether the lone pair on the third nitrogen is involved in coordination to a metal centre.

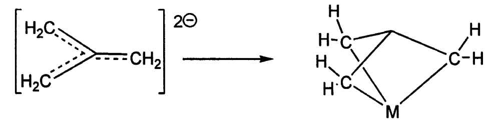


Fig. 47. Distortion of the trimethylenemethane system on coordination in the η^3-coordination mode.

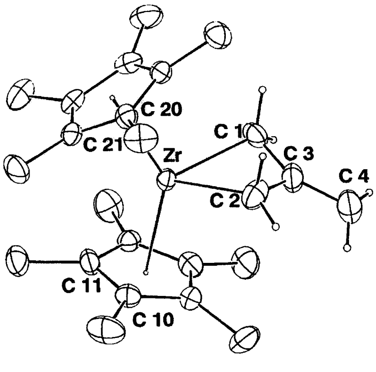


Fig. 48. The molecular structure $[Cp_2Zr\{\eta^2\text{-}(CH_2)_2C{=}CH_2]$ the only example of a chelating trimethylenemethane ligand. Reproduced from Ref. [69] with permission of Wiley–VCH.

References

[1] G.S.H. Nöth, J. Deberitz, Angew. Chem. Int. Ed. Engl. 7 (1968) 293.
[2] A. Gobbi, G. Frenking, J. Am. Chem. Soc. 115 (1993) 2362.
[3] (a) J. Klein, Tetrahedron 39 (1983) 2733. (b) I. Agranat, W.C. Hernden, T.P. Radhakrishnan, A. Skancke, Chem. Phys. Lett. 118 (1991) 117. (c) A. Skancke, J. Chem. Phys. 98 (1994) 5234.
[4] S. Patai, Z. Rappoport, The Chemistry of Amidines and Imidinates, vol. 2, Wiley, New York, 1991 (Chapter 10).
[5] R. Mehrota, Compr. Coord. Chem. 2 (1987) 281.
[6] For example see: (a) C.N. Morimoto, E.C. Lingafelter, Acta Crystallogr. Sect. B 26 (1970) 335. (b) D.M. Halepoto, L.F. Larkworthy, D.C. Povey, G.W. Smith, V. Ramdas Polyhedron 14 (1995) 1453. (c) K. Kopka, R. Mattes, Z. Naturforsch. Teil B 51 (1996) 1675.
[7] For example see: (a) A.S. Batsanov, P. Hubberstey, C.E. Russell, J. Chem. Soc. Dalton Trans. (1994) 3189. (b) M. Fernanda, N.H. Carvalho, A.J.L. Pombeiro, A. Hills, D.L. Hughes, R.L. Richards, J. Organomet. Chem. 469 (1994) 179. (c) M.J. Begley, P. Hubberstey, J. Stroud, J. Chem. Soc. Dalton Trans. (1996) 2323.
[8] M. Mitewa, Coord. Chem. Rev. 140 (1995) 1.
[9] R.S. Drago, R. Longhi, Inorg. Chem. 4 (1965) 11.
[10] R. Snaith, K. Wade, B.K. Wyatt, J. Chem. Soc. (A) (1970) 380.
[11] E.M.A. Ratilla, N.M. Kostic, J. Am. Chem. Soc. 110 (1988) 4427.
[12] E.M.A. Ratilla, B.K. Scott, M.S. Moxness, N.M. Kostic, Inorg. Chem. 29 (1990) 918.
[13] N. de Vries, C.E. Costello, A.G. Jones, A. Davison, Inorg. Chem. 29 (1990) 1348.
[14] W.P. Fehlhammer, R. Metzner, W. Sperber, Chem. Ber. 127 (1994) 829.
[15] A. Luna, B. Amekraz, J.-P. Morizur, J. Tortajada, O. Mó, M. Yáñez, J. Phys. Chem. A 101 (1997) 5931.
[16] W. Schneider, A. Bauer, A. Schier, H. Schmidbaur, Chem. Ber. Recl. 130 (1997) 1417.
[17] P.J. Bailey, K.J. Grant, S. Pace, S. Parsons, L.J. Stewart, J. Chem. Soc. Dalton Trans. (1997) 4263.
[18] O. Angelova, P.J. Bailey, N. Mincheva, M. Mitewa, T. Todorov, J. Coord. Chem. 50 (2000) 169.
[19] L. Coghi, A. Mangia, M. Nardelli, G. Pelizzi, L. Sozzi, J. Chem. Soc. Chem. Commun. (1968) 1475.
[20] P. Hubberstey, C.P. Falshaw, J. Chem. Res. (S) (M) 176 (1982) 1809.
[21] (a) M.J. Begley, P. Hubberstey, P.H. Walton, J. Chem. Soc. Chem. Commun. (1989) 502. (b) M.J. Begley, P. Hubberstey, P.H. Walton, J. Chem. Soc. Dalton Trans. (1995) 957.
[22] M.J. Begley, O. Eisinstein, P. Hubberstey, S. Jackson, C.E. Russell, P.H. Walton, J. Chem. Soc. Dalton Trans. (1994) 1935.
[23] J. Pickardt, B. Kühn, Z. Naturforsch. Teil B 51 (1996) 1701.
[24] K.T. Leffek, A. Jarczewski, Can. J. Chem. 69 (1991) 1238.
[25] B. Brzezinski, A. Jarczewski, M. Stanczyk, G. Zundel, J. Mol. Struct. 297 (1993) 81.
[26] H. Zawadski, M. Penkowski, Pol. J. Chem. 69 (1995) 1409.
[27] M.F.C. Guedes da Silva, C.M.P. Ferreira, E.M.P.R.P. Branco, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, R.A. Michelin, U. Belluco, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo, V.Y. Kukushkin, Inorg. Chim. Acta 265 (1997) 267.
[28] W.O. Lin, C.N. Guimãres, M.C. De Souza, J.B.N. Da Costa, H.G. Aly, Phosphorous Sulfur Silicon 92 (1994) 1.
[29] J. Münchenberg, A.K. Fischer, H. Thönnessen, P.G. Jones, R. Schmutzler, J. Organomet. Chem. 529 (1997) 361.
[30] J. Münchenberg, H. Thönnessen, P.G. Jones, R. Schmutzler, Chem. Ber. Recl. 130 (1997) 1825.
[31] J. Barker, M. Kilner, Coord. Chem. Rev. 133 (1994) 219.
[32] (a) P.J. Bailey, S.F. Bone, L.A. Mitchell, S. Parsons, K.J. Taylor, L.J. Yellowlees, Inorg. Chem. 36 (1997) 867; Erratum, Inorg. Chem. 36 (1997) 5420.
[33] P.J. Bailey, K.J. Grant, L.A. Mitchell, S. Pace, A. Parkin, S. Parsons, J. Chem. Soc. Dalton Trans. (2000) 1887.
[34] M.B. Dinger, W. Henderson, J. Chem. Soc. Chem. Commun. (1996) 211.
[35] M.K.T. Tin, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 38 (1999) 998.

[36] I. Pattison, K. Wade, B.K. Wyatt, J. Chem. Soc. (A) (1968) 837.
[37] W. Clegg, R. Snaith, H.M.M. Shearer, K. Wade, G. Whitehead, J. Chem. Soc. Dalton Trans. (1983) 1309.
[38] D.P. Fairlie, W.G. Jackson, Inorg. Chem. 29 (1990) 140.
[39] T. Jenke, H. Stoeckli-Evans, U. Bodensieck, G. Süss-Fink, J. Organomet. Chem. 401 (1991) 347.
[40] H.-K. Yip, C.-M. Che, Z.-Y. Zhou, T.C.W. Mak, J. Chem. Soc. Chem. Commun. (1992) 1369.
[41] D. Stalke, M.A. Paver, D.S. Wright, Angew. Chem. Int. Ed. Engl. 32 (1993) 428.
[42] P.J. Bailey, L.A. Mitchell, S. Parsons, J. Chem. Soc. Dalton Trans. (1996) 2839.
[43] J.L. Bear, Y. Li, B. Han, K.M. Kadish, Inorg. Chem. 35 (1996) 1395.
[44] F.A. Cotton, D.J. Timmons, Polyhedron 17 (1998) 179.
[45] F.A. Cotton, L.M. Daniels, C.A. Murillo, D.J. Timmons, J. Chem. Soc. Chem. Commun. (1997) 1449.
[46] F.A. Cotton, J.H. Matonic, C.A. Murillo, J. Am. Chem. Soc. 119 (1997) 7889.
[47] F.A. Cotton, X. Feng, D.J. Timmons, Inorg. Chem. 37 (1998) 4066.
[48] P.J. Bailey, R.O. Gould, C.N. Harmer, S. Pace, A. Steiner, D.S. Wright, J. Chem. Soc. Chem. Commun. (1997) 1161.
[49] S.D. Robinson, A. Sahajpal, J. Chem. Soc. Dalton Trans. (1997) 3349.
[50] K.T. Holman, S.D. Robinson, A. Sahajpal, J.W. Steed, J. Chem. Soc. Dalton Trans. (1999) 15.
[51] J.R. da S. Maia, P.A. Gazard, M. Kilner, A.S. Batsanov, J.A.K. Howard, J. Chem. Soc. Dalton Trans. (1997) 4625.
[52] B. Srinivas, C.-C. Chang, C.-H. Chen, M.Y. Chiang, I.-T. Chen, Y. Wang, G.-H. Lee, J. Chem. Soc. Dalton Trans. (1997) 957.
[53] C.-C. Chang, C.-S. Hsiung, H.-S. Su, B. Srinivas, M.Y. Chiang, G.-H. Lee, Y. Wang, Organometallics 17 (1998) 1595.
[54] S.L. Aeilts, M.P. Coles, D.C. Swenson, R.F. Jordan, V.G. Young, Jr., Organometallics 17 (1998) 3265.
[55] T. Chivers, M. Parvez, G. Schatte, J. Organomet. Chem. 550 (1998) 213.
[56] G.R. Giesbrecht, A. Shafir, J. Arnold, J. Chem. Soc. Dalton Trans. (1999) 3601.
[57] M.K.T. Tin, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 38 (1999) 5788.
[58] M.K.T. Tin, N. Thirpathi, G.P.A. Yap, D.S. Richeson, J. Chem. Soc. Dalton Trans. (1999) 2947.
[59] J.M. Decams, G.G. Hubert-Pfalzgraf, V. Vaissermann, Polyhedron 18 (1999) 2885.
[60] Y. Zhou, G.P.A. Yap, D.S. Richeson, Organometallics 17 (1998) 4387.
[61] N.J. Bremer, A.B. Cutcliffe, M.F. Farona, W.G. Kofron, J. Chem. Soc. (A) (1971) 3264.
[62] P.J. Bailey, A.J. Blake, M. Kryszczuk, S. Parsons, D. Reed, J. Chem. Soc. Chem. Commun. (1995) 1647.
[63] P.J. Bailey, L.A. Mitchell, P.R. Raithby, M.-A. Rennie, K. Verhorevoort, D.S. Wright, J. Chem. Soc. Chem. Commun. (1996) 1351.
[64] G. Rodriguez, C.K. Sperry, G.C. Bazan, J. Mol. Catal. (A) 128 (1998) 5.
[65] M.B. Dinger, W. Henderson, B.K. Nicholson, J. Organomet. Chem. 556 (1998) 75.
[66] A.J. Blake, J.M. McInnes, P. Mountford, G.I. Nokonov, D. Swallow, D.J. Watkin, J. Chem. Soc. Dalton Trans. (1999) 379.
[67] M.D. Jones, R.D.W. Kemmitt, Adv. Organometal. Chem. 27 (1987) 279.
[68] P.J. Bailey, K.J. Grant, S. Parsons, Organometallics 17 (1998) 551.
[69] G.E. Herberich, C. Kreuder, U. Englert, Angew. Chem. Int. Ed. Engl. 33 (1994) 2465.