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The coordination chemistry of the amidine ligand

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CONTENTS

ABSTRACT

Amidines, R′NH–C(R)=NR′, as for the isoelectronic carboxylic acids, form a large number of transition metal derivatives, the metals varying from early metals in high oxidation states to the later metals in lower oxidation states. Various bonding modes for the amidino group are involved, and are reviewed with reference to other aza-allyl systems. Much current interest arises from the ability of the ligand to bridge between metals, facilitating metal–metal bonding, and from the use of unsymmetrically substituted amidino groups to produce chiral complexes. Methods of synthesis are reviewed, together with infrared and NMR spectroscopic, mass spectrometric and thermal analysis data. The complexes are

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introduced systematically according to their Period Group, making easy access to information on specific metal complexes. Mixed-metal complexes containing amidino groups bridging between different metals are considered separately. X-ray crystallographic data is collated in a table, thus providing an accessible source for reference purposes. Source material for the review amounts to about 300 references.

1. INTRODUCTION

Though large numbers of processes in the chemical industry involve heterogeneous catalysis, the use of homogeneous catalysis is more limited but expanding. Notable examples of important homogeneous catalytic processes include, inter alia, the Wacker process [1], which involves the palladium-catalysed oxidation of ethene, and the Monsanto process which produces ethanoic acid from methanol via carbonylation involving a rhodium catalyst [2]. Such applications are attributed to the exponential growth in studies of metal–alkene, metal–allyl, and metal–alkyne complexes, etc., which are important in catalytic processes [3], and several reviews in these areas of chemistry have been published [4–14].

The large number of studies has allowed various general types of organometallic reaction, such as ligand cleavage to generate coordinatively unsaturated compounds, migratory insertion, oxidative addition and reductive elimination, etc. to be well documented. This in turn has allowed many catalytic processes to be formulated as a series of stages involving these model reaction types, and has led to their better understanding. The principles which apply to reactions of hydrocarbons also apply to systems containing heteroatoms, although account has to be taken also of any additional coordinating ability of the heteroatoms. Thus the heteroatom ligand systems relating to allenes [15–18], alkynes, alkenes [19–22], allyls [23,294], etc., such as the aza-allyl systems (see Table 1), have attracted much interest, and it is the amidine ligand in particular which is the subject of this review.

Interest in catalytic processes involving small molecules containing heteroatoms, such as nitrogen [40,41], has been directed towards adding value to organo-

TABLE 1

Examples of pseudo-allyl ligands

Group	Name	Ref.
>C–C–C<	Allyl	
–N–N–N–	Triazeno	24–27,50
O–C–O	Carboxylato	28–31
S–C–S	Dithiocarboxylato	32–33
C–N–N–	Hydrazones	34–35
–N–S–N–	Sulphurdiimino	36
>C–N–C<	Aza-allyl	37–39
–N–C–N–	Amidino	293,298

nitrogen chemicals, e.g. the commercial pathway to glutamic acid from acrylonitrile [42,43], and though some of the chemistry associated with the carbon ligand systems is applicable to the isoelectronic heteroatom groups, account has to be taken of the chemistry of the heteroatom. This is illustrated by the allyl group which often bonds to metals using its π-system, whereas pseudo-allyls, such as amidines, prefer to bond through the hetero-atom lone pairs, giving other coordination possibilities.

Though there has been much interest in the variety of bonding possibilities associated with organonitrogen complexes, the amount of data on organonitrogen complexes is limited compared with that of the carbo groups. There is an increasing interest in pursuing the study of important pseudo-allyls such as amidines, the subject of this review. Emphasis here is placed on transition-metal derivatives, main group metal compounds being mentioned only when they impinge on the synthesis of the former.

Amidines (Fig. 1), first synthesised by Gerhardt [44] in 1858 by the reaction of aniline with *N*-phenylbenzimidyl chloride, are named after the acid or amide obtained from it after hydrolysis. Thus, when $R' = H$, the compound is known as a formamidine; $R' = CH_3$, acetamidine; $R' = C_4H_9$, butyramidine; and $R' = C_6H_5$, benzamidine. It should be noted that the chemical literature systematically names amidines as amides of the corresponding imidic acid, e.g. hexanimidamide is the name of the amidine derived from hexanoic acid by replacement of the carboxyl group by $-C(:NH)NH_2$. Thus, acetamidine is named ethanimidamide, and formamidine is named methanimidamide in the synthesis literature.

Amidines act as two-electron donors via the more basic and less sterically crowded imino lone pair, to form simple adducts such as $CoCl_2(AmH)_2$ and $PdCl_2(AmH)_2$, where AmH = amidine, but a more interesting group is formed when the R_4 group is displaced to form the amidino group, $R^2NC(R^1)NR^3$, which is isoelectronic with the ligands in Table 1.

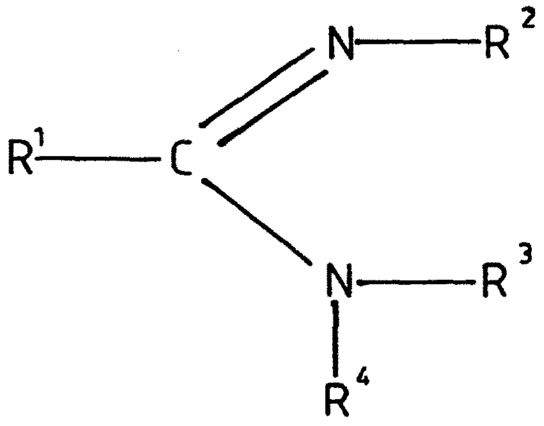


Fig. 1. The general structure of an amidine.

2. METAL–AMIDINE BONDING MODES

The four types of metal-to-allyl group bonding modes (Fig. 2), are described below.

(a) σ-Allyl. σ Bonding occurs between a terminal carbon atom and the metal atom, an uncoordinated localised double bond remaining between the other two carbon atoms, e.g. (σ-CH_2=$CHCH_2$)$Mn(CO)_5$ [45], (σ-CH_2=$CHCH_2$)(C_5H_5)-$Mo(CO)_3$ [46].

(b) μ-Allyl. A bridge occurs between two metal atoms, the allyl group being σ-bonded to the first metal atom through a terminal carbon atom, and to the second metal atom by interaction of the double bond, e.g. (μ-C_3H_5)$_4Mo_2$ [47], and [(μ-C_3H_5)PtCl)]$_4$ [48].

(c) η^3-Allyl. Delocalised bonding occurs between the three carbon atoms forming a multicentre bond with the metal. The three carbon atoms of the allyl group occur in a plane above the metal, all metal-to-carbon distances being approximately equal, and the metal formally receives three electrons from the ligand, e.g. (η^3-C_3H_5)$Fe(CO)_3$ [49].

(d) σ,π-Allyl. The group bonds to the metal using a combination of σ and π interactions, e.g. (η^3-C_4H_7)$PdCl(PPh_3)$ [51]. Here the carbon atoms are in different environments, though interchange between terminal σ- and π-bound carbon atoms often occurs in solution.

Replacement of the two terminal carbon atoms of the allyl group with oxygen atoms gives the carboxylato group, and replacement of all three carbon atoms with isoelectronic nitrogen groups gives the triazeno group. The bonding modes are

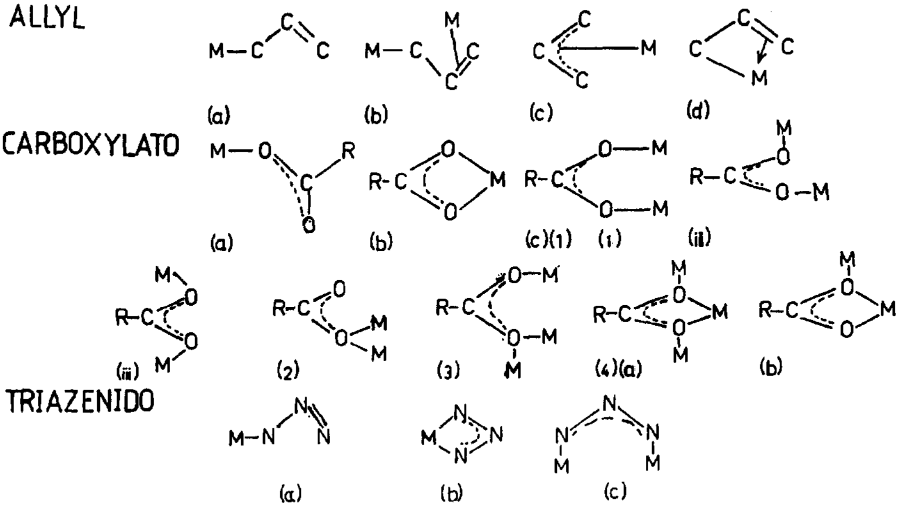


Fig. 2. Allyl and pseudo-allyl bonding modes.

correspondingly modified (Fig.2). The carboxylato group can coordinate as (a) a monodentate ligand, e.g. $Co(O_2CCH_3)_2 \cdot 4H_2O$ [28]; (b) as a chelating ligand, e.g. $(\eta^6\text{-}C_6H_6)Mo(C_3H_5)(O_2CR)$ [52]; (c) as a μ^2-bridging ligand of types (i) *syn–syn*, e.g. $[Pd_3(O_2CCH_3)_6(0.5H_2O)$ [30], (ii) *syn–anti*, e.g. $Cu(O_2CH)_2$ [53], (iii) *anti–anti*, e.g. $Mn(O_2CCH_3)_2(H_2O)_4$ [54]; or bridging through one atom e.g. $[Hg(O_2CCH_3)_2\{(C_6H_{11})_3P)\}]$ [55]. Additional bridging may also occur as for, for example, $Cu(O_2CCH_3)$ [56], and through mixed arrangements involving chelation and bridging, as for $(CH_3)_2Tl(O_2CCH_3)$ [57], and $Cd(O_2CCH_3)_2(H_2O)_2$ [58]. These bonding modes are discussed in detail in several reviews [59–61].

The triazeno group shows (a) monodentate, e.g. $Pt(PPh_3)_2(PhN_3Ph)_2 \cdot C_6H_6$ [62]; (b) chelating, e.g. $C_5H_5Mo(CO)_2(ArN_3Ar)$ [63]; and (c) bridging, e.g. $Ni_2(\mu\text{-}ArN_3Ar)_4$ [64] modes of bonding (Fig. 2). All the bonding modes have been characterised by X-ray crystallography.

For the amidino ligand, many of the possible bonding modes illustrated in Fig. 3 have been established by X-ray crystallography. In the course of this review, we shall discuss amidino complexes, the synthetic methods used to produce them, structural aspects, spectroscopic characteristics, and industrial applications. The bonding modes are.

(a) Monodentate. One nitrogen is σ-bonded to the metal, the other nitrogen, which is double bonded to the central carbon atom, remaining unattached. Two examples have been characterised by X-ray crystallography, $PtC_6H_3(CH_2N\{CH_3\}_2)_2(CH_3C_6H_4NCHNC_6H_4CH_3)$ [65], and $HgC_6H_5(p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p)$ [66].

(b), (c), (d) Chelate complexes. In this bonding mode, the relatively small size of the four-membered M(NCN) ring introduces steric strain and distortion of the

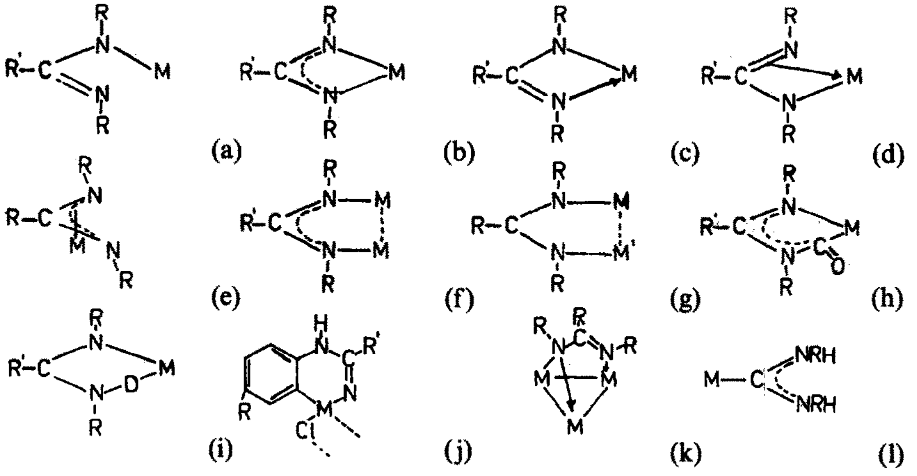


Fig. 3. Possible amidine bonding modes.

valence angles. This class may be sub-divided as follows; (i) σ,σ-symmetrical attachment for which the NCN bonding is delocalised, e.g. $Pt[C_6H_5NC(C_6H_5)NC_6H_5]_2$ [67] characterised by X-ray crystallography; (ii) σ,σ-unsymmetrical attachment, in which both nitrogens bond to the metal, but one nitrogen bonds formally via the imine lone pair of electrons, e.g. $CH_3TaCl_2\{C_6H_{11}NC(CH_3)NC_6H_{11}\}$ [268], characterised by X-ray crystallography; (iii) one nitrogen σ bonds to the metal whilst the localised double bond interacts in an alkene-type manner. No amidine complexes of this type have been characterised.

(e) n^3-Allyl. This type of amidine linkage is not yet known.

(f), (g) Bridging. This usually produces metal–metal bonding and involves formation of a M_2NCN ring. The metal atoms may be the same as in $Mo_2\{PhNC(Ph)NPh\}_4$ [68], or different as in $[2,6\text{-}(CH_3)_2NCH_2)_2C_6H_3]Pt[\mu\text{-}p\text{-}CH_3C_6H_4NC(H)NPr\text{-}i]HgBrCl]$ [70].

(h), (i) Carbamoyl/insertion complexes. Insertion of a carbonyl group into the metal-to-nitrogen amidine bond results in a carbamoyl complex, e.g. $Re(CO)_4[CON(Ph)C(Ph)NPh]$ [71]. Insertion of CH_2, and C_6H_5CN has also been found. In the first case, CH_2 is inserted between the metal-to-nitrogen bond of a chelating amidine, to form the complex $[W_2(\mu\text{-}CO)_2\{\mu\text{-}HC(N\text{-}3,5\text{-}xylyl)_2\}_2\{HC(N\text{-}3,5\text{-}xylyl)_2\}\{(N\text{-}3,5\text{-}xylyl)CHN(3,5\text{-}xylyl)CH_2\}]$ [72]. In the latter case, the treatment of $Pt(PhCN)_2Cl_2$ with $HN(Li)C(C_6H_5)NH$ results in nucleophilic attack at the nitrile to form $Pt\{HNC(C_6H_5)NC(C_6H_5)NH\}_2$ having six-membered rings as established by X-ray crystallography [73,83].

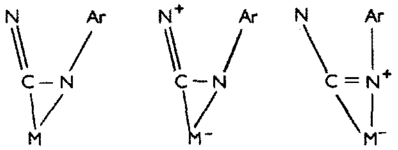
(j) Ortho-metallation. If a nitrogen substituent is an aryl group, ortho-metallation may occur, forming a reasonably stable six-membered metallocycle. A six-membered ring has been established for $(\pi\text{-}C_5H_5)Pd\{CH_3C_6H_3N(H)C(CH_3)$ Ntolyl-$p\}$ [73], but a five-membered ring is indicated for $Re(CO)_3\{PhNC(C_6H_4)NHPh\}\{PhNC(Ph)NHPh\}$ by spectroscopic methods [74].

(k) Cluster-capping. The X-ray structure of $[Os_3(\mu\text{-}H)(CO)_9\{PhNC(Ph)NH\}]$ [75] shows the amidino ligand capping one triangular face of osmium atoms, and formally donating five electrons to the cluster.

(l) Carbene. This mode of bonding is simply included for completeness, since the complexes should be regarded more as carbenes than amidino complexes, e.g. $[(CH_3NC)_4Ru{=}C(NHCH_3)_2][PF_6]$ [76].

(m) Metallo-amidine. A recent extension to these bonding modes has been furnished by Chisholm et al. [209], albeit a rather esoteric combination of amidine and carbene modes that have already been described. The so-called metallo-amidine $Mo(\eta^2\text{-}Me_2NCN\text{-}2,6\text{-}Me_2C_6H_3)_4$ was formed from the reaction of $Mo(NMe_2)_4$ with $2,6\text{-}Me_2C_6H_3NC$. The X-ray crystal structure indicates a bonding mode having a contribution from the resonance forms shown below.

The amidine ligand may also form simple salts, e.g. $[PhC(NH_2)_2]\{cis\text{-}(OC)_4Re(CH_3CO)_2\}$ [77], the structure of which has been established by X-ray crystallography.



3. SYNTHETIC METHODS FOR THE PREPARATION OF AMIDINE–TRANSITION METAL COMPLEXES

For the synthesis and properties of the ligands there are extensive reviews [78–80].

(1) Reaction of a lithiated amidine with a metal halide in situ [67].

$$n\text{-butyl-Li} + [\mathrm{PhN(H)C(Ph)NPh}] \xrightarrow{\mathrm{THF/0^{\circ}C}} [\mathrm{PhN(Li)C(Ph)NPh}]$$

$$2[\mathrm{PhN(Li)C(Ph)NPh}] + \mathrm{Pt(PhCN)_2Cl_2} \xrightarrow{\mathrm{THF}} \mathrm{Pt(PhNC(Ph)NPh)_2} + \mathrm{LiCl}$$

Alternatively, another Group 1 derivative may be used [81].

$$\mathrm{K(ArNC(H)NAr)} + \mathrm{C_5H_5Mo(CO)_3Cl} \rightarrow$$
$$\mathrm{C_5H_5Mo(CO)_2(ArNC(H)NAr)} + \mathrm{KCl} + \mathrm{CO}$$

(2) Reaction of an amidine with a metal halide [82].

$$\mathrm{C_5H_5Mo(CO)_3Cl} + 2[\mathrm{PhN(H)C(CH_3)NPh}] \rightarrow$$
$$\mathrm{C_5H_5Mo(CO)_2(PhNC(CH_3)NPh)} + (\mathrm{PhNHC(CH_3)NHPh})^{+}\mathrm{Cl}^{-}$$

(3) Reaction of amidines with metal carbonyls in air with displacement of carbonyl groups [81].

$$2\mathrm{Mo(CO)_6} + 4[\mathrm{PhN(H)C(Ph)NPh}] \xrightarrow{\mathrm{Air}} \mathrm{Mo_2[PhNC(Ph)NPh]_4} + 12\mathrm{CO}$$

(4) The displacement of silver halides by the reaction of silver amidines with metal halides [81].

$$\mathrm{Ag(PhNC(H)NPh)} + \mathrm{C_5H_5Mo(CO)_3Cl} \rightarrow$$
$$\mathrm{C_5H_5Mo(CO)_2(PhNC(H)NPh)} + \mathrm{AgCl} + \mathrm{CO}$$

(5) The reaction of a carbodiimide with a metal hydride [262].

$$\mathrm{OsH_2(CO)(PPh_3)_3} + \mathrm{Pr^iN{=}C{=}NPr^i} \rightarrow$$
$$\mathrm{OsH(CH_2{=}C(CH_3)NC(H)NCH(CH_3)_2(CO)(PPh_3)_2}$$

(6) Reactions using copper amidines [81].

$$\mathrm{MoC_5H_5(CO)_3Cl + Cu[\mathit{p}\text{-}tolylNC(H)Ntolyl\text{-}\mathit{p}]} \xrightarrow[\text{Room temp., 1 week}]{\text{Benzene}}$$
$$\mathrm{[MoC_5H_5(\mathit{p}\text{-}tolylNC(H)Ntolyl\text{-}\mathit{p})(CO)_2] + CuCl + CO}$$

(7) Reactions of metal amides with nitriles [85].

$$\mathrm{Ti(N(CH_3)_2)_{\mathit{x}} + \mathit{y}CH_3CN \rightarrow Ti(N{:}C(CH_3)N(CH_3)_2)_{\mathit{y}}(N(CH_3)_2)_{\mathit{x}-\mathit{y}}}$$

(8) Reactions of metal alkyls with amidines [178].

$$\mathrm{Zn(Et)_2 + 2(PhNC(Ph)N(H)Ph)} \xrightarrow[\text{THF}]{-196^{\circ}\text{C}} \mathrm{[Zn(PhNC(Ph)NPh)_2]_{\mathit{n}} + 2EtH}$$

4. MASS SPECTROSCOPY

Parent ion and CO loss fragmentation studies have been reported by a number of workers [69,71,74,75,82,90,91,111–114,126,127,160,271,277,286,297], but only three groups, those of Vrieze, Kilner, and Brunner have studied the mass spectra of amidine compounds in any detail.

Vrieze [88] studied the spectra of molybdenum amidines, viz.

$$\begin{tikzcd}
 & & {[H_2NR]^+} \\
{Mo(CO)_5(Am)^+} \arrow[r, "-5CO", "\text{sequential loss}"'] & {MoAm^+} \arrow[ur] \arrow[dr] & \\
 & & {[HNR]^+}
\end{tikzcd}$$

where Am = diarylformamidino.

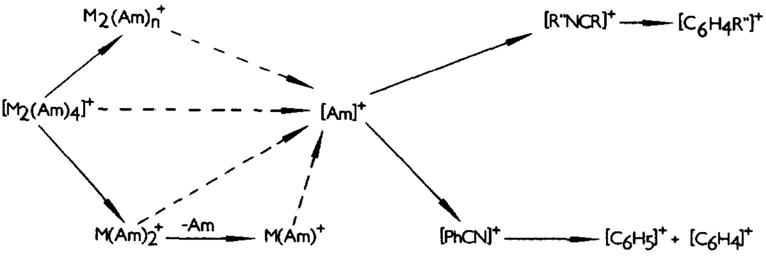
Brunner et al. have also studied the spectra of molybdenum complexes [100,102,106], the ligands being asymmetric N,N'-disubstituted benzamidines, viz.

$$\mathrm{Mo(C_5H_5)(CO)_2\{PhCH(R)N{-}C(Ph){-}NCH(R')Ph\}^+} \xrightarrow{-2\text{CO, sequential loss}}$$
$$\mathrm{Mo(C_5H_5)\{PhCH(R)N{-}C(Ph){-}NCH(R')Ph\}^+}$$

This was followed by ligand breakdown at the metal with fragmentation dependant on the amidine substituents. The carbamoyl [100] complexes were also studied, and exhibited similar characteristics, except for the loss of an extra CO group initially.

Kilner's group has studied a number of systems [73,147]. It was found that $Pd_2(Am)_4$, $Pt(Am)_2$, and $Ni_2(Am)_4$ (Am = N,N'-diarylamidino-) fragmented as described in Scheme 1.

Study of O-metallated $[(Pd\{ArN{-}C(CH_3){-}NAr)Cl]_n$ complexes by Kilner and co-workers [73,148] using FAB mass-spectroscopy showed that the chloride bridges of the dimers were cleaved by the thiodiglycol mulling agent and ions corresponding to those shown in Fig. 4 were observed. The amidine ligands themselves have also been studied [238–244].



Scheme 1.

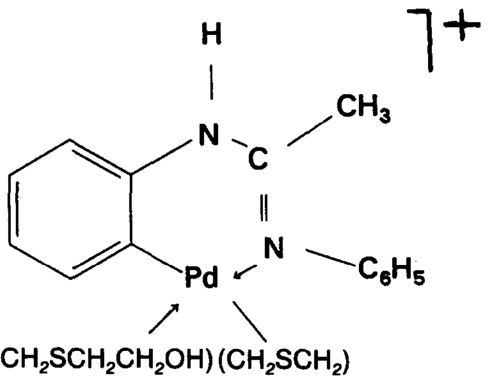


Fig. 4. Proposed structure of the mass spectral ion derived from $[Pd\{_6H_4NHC(CH_3)NC_6H_5\}Cl]_n$ in thioglycol.

5. INFRARED SPECTROSCOPIC DATA FOR CRYSTALLOGRAPHICALLY CHARACTERISED AMIDINE COMPLEXES

Infrared data are presented in most papers concerned with the chemistry of amidino complexes. However, the data associated with complexes that have also been characterised by X-ray crystallography are more revealing (Table 2).

Though the data do not encompass every bonding mode, there are clearly trends which allow use of the data as a diagnostic tool. Vrieze and co-workers [194] have indicated that, for the [*p*-tolylNC(H)Ntolyl-*p*] ligand in the monodentate mode of bonding, the following absorptions are characteristic: 1200, 1310–1320, 1550–1560 and 1610 cm^{-1}. A similar analysis of the spectra of complexes of the same ligand, but in the bridging mode, shows absorptions at 1470–1500, 1545–1570, 1580–1605, and 1610–1620 cm^{-1}. Further, chelating [*p*-$RC_6H_4NC(CH_3)NC_6H_4R$-*p*] ligands show three characteristic bands at 1543–1570, 1621–1624, and 1644–1646 cm^{-1}. A further rationalisation of the above bands has been carried out by Kilner and co-workers [67], and is based on the work of Prevorsek [195] for the free amidine ligands. Bands in the ca. 1640 region may be assigned to ν_{asym}(NCN), and those at ca. 1588 to ν(C=N). Both bands may be designated amidine I bands. Bands around 1390–1520 are designated amidine II-type absorptions, and are described as a com-

TABLE 2

Infrared spectroscopic data for crystallographically characterised amidine complexes

Complex	Structure[a]	Medium[b]	Ref.	Bands[c]
$[C_6H_{11}NC(CH_3)NC_6H_{11}]_2TaCH_3Cl_2$	c,b	Soln.	86	1646w 1624w 1543s 1560s
$[C_3H_7NC(CH_3)NC_3H_7]_2TaCl_3$	b	Soln.	86	1644m 1596wm
$[C_6H_{11}NC(CH_3)NC_6H_{11}]_2TaCl_3$	c,b	Soln.	171	1528ms 1533m 1598s
$[C_3H_7NC(CH_3)NC_3H_7]_2TaCH_3Cl_2$	c	Soln.	86	1649m 1531m 1590w
$Re(PPh_3)_2(CO)_2[C_6H_5NC(H)NC_6H_5]$	b	NJM	112	1520vs 1268vs 1230m
$RuCl(PPh_3)_2(CO)[CH_2{=}C(CH_3)NC(H)NCH(CH_3)_2]$	c	Soln.	262	1550 1250
$PPh_4[Cl_5Os(NC(CCl_3)NCCl(CCl_3)_2CH_2Cl_2)]$	ion	NJM	75	1685s 1616m 1412m
$Pd[CH_3C_6H_4NC(CH_3)NC_6H_4CH_3]_2$	b	NJM HXB	73	1624s 1593ms 1570m
$Pd(C_5H_5)(CH_3C_6H_4N(H)C(CH_3)NC_6H_4CH_3)$	j	KBr	73	1550m 1530msbr
$Pt[C_6H_5NC(C_6H_5)NC_6H_5]_2$	b	NJM HXB	67	1621w 1589s
$Pt[(C_6H_5)_2C_2N_3H_2]_2 \cdot 0.75C_6H_5CH_3$	i	KBr	83	1630m 1582w 1560w 1530s
$Cu_2[C_6H_5NC(C_6H_5)NC_6H_5]_4$	g	KBr	167	1568-1463 and 1263-1231
$Zr(C_5H_5)[C_6H_{11}NC(H)NC_6H_{11}]Cl$	c	NJM	84	1550
$MoCl_4[iC_3H_7NC(H)NC_3H_7\text{-}i]$	b	Soln.	111	1644sm 1459sh 1450m 1381sh 1368s 1355mbr 1312mw
$FeCl_6[HC(NH_2)_2]_3$	salt		126	1713vs 1330m
$Tc(P(CH_3)_2C_6H_5)_2(CO)_2[C_6H_5NC(CH_3)NC_6H_5]$	b	NJM	204	1260
$Rh_2[p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p](O_2CCF_3)_2(H_2O)_2$	b	KBr	210	1570s
$Rh_2(CH_3C_6H_4NC(H)NC_6H_4CH_3]_4$	f	KBr	217	1580vs
$Na[(NH_3)_3Co[\mu\text{-}OH,\mu\text{-}NH_2\mu\text{-}CH_3C(NH)_2]Co(NH_3)_3\text{-}[S_2O_6]_2H_2O]$	f	NJM	221	1630 1580
$Ni_2[CH_3C_6H_4NC(H)NC_6H_4CH_3]_4 \cdot 2H_2O$	f	NJM	213 222	1620s 1590s 1545m 1500s

$Ni_2[CH_3C_6H_4NC(H)NC_6H_4CH_3]_4 \cdot 2BF_4$	f	NJM	213 222	1620s 1590s 1545m
$Pd[CH_3C_6H_4NC(H)C_6H_4CH_3]_2PF_6$	f	NJM	213 222	1580s 1560s 1490m
$Ir_2[CH_3C_6H_4NC(H)NC_6H_4CH_3](NH\text{-}p\text{-}C_6H_4CH_3)(C_8H_{14})_2$	f	NJM	229	1885w 1645w 1605w 1560s 1500s
$Ag_2[CH_3C_6H_4NC(H)NC_6H_4CH_3]_2$	f	NJM	235	1610w 1580s 1550s
$V[CH_3C_6H_4NC(H)NC_6H_4CH_3]_2(C_5H_5N)_2$	b	NJM	230	1570m 1535s 1500s
$V(C_5H_5)[CH_3C_6H_4NC(H)NC_6H_4CH_3]_2$	b	NJM	230	1605w 1540s 1505s 1510s
$Cu_2[CH_3C_6H_4NC(H)NC_6H_4CH_3]_2$	f	NJM	235	1610w 1580s 1550s 1510s
$Rh_2[CH_3C_6H_4NC(H)NC_6H_4CH_3]_3(NO_3)(C_5H_5N)$	f	KBr	245	1580vs
$W(CO)_5[(NH{=}C(C_6H_5))N(CH_3)_2]$	a	NJM	223	1602m
$Mo_2[CH_3C_6H_4NC(H)NC_6H_4CH_3]_4PF_6$	f	NJM	247	1560s 1540s 1520s 1470s
$MoO_2[(CH_3)_3SiNC(C_6H_5)NSi(CH_3)_3]_2$	b	NJM	249	1600m
$TiCl_2[(CH_3)_3SiNC(C_6H_5)NSi(CH_3)_3]_2$	b	NJM	249	1600m
$Mo_2[CH_3C_6H_4NC(H)NC_6H_4CH_3]_4$	f	NJM	247	1550s 1510s 1460s
$\{Ti[C_6H_5C(NSi(CH_3)_3)_2Cl_3]\}_2$	b	NJM	259	1550 1360
$\{Zr[C_6H_5C(NSi(CH_3)_3)_2Cl_3]\}_2$	b	NJM	259	1550 1310
$\{Cu[C_6H_5C(NSi(CH_3)_3)_2]\}$	f	NJM	260	1470 1395
$\{C_6H_5C(NSi(CH_3)_3)_2CuCl[C_6H_5C(NSi(CH_3)_3(NHSi(CH_3)_3]\}$	a	NJM	261	1630 1560
$[FeCl_4][C_6H_5C\{NHSi(CH_3)_3\}_2]_2$	ion	NJM	273	1565
$AuCl_2(C_6H_5C\{NSi(CH_3)_3\}_2$	b	NJM	271	1565
$[Rh_2(CH_3C_6H_4NC(H)C_6H_4CH_3)_2(\mu\text{-}P(C_6H_5)_2C_5H_4N)_2(O_2CCF_3)_2]$	f	KBr	274	1562
$TaC_5(CH_3)_5F_3([NSi(CH_3)_3]_2CC_6H_4OCH_3$	b	NJM	277	1610, 1520, 1455

TABLE 2 (*continued*)

Complex	Structure[a]	Medium[b]	Ref.	Bands[c]
$Ag_2[(C_6H_5C(NSi(CH_3)_3)_2]_2$	f	NJM	284	1470, 1405
$Au_2[(C_6H_5C(NSi(CH_3)_3)_2]_2$	f	NJM	284	1530, 1302
$[Au(C_6H_5NC(H)NC_6H_5)]_4$	f	NJM	285	1567
$Hg[(C_6H_5C(NSi(CH_3)_3)_2]_2$	b	NJM	291	1555, 1172
$Ru_2(p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p)_4$	f	NJM	288	1608, 1505, 1177
$FeCl(C_6H_5C(NSi(CH_3)_3)_2)_2$	b	NJM	289	1436, 1394
$Rh_2(p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p)(O_2CCF_3)((C_6H_5)_2\text{-}P(CH_2)_2P(C_6H_5)(C_6H_4))(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2\text{-}CF_3COO \cdot 0.5H_2O$	f	NJM	294	1568
$\{PdCl_3NH(NH_2)C{-}C_6H_5\}(P(C_6H_5)_4)$	f	NJM	295	1555
$[Pd(C_3H_5)C_6H_5{-}C(NH)_2]_2$	f	KBr	296	1565 1485 1285
$Cr[C_6H_5C(NSi(CH_3)_3)_2)_2$	b	NJM	297	1245 1172 985

[a] See Fig. 3 for bonding types a, b, c, f, g, i, j.

[b] NJM = nujol mull; HXB = hexachlorobutadiene mull, KBr = potassium bromide disc; soln = solution.

[c] v = very; s = strong; m = medium; br = broad; sh = shoulder; w = weak.

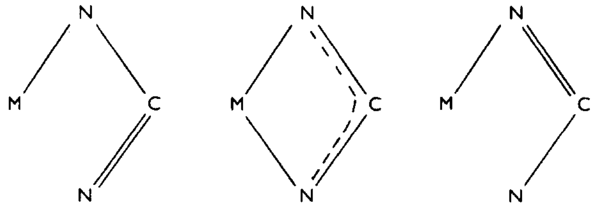
plex mixture of ν(C–N) and δ(N–H) modes. Also of note is the amidine III band, which may be described as a complex mixture of ν(C–N), δ(N–H), and ν(C–C) vibrations and occurs around 1240–1400 cm^{-1}.

6. THERMAL ANALYSIS OF AMIDINE COMPLEXES

This subject has only been addressed by Kilner's group and results indicate breakdown mechanisms which involve either loss of whole amidine groups or partial ligand breakdown whilst the ligand remains still attached to the metal.

7. NMR STUDIES OF AMIDINE COMPLEXES

Many NMR studies are reported in the literature, and in this review it is more appropriate to discuss each report in the context of the relevant metal. However, it is noteworthy that a number of solution studies of complexes having monodentate amidines indicate the occurrence of a fluxional intramolecular process involving a chelated intermediate, viz. [66].



8. A SURVEY OF AMIDINE COMPLEXES

8.1 *Scandium, yttrium and lanthanum*

No complexes or salts of these metals have been reported.

8.2 *Titanium, zirconium, and hafnium*

Early work involved the reaction of metal dialkylamides with acetonitrile to give dark-brown, air-sensitive, insoluble compounds [85].

$$M(N(CH_3)_2)_x + yCH_3CN \rightarrow M\{N{:}C(CH_3)N(CH_3)_2\}_y(N(CH_3)_2)_{x-y}$$

(M = Ti, Zr, Ta). The proposed structure is shown in Fig. 5. A characteristic ν(N–C–N) infrared band occurs at 1577–1587 cm^{-1}.

As part of their study of the coordination chemistry of the trimethylsilylbenzam-

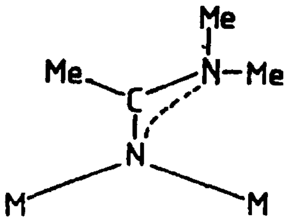


Fig. 5. Proposed structure of the bridging ligand derived from metal dialkylamides and acetonitrile (M = Ti, Zr, Ta).

idinato ligand, Dehnicke and co-workers [258] reacted it with titanium and zirconium tetrachlorides, viz.

$$\{C_6H_5{-}C(NSiMe_3)[NSiMe_3]_2]\} + MCl_4 \rightarrow C_6H_5{-}C(NSiMe_3)_2MCl_3 + ClSiMe_3$$

(M = Ti, Zr). The complexes were characterised using X-ray crystallography, and infrared spectroscopy. Both complexes were found to be centrosymmetric and dimeric, with bridging chlorides and bidentate amidino groups.

Roesky et al. [249] have also investigated the reaction of the same ligand with titanium and hafnium tetrachlorides. The $Li\{(C_2H_5)_2O\}(Me_3SiNC(C_6H_5)NSiMe_3)$ salt yielded $MCl_2(Me_3SiNC(C_6H_5)NSiMe_3)_2$ complexes, which were characterised by elemental analysis, infrared, NMR, and mass spectroscopy. The titanium complex was found to be centrosymmetric with chelating amidino ligands by X-ray crystallography.

$Ti(C_5H_5)Cl_3$ was found to react with one equivalent of $Na(C_6H_5C(NSi(CH_3)_3)_2)\cdot 0.5C_2H_5O$ to yield $Ti(C_5H_5)Cl_2(C_6H_5C(NSi(CH_3)_3)_2)$ [297].

As part of a wider study of the reactions of zirconium complexes with carbon dioxide-model heterocumulenes, a number of amidino complexes were isolated. The reaction of carbodiimides {RNCNR; R = C_6H_{11}, p-$CH_3C_6H_4$} with $[C_5H_5ZrH(Cl)]$ yielded the formamidino complexes $[C_5H_5Zr(Cl)RNC(H)NR]$, one of which (R = C_6H_{11}) was shown by X-ray crystallography [84] to have a bidentate amidino group.

Further, $[Cp_2ZrR_2]$ (R = Me, $C_6H_5CH_2$, Ph), when reacted with *p*-tolylcarbodiimide, provided the acetamidino and benzamidino complexes $[Cp_2Zr(R)\{p\text{-}MeC_6H_4NC(R)NC_6H_4Me\text{-}p\}]$ (R = CH_3, Ph), but no reaction occurred for R = $C_6H_5CH_2$ [196]. The salt $TiF_6[CH_3C(NH_2)_2]_2$ has been prepared by addition of acetamidinium fluoride to an aqueous solution of H_2TiF_6 [275].

Initial work [197] on the reaction of $TiCl_4$ and *N,N'*-diarylamidines yielded dark-purple, air- and moisture-sensitive solids thought to be chloride-bridged dimers.

8.3 Vanadium, niobium, and tantalum

Cotton and Poli's [230] initial attempts to synthesise complexes containing the difficult-to-form vanadium–vanadium bonded core unit using formamidinato ligands met with little success. The reaction of VCl_2Py_4 and two equivalents of lithio-amidine (LiAm) in toluene yielded $V(Am)_2Py_2$, containing bidentate amidine groups, ($Am = CH_3C_6H_4NC(H)NC_6H_4CH_3$, Py = pyridine). Further, the reaction of $V(C_5H_5)_2$ with two molar equivalents of amidine (AmH) in refluxing toluene yielded the mononuclear vanadium(III) complex, $V(C_5H_5)(Am)_2$. However, recent work with the *N*,*N'*-di-*p*-tolylformamidinato ligand [286] has proven the usefulness of amidine ligands in promoting M–M bonding, as exemplified by Cotton and Poli's synthesis of the first V(II)–V(II) σ^2,π^4-triple-bonded complex. X-ray crystallography indicated a V_2(amidinato)$_4$ structure with four bridging ligands, and a short V–V distance of 1.978(2) Å. Further, it was noted that the magnetic anisotropy γ value of 7300×10^{-36} m^3 molecule^{-1}, is the highest known for any M_2(amidinato)$_4$ complex.

The reaction of Me_xMCl_{5-x} (M = Nb, Ta; $x = 1, 2, 3$) with carbodiimides (RNCNR, R = isopropyl, cyclohexyl, *p*-tolyl) gives products of the types $MCl_4\{RNC(Me)NR\}$, $MeMCl_3\{RNC(Me)NR\}$, and $MCl_3\{RNC(Me)NR\}_2$. Infrared bands assigned to ν(CN) were observed at 1635–1506 cm^{-1} [86]. A number were later characterised by X-ray crystallography [169–172], both symmetrical and unsymmetrical bidentate modes of bonding being found (see Table 3, below).

Other niobium and tantalum complexes have been synthesised by reacting acetamidine hydrochloride with the metal(V) chlorides in the presence of a large excess of acetonitrile. The resultant $\{CH_3C(NH_2)_2\}MCl_6 \cdot 2CH_3CN$ compounds then ligand exchange with SCN^- yielding $\{CH_3C(NH_2)_2\}M(NCS)_6 \cdot 2CH_3CN$ [87]. MCl_5 (M = Nb, Ta) have also been found to react with $(C_2H_5)_2NH$ (equimolar amounts) in acetonitrile under refluxing conditions to yield $MCl_5\{(C_2H_5)_2NH\}\{NHC_2H_5\}\{CH_3CN\}$ [299]. When this mixture was refluxed for one hour, cooled to room temperature, and $(C_6H_5)_4PCl$ added, $MCl_4\{C_2H_5NC(CH_3)NC_2H_5\}\{(C_2H_5)_2NH\}$ inter alia was obtained.

Carbodiimides insert into metal–hydrogen bonds to yield formamidine complexes [252].

$$[(C_5H_5)MLH] + CH_3C_6H_4NCNC_6H_4CH_3 \rightarrow$$

$$[(C_5H_5)ML(CH_3C_6H_4NC(H)NC_6H_4CH_3]$$

($L = CO$ or $P(CH_3)_2Ph$, M = Nb, Ta). The complexes are thought to contain monodentate amidino groups, and upon irradiation become bidentate.

Glushkova et al. [228] studied the addition reactions of nitriles with tantalum pentachloride in the presence of amines. The reaction of $TaCl_5$ with RCN (R = CH_3, C_2H_5, C_6H_5) in carbon tetrachloride containing $(C_2H_5)_2NH$ yielded

$Cl_4Ta\{NC_2H_5C(R){:}NC_2H_5\}\{HN(C_2H_5)_2\}$ and $HTaCl_6$. A similar reaction in the presence of $(C_2H_5)_3N$ yielded $Cl_4Ta\{N{:}C(Cl)NR\}\{HN(C_2H_5)_2\}$.

The tantalum complex $[TaCl_4NC(C_6H_5)N\{Si(CH_3)_3\}_2]_2 \cdot 2CH_2Cl_2$, described in an initial publication [249] as part of Dehnicke and co-workers' study of *N,N,N'*-tris(trimethylsilyl)benzamidine has now had its X-ray crystal structure reported [269]. The complex is a centrosymmetric dimer with bridging chlorides and imido nitrogen-bonded amidino groups. As part of a synthetic study of vanadium(II) amides, Gambarotta and co-workers [276] synthesised $V(Me_2NCH_2CH_2NMe_2)(PhNCHNPh)_2$ from $V(Me_2NCH_2CH_2NMe_2)_2Cl_2$ and sodium *N,N'*-diphenylformamidinate.

A number of tantalum complexes have been prepared from the reaction of $\{C_5(CH_3)_5\}TaF_4$ with lithio derivatives of para-substituted benzamidines, yielding $\{C_5(CH_3)_5\}TaF_3\{[NSi(CH_3)_3]_2CC_6H_4R\}$ complexes where ($R = H$, CF_3, $N(CH_3)_2$, CH_3, CN, OCH_3) [277]. The complex $\{C_5(CH_3)_5\}TaF_3([NSi(CH_3)_3]_2CC_6H_4OCH_3\}$, characterised by X-ray crystallography, has the tantalum atom in a pseudo-trigonal bypyramidal arrangement with the amidino group bound as a symmetrical bidentate group.

8.4 Chromium, molybdenum, and tungsten

The chemistry of amidine complexes of these metals is extensive. A number of carbonyl displacement reactions of $M(CO)_6$ complexes have been carried out, but with mixed success. The preparation of dimeric complexes follows the related synthesis of the carboxylates which is undertaken in air, viz.

$$M(CO)_6 + \{R'N(H)C(R)NR'\} \rightarrow M_2\{R'NC(R)NR'\}_4 + CO$$

($M = Cr$, Mo, W; $R = H$, Me, Ph; $R' =$ aryl). The formamidine complexes were investigated by Vrieze and co-workers [88]. The tungsten derivative was not $W_2\{R'NCHNR'\}_4$ as anticipated but $[W_2(\mu\text{-}CO)_2\{HC(NR')_2\}_2\{R'NCHN(R')CH_2\}]$, ($R' =$ 3,5-xylyl), a novel complex containing a CH_2 group inserted in a chelating formamidino group, two bridging carbonyl groups, and two bridging formamidino groups. The structure was confirmed by X-ray crystallography [72,88]. The reaction of the above tetrakisamidino complexes with more hexacarbonyl yielded the following: (1) for Mo, $Mo_2\{HC(NR')_2\}_2\{HC(NR')_2Mo(CO)_3\}_2$ and $Mo_2\{HC(NR')_2\}_3\{HC(NR')_2Mo(CO)_3\}$, and (2) for Cr, $Cr_2\{HC(NR')_2\}_3\{HC(NR')_2Cr(CO)_3\}$. The $M(CO)_3$ fragment is bonded to one of the aromatic groups. In solution, the complexes show monomer–dimer equilibria, which are very dependent on the nature of the substituent R'.

With benzamidines, the tetrakisamidinomolybdenum compound has been characterised crystallographically [69], but the chromium product, a red insoluble crystalline material which analysed as Cr_2(amidinato)$_4$, was distinctly different from the molybdenum compound, and could not be obtained as crystals. The reaction with tungsten carbonyl gave a red crystalline solid which was not fully characterised [69].

The tetraethylammonium salts of the formamidino–metal carbonyl anions $[\mathrm{M(CO)_4\{HC(NR)_2\}}]^-$ (M = Cr, Mo, or W; R = aryl, *t*-but), have been made via the 1:1 reaction of $\mathrm{NEt_4[M(CO)_5Cl]}$ with potassium formamidines [89]. The reaction of $\mathrm{NEt_4[M(CO)_5Cl]}$ with *N*,*N*′-dimethylformamidine yielded the carbamoyl derivative $\mathrm{NEt_4[M(CO)_4\{CH_3NC(H)N(CO)CH_3\}]}$ M = Cr, Mo, W). Fluxional behaviour of the terminal carbonyls was indicated in solution by ^{13}C NMR, and when the complexes are heated with triphenylphosphine or pyridine, carbonyl substitution occurs to give $\mathrm{NEt_4[\mathit{fac}\text{-}M(CO)_3L\{HC(NR)_2\}]}$ (M = Mo, W).

Cotton found amidines ideal for the promotion of metal–metal bonding because of their bridging characteristics. The complexes were produced by the reaction of lithioamidines with tetrakis acetate–metal complexes, and were characterised by X-ray crystallography and accurate mass spectrometry. The following were prepared: (i) $\mathrm{Cr_2\{CH_3NC(Ph)NCH_3\}_4}$ [90]; (ii) $\mathrm{Mo_2\{[2,6\text{-xylylN}]_2CCH_3\}_2(CH_3CO_2)_2\cdot 4THF}$ [91]; (iii) $\mathrm{Mo_2\{(PhN)_2CCH_3\}_3(CH_3CO_2)}$ [91]; and (iv) $\mathrm{W_2\{(PhN)_2CCH_3\}_2(dmph)_2\cdot 2THF}$ [92] (dmph = the anion of 2,4-dimethyl-6-hydroxypyrimidine).

More recently, Cotton et al. have used amidines in their studies of stable $\mathrm{Mo_2L_4^+}$ systems [247]. The complex $\mathrm{Mo_2(Am)_4}$ ($\mathrm{Am = CH_3C_6H_4NC(H)NC_6H_4CH_3}$) was synthesised by two different routes. The first was by the reaction of $\mathrm{Mo_2(O_2CCH_3)_4}$ with lithioamidine, and the second via the metal carbonyl and amidine [88]. Addition of $\mathrm{AgPF_6}$ to these complexes produced the cationic derivatives [247]. It had been noted that complexes of this type, characterised by X-ray crystallography, had vacant sites within the unit cell suitable for accommodating other species such as ions. Reaction of $\mathrm{Mo_2(Am)_4}$ with $\mathrm{AgPF_6}$ yielded the desired product, $\mathrm{Mo_2(Am)_4PF_6}$, the X-ray crystal structure determination showing the $\mathrm{PF_6^-}$ ion occupying the previously vacant sites. The structures of the cationic and neutral complexes were found to be very similar, though the Mo–Mo distances did, however, differ, being 2.085 Å for the molecule and 2.122 Å for the cation. Further, Cotton undertook molecular orbital calculations to interpret the electronic absorption spectra of the two complexes. It should be noted also that HNC(H)NH was a satisfactory and valid model for the phenyl-substituted formamidino group.

Cyclopentadienyl metal amidine complexes of this group have been well studied, Vrieze documenting the formamidines, Kilner the formamidines, acetamidines, and benzamidines, and Brunner the asymmetric benzamidines.

Molybdenum and tungsten formamidine cyclopentadienyl complexes were produced by a number of routes, the molybdenum systems being the most extensively studied.

$$(1)\ \mathrm{MoCp(CO)_3Cl + M\{HC(\mathit{N}\text{-}\mathit{p}\text{-tolyl})_2\}} \xrightarrow[\text{Room temp., 1 h}]{\text{Benzene}} \mathrm{MoCp\{HC(\mathit{N}\text{-}\mathit{p}\text{-tolyl})_2\}(CO)_2}$$

$$+\ \mathrm{MoCp\{HC(\mathit{N}\text{-}\mathit{p}\text{-tolyl})N(CO)\text{-}\mathit{p}\text{-tolyl}\}(CO)_2 + KCl + CO}$$

(M = K, Ag, or Cu; Cp = C_5H_5). The complexes were separated by chromatography.

$$\text{(2)}\ \mathrm{MoCp(CO)_3Cl + M\{HC(}N\text{-}p\text{-}\mathrm{tolyl)_2\}} \xrightarrow[\text{1 week, dark}]{\text{Benzene, room temp.}}$$

$$\mathrm{MoCp\{HC(}N\text{-}p\text{-}\mathrm{tolyl)_2\}(CO)_2 + MCl + CO}$$

$$\mathrm{\{MoCp(CO)_3\}_2 + M\{HC(}N\text{-}p\text{-}\mathrm{tolyl)_2\}} \xrightarrow[\text{reflux, 3 weeks}]{\text{Benzene}}$$

$$\mathrm{MoCp\{HC(}N\text{-}p\text{-}\mathrm{tolyl)_2\}(CO)_2 + 2CO}$$

$$\text{(3)}\ \mathrm{MoCp(CO)_3Cl + 2HC(}N\text{-}p\text{-}\mathrm{tolyl)(NH\text{-}}p\text{-}\mathrm{tolyl)} \xrightarrow[\text{24 h, room temp.}]{\text{Benzene, } h\nu}$$

$$\mathrm{MoCp\{HC(}N\text{-}p\text{-}\mathrm{tolyl)\}_2(CO)_2 + \{HC(NH\text{-}}p\text{-}\mathrm{tolyl)_2\}Cl + CO}$$

$$\text{(4)}\ \mathrm{MCp(CO)_3Cl + HC(NHCH_3)(NCH_3) \rightarrow [MCp\{HC(NCH_3)N(CO)CH_3\}(CO)_2}$$

$$\xrightarrow{h\nu} \mathrm{[MCp\{HC(NCH_3)_2\}(CO)_2]}$$

(M = W, or Mo).

Using symmetrically substituted potassium formamidines, the complexes $\mathrm{MCp\{HC(NR)_2\}(CO)_2}$ and $\mathrm{MCp\{HC(NR)N(CO)R\}(CO)_2}$ (M = Cr, Mo, W) were formed [93], and were separated by column chromatography. The novel chromium analogues were prepared in situ from $\mathrm{CrCp(CO)_3I}$. One type of complex $\mathrm{MCp\{HC(NPh)N(CO)Ph\}(CO)_2}$ (M = Cr, Mo) showed on the NMR time scale terminal CO exchange. Others, e.g. [WCp{HC(NPh)N(CO)-*t*-Bu}$\mathrm{(CO)_2}$], were stereochemically rigid. Product relative molar ratios were found to be highly dependant on the molar ratios of the starting materials. As an extension to this work, complexes of the type [MCp{HC(*N*-*p*-tolyl)$_2$}(CO)L], (Mo, W; L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{SbPh_3}$, $\mathrm{P(OPh)_3}$, $\mathrm{P(OMe)_3}$) were prepared by the reaction of $\mathrm{MCp(CO)L_2Cl}$ with potassium *N*,*N*′-di-*p*-tolylformamidine [94]. The reaction of the dimer $\mathrm{\{MoCp(NO)X_2\}_2}$ (X = Cl, Br, and I) with the parent formamidine yielded the complexes MoCp{HC(*N*-*p*-tolyl)$_2$}(NO)X. The effects of both L and X on ^{13}C NMR frequencies were noted, L appearing to destroy correlation in the ^{13}CO frequencies which had been previously found for $\mathrm{M(CO)_5L}$ complexes. This was attributed to the influence of L on the stereochemistry.

Kilner and co-workers [82,95–97] found that both lithioamidines and parent amidines reacted with various metal cyclopentadienyl complexes (M = W and Mo) in the following ways.

$$\text{(1)}\ \mathrm{MoCp(CO)_3Cl + Li\{R'NC(R)NR'\} \rightarrow \underset{\text{yellow/carbamoyl}}{\{MoCp(CO)_2CON(R')C(R)NR'\}(I)}}$$

$$\text{or } \mathrm{H_2NC(Ph)NH}$$

(R = H, R′ = Ph; R = Me, R′ = H, Ph, *p*-tolyl; R = Ph, R′ = Me).

(2) $MoCp(CO)_3Cl + R'NHC(R)NR' \rightarrow MoCp(CO)_2\{R'NC(R)NR'\}$(II)

(3) $MoCp(CO)_2(PPh)_3Cl + Li\{R'NC(R)NR'\} \rightarrow$ (II)

The postulated mechanism for reaction (1) is that of nucleophilic attack at a coordinated carbonyl group, whereas for (2) attack is at the metal centre. Decarbonylation from I to II was achieved in small yields by thermolysis and UV photolysis. Infrared data supported the generation of $[C_5H_5Mo(CO)_3\{RNCRN(CH_3)R'\}]^+I^-$ in photolytic reactions carried out in the presence of methyl iodide. Attempts at insertion of carbon monoxide into metal–nitrogen bonds of $MC_5H_5(CO)_2(\{R'NC(R)NR'\}$ (M = W, and Mo), proved unsuccessful [97]. The *N,N'*-diphenylacetamidino complex, characterised by X-ray crystallography [98], has a symmetrically bound delocalised NCN system with the metal lying essentially in the same plane.

Brunner et al. through their interest in asymmetric catalysis have studied a number of related optically active molybdenum cyclopentadienyl amidino complexes [99–108]. The reaction of $MoC_5H_5(CO)_3Cl$ with unsymmetrical [R'NHC(R)NR″] amidines in pyridine gave $MoC_5H_5(CO)_2\{R'NC(R)NR''\}$ complexes. Work with lithioamidines yielded products similar to those previously described by Kilner and co-workers [98]. Brunner and Wachter [105] also found that the reaction of lithiated amidines, carbon disulphide and $MoC_5H_5(CO)_3Cl$ results in the formation of (a) and (b) shown in Fig. 6 (R = CH_3 and C_6H_5; when R = C_6H_5, only (a) is formed).

Brunner's investigations have shown that $MoC_5H_5(CO)_3Cl$ and amidines react to form the previously described type-II complexes, but by his use of unsymmetrical amidines, a molybdenum chiral centre was formed, and with racemic chiral amidines, diastereoisomeric pairs of enantiomers were obtained which were separated by fractional crystallisation. The conformations of the complexes were determined by various methods, including X-ray crystallography [99,102,103], ^1H high-field nuclear Overhauser effect difference spectroscopy [107], and circular dichroism measurements [104,106]. Of the four optically active compounds determined by X-ray crystallography, the configuration shown in Fig. 7 was the most preferred.

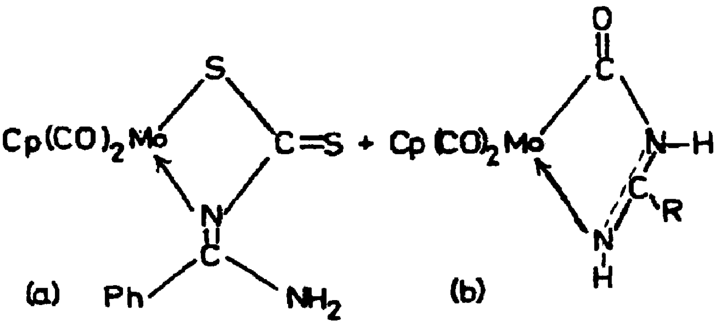


Fig. 6. Proposed structures of products from the reaction of $MoC_5H_5(CO)_3Cl$, LiNHC(R)NH and CS_2.

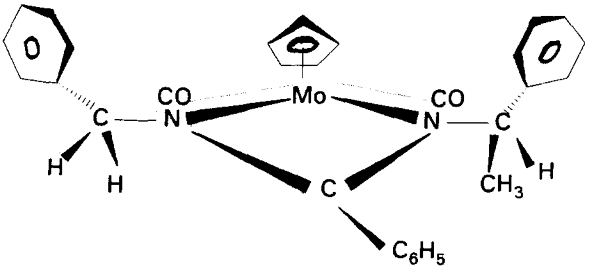


Fig. 7. Preferred configuration for $MoC_5H_5(CO)_2\{PhCH_2NC(Ph)NCH(CH_3)Ph\}$.

Draux and Bernal [212] have extended the work on the solid state structures of Brunner's optically active molybdenum benzamidines to assess the effect of methylation of the cyclopentadiene ring on the equilibria between preferred and non-preferred diastereoisomers. Two complexes $[\eta^5\text{-}(CH_3)C_5H_4]Mo(CO)_2[(S)HCC_6H_5\text{-}(CH_3)NC(C_6H_5)NCH_2C_6H_5]$ and $[\eta^5\text{-}(CH_3)C_5H_4]Mo(CO)_2[(S)HC(C_6H_5)\text{-}(CH_3)NCC_6H_4N(R)CHC_6H_5(CH_3)]$, were characterised by X-ray crystallography. The ring substituent methyl group was found not to affect the equilibrium position. Clearly, the work is of importance, particularly in the field of asymmetric catalysis, in providing insight into the way in which chiral information may be transmitted.

As part of their study of the trimethylsilylbenzamidine ligand, Roesky et al. [249] reacted $((CH_3)_3SiNC(C_6H_5)NSi(CH_3)_3)LiO(C_2H_5)_2$ with MO_2Cl_2 (M = W, Mo) to yield $Mo_2\{(CH_3)_3SiNC(C_6H_5)NSi(CH_3)_3\}_4$. The complexes were characterised via infrared spectroscopy, mass spectroscopy, and ^{13}C NMR, and the molybdenum complex was shown by X-ray crystallography to be centrosymmetric with two bidentate amidino groups.

Raubenheimer et al. [223] noted that the aminolysis of the complex $[(CO)_5W\{NH{=}C(OCH_3)C_6H_5\}]$ with diethylamine yielded the monodentate amidinato complex $[(CO)_5W\{NH{=}C(C_6H_5)N(CH_3)_2\}]$. The complex was synthesised as a mixture of E and Z isomers, but recrystallisation from diethyl ether/hexane yielded only crystals of the E isomer, characterised by X-ray crystallography.

N,N'-di-*p*-tolylcarbodiimide was found to undergo a β-insertion reaction with *trans*-$[WH(CO)_2(NO)(P(C_6H_5)_3)_2]$, yielding the bidentate formamidinato complex *trans*-$[W(CO)(NO)(P(C_6H_5)_3)_2\{CH_3C_6H_4NC(H)NC_6H_4CH_3\}]$ [224], characterised by IR spectroscopy, elemental analysis, and ^1H NMR. The observed ^1H NMR spectrum was complex because one nitrogen atom was coordinated trans to CO whilst the other was trans to NO. The proton on the N–C–N fragment was observed as a triplet, due to coupling with phosphorus ($^4J_{Ph} = 4$ Hz). No addition of CO occurred under 1 atm pressure of CO. The authors also claim $W(CH_3C_6H_4NNNC_6H_4CH_3)(CO)(NO)(PPh_3)_2$ may be synthesised from 1,3-di-*p*-tolylformamidine and $[WH(CO)_2(NO)(PPh_3)_2]$, obviously a manuscript error!

As previously noted, Chisholm et al. [209] synthesised the metal–amidine complex $Mo_2\{(CH_3)_2NCN\text{-}2,6\text{-}(CH_3)_2C_6H_3\}_4$ from the reaction of $Mo_2(N(CH_3)_2)_4$

and 2,6-$(CH_3)_2C_6H_3NC$. The complex, characterised by X-ray crystallography, has two types of amidino ligand, one type having shorter M—C and M—N distances than the other. Each type of group has an n^2 interaction with the metal [see Sect. 2(m)].

The reaction of Mo(V) species with amidines in the presence of isocyanate has been used for the extraction and spectrophotometric determination of molybdenum in various ores and minerals [227]. The amidines are of the type $[XC_6H_4N(H)C(C_6H_4\text{-}m\text{-}Cl)NC_6H_4Cl]$, (where X = H; o-$CH_3$; m-$CH_3$; p-$CH_3$; o-Cl; m-Cl; p-Cl). *N*-*m*-tolyl-*N′*-*p*-chlorophenyl-*o*-chlorobenzamidine hydrochloride was found to be the most successful extractor.

Dehnicke and co-workers [111] found that $MoCl_5$ reacted with di-isopropylcarbodiimide to yield $MoCl_4\{$i-propylNC(Cl)N-i-propyl$\}$, the structure of which was shown by X-ray crystallography to contain a bidentate amidino group.

During studies [231] of new nitrile complexes of the type $[MCp_2X(NCR)][PF_6]$ (M = Mo, W; Cp = cyclopentadiene; X = SR, halides; R = Me, Et, Ph), Calhorda et al. found that the tungsten complexes add NHR'_2 to give the amidine complexes $[WCp_2X(HNC(CH_3)NR'_2)][PF_6]$ (R′ = Me or H; X = SPh, Br). The nature of the complex was determined by infrared spectroscopy and NMR deuteration studies.

In a series of theoretical studies of amidino complexes, Davy and Hall [253] applied a general valence band calculation approach to the bonding in a series of dichromium(II) complexes. It was found that, though absolute values could not be determined for Cr—Cr bond lengths in the series of formamidino, formamido, and formato complexes, a general trend of bond length extension from amidinato to formato was predicted and borne out by experimental values. The model amidinato complex used was $Cr_2\{HNC(H)NH\}_4$. In another theoretical study, focus was on the effect of bridging amidino ligands on Cr(II)—Cr(II) bond lengths [202]. It was concluded that two effects were important, the inductive effect of the ligand and the presence or absence of axial ligands.

Albert and Davies [272] have recently extended their work on asymmetric synthesis by using chromium tricarbonyl formamidine complexes. The carbanions of formamidines derived from *N*-methylbenzylamine, L-valinol, and L-leucinol, undergo electrophilic benzylic methylation with poor selectivity, whereas on complexation, significant improvements in stereoselectivity were found.

Dias and Querios [278] have recently described the synthesis and characterisation of a number of molybdenum dicyclopentadienyl amidino complexes. $[Mo(C_6H_5)_2Br_2]$ reacts with the diarylamidines ArN(H)C(X)NAr (Ar = C_6H_5, p-$CH_3OC_6H_4$, p-$CH_3C_6H_4$, p-FC_6H_4; X = H, CH_3, C_6H_5) in ethanol containing triethylamine to yield $[Mo(C_5H_5)_2\{ArNHC(X)NAr\}]^+PF_6^-$. The complexes were characterised by elemental analysis, infrared spectroscopy and NMR, the data indicating bidentate amidinato ligands. Cyclic voltammetry studies showed that the formal oxidation potentials of the complexes are dependant on the central ligand substituent. The order of increasing ease of oxidation, formamidine < acetamidine < benzamidine was explained in terms of the electron-releasing inductive effect of the methyl group and the phenyl group's overall supply of electrons via the ring π system.

Dehnicke et al. [290] synthesised a mixed ligand amidinato–carboxylato complex $Mo_2(O_2CC_6H_5)_2\{C_6H_5C(NSi(CH_3)_3)_2\}_2$ from $Mo_2(O_2CC_6H_5)_4$ and *N,N,N'*-tris(trimethylsilyl)benzamidine. The X-ray structure of the complex indicated a dimeric Mo—Mo core with surrounding bidentate bridging carboxylato and amidinato ligands.

The crystal structure of $W(\eta^5\text{-}C_5H_5)_2Br\{H_2NC(CH_3)NH\}(PF_6)$ [292] shows the tungsten atom coordinated in a distorted tetrahedral environment by two cyclopentadienyl rings, a bromine and the imino nitrogen atom of the acetamidine ligand.

Noltmeyer and co-workers [297] have synthesised $Cr\{C_6H_5C(NSi(CH_3)_3)_2\}_2$ from $Cr_2Cl_2(C_4H_8O)_2$ and $NaSiMe_3$. The product was characterised by X-ray crystallography and found to have two bidentate amidino ligands. The 4-trifluoromethylbenzamidinato analogue was also prepared.

8.5 Manganese, technetium, and rhenium

Kilner and co-workers [97,109,110] found that the reaction of lithioamidines with $Mn(CO)_5X$ (X = Cl, Br, I) yielded the carbamoyl complexes $Mn(CO)_4\{CON(R')C(R)NR'\}$. The failure to insert CO into the Mn—N amidine bonds under high CO pressures favours a mechanism proceeding by nucleophilic attack at a carbonyl group of $Mn(CO)_5Br$. In contrast to other carbamoyls, these amidino carbonyl groups can be decarbonylated by UV irradiation to form $Mn(CO)_4\{R'NC(R)NR'\}$ complexes. Thermolysis of the carbamoyls also caused decarbonylation, but when achieved under a high carbon monoxide pressure, the first example of an amino–manganese carbonyl complex, $Mn(CO)_5\{N(Ph)\text{-}C(Ph){:}NPh)$ was also formed.

Abel and Skittrall [200] have investigated the analogous formamidine complexes. Both the monomeric and dimeric carbonyl halides $Mn(CO)_5X$ and $[Mn(CO)_4X]_2$ yield $Mn(CO)_4\{RNC(H)NR\}$ and $Mn(CO)_4\{CON(R)C(H)NR\}$ complexes, the former resulting from decarbonylation of the carbamoyl complex in low yield. Using analogous rhenium monomeric and dimeric carbonyl chlorides, similar carbamoyl and formamidino complexes to those described for manganese were formed.

The first amidino complexes of technetium have been reported by Magon and co-workers [204]. They were formed by the reaction of technetium phosphine complexes with lithioamidines:

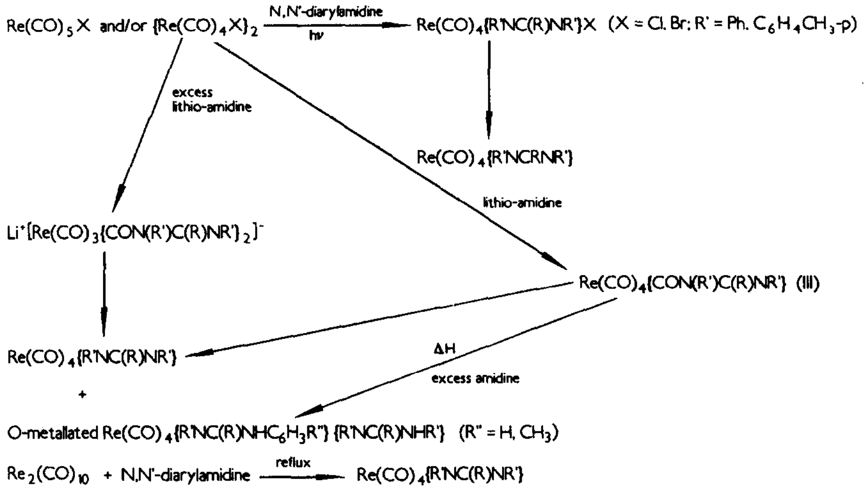
$$\textit{mer}\text{-}Tc(PMe_2Ph)_3(CO)_2Cl + Li[ArNC(X)NAr] \rightarrow$$

$$\textit{trans}\text{-}Tc(PMe_2Ph)_2(CO)_2\{ArNC(X)NAr\}$$

(Ar = C_6H_5, X = CH_3; Ar = p-CH_3–C_6H_4, X = H). The structures of *trans*-$Tc(PMe_2Ph)_2(CO)_2\{C_6H_5NC(CH_3)NC_6H_5\}$ and $Tc(PMe_2Ph)_2(CO)_2$-(p-$CH_3C_6H_4NNNC_6H_4CH_3$-p}, were determined by X-ray crystallography, allowing a comparison of pseudo-allyl; amidino and triazenido ligands in a similar molecular environment. Similar Tc–N distances (2.186(6) Å triazine; 2.203(1) Å amidine averages) were noted, but the coordination geometry of the ligands differ in that the central amidino carbon is slightly out of the plane containing the metal and two nitrogen atoms, whereas the four atoms in the triazeno case are co-planar.

Cotton et al. [112] as part of their studies of metal–metal bonding, reacted tetrabutylammonium octachlorodirhenate and the amidines, *N*,*N*′-diphenylacetamidine, and *N*,*N*′-dimethylbenzamidine, in the melt to yield $Re_2Cl_4\{(PhN)_2CCH_3\}_2$ and $Re_2\{(MeN)_2CPh\}_4Cl_2$, respectively. The complexes were characterised by mass spectroscopy and X-ray crystallography, which showed metal–metal bonded complexes with bridging amidino groups. Further, Cotton and Shrive also found [114] that $(Bu_4N)_2Re_2Cl_8$, on fusing with *N*,*N*′-diphenylbenzamidine, yielded after recrystallisation two products, $Re_2(N_2CPh_3)_2Cl_4$ and $Re_2(N_2CPh_3)_2Cl_4 \cdot THF$, shown by X-ray crystallography to have amidino groups bridging a metal–metal bonded Re_2 unit.

Clark and Kilner [71,74] have extensively investigated rhenium carbonyl complexes of the *N*,*N*′-diarylamidines, viz.



$Re(CO)_3(L)\{R'NC(R)NR'\}$ (**IV**) complexes were prepared by decarbonylation of **III** or by the reaction of $Re(CO)_4LBr$ with amidines in refluxing toluene (L = PPh_3 or $AsPh_3$). The reaction stops at the intermediate compound $Re(CO)_3(PPh_3)\{R'NC(R)N(CH_3)R'\}Br$ when a *N*,*N*,*N*′-trisubstituted amidine is used. Related complexes were made by reacting **IV** with hydrobromic acid.

$$\mathrm{Re(CO)_5X + amidine \xrightarrow{monoglyme/reflux}}$$
$$\mathrm{Re(CO)_3\{R'NC(R)NHC_6H_3R''\text{-}\mathit{p}\}\{R'NC(R)NHR'\}}$$

($R = H$, $R' = C_6H_5$, $R'' = H$; $R = CH_3$ or C_6H_5, $R' = C_6H_4CH_3\text{-}p$, $R'' = CH_3$; $R = CH_3$ or Ph, $R' = C_6H_5$, $R'' = H$). These complexes contain six-membered *O*-metallated rings. Benzamidines ($R = C_6H_5$) produce in addition isomeric complexes in which ortho-metallation of the skeletal carbon substituent occurs to give complexes having five-membered ortho-metallated rings. A 1,3-proton shift mechanism for ortho-metallation was eliminated, and the complexes and their reaction schemes are discussed on the basis of infrared and ^1H, ^{13}C NMR data.

Toniolo and co-workers [201] found that $Re(CO)_3(PPh_3)_2Cl$ reacted with Li(ArNC(H)NAr) (Ar = $p\text{-}CH_3C_6H_4$, C_6H_5, $p\text{-}ClC_6H_4$, $o\text{-}FC_6H_4$) in refluxing tetrahydrofuran to yield the complexes $Re(CO)_2(PPh_3)_2\{ArNC(H)NAr\}$. Significant infrared bands in the region 1620–1218 cm^{-1} were reported, and one of the complexes (Ar = Ph) was shown by X-ray crystallography to have a symmetrically bound delocalised amidino group. This initial work has been extended by Zanello et al. [232]. The electrochemistry of a series of Re(I) complexes, viz. $[Re(CO)_2(PPh_3)_2\{(ArN)_2CH\}]$ (Ar = C_6H_5, $C_6H_4CH_3$, $C_6H_4Cl\text{-}p$, $C_6H_4F\text{-}p$) was studied in dichloromethane, acetonitrile and acetone. The Re(I) to Re(II) electrode potentials, which occur in the range +0.06 to +0.09 V (vs. SCE), were found to depend upon aryl group electron-donating ability. The electrochemically generated Re(II) complexes were stable at temperatures below 0°C and were characterised by ESR, infrared and UV-vis. spectroscopy. They were found to be isostructural with the Re(I) complexes. At higher temperatures, two parallel reactions were postulated to explain the instability of the Re(II) complexes: (1) photochemical and/or thermal induction of self-reduction to Re(I); (2) intramolecular oxidation of the amidino ligand by Re(II) followed by partial decomplexation of the CO and the oxidised amidino ligand.

The benzamidinium salt of a rhenium-2,4-pentanedionate anion has been characterised by X-ray crystallography [77]. $Tc\{P(CH_3)_2(C_6H_5)\}_2(CO)_2(C_6H_5NC(H)NC_6H_5)$, previously synthesised by Marchi et al. [204], was recently used in the context of structure and stability relationships for technetium radiopharmaceuticals. Wei et al. [279] applied the solid angle factor sum model, which indicated that the packing around the metal in this complex had reached a limit.

A sensitive method for the determination of Re(IV), described by Gosh et al. [280], is based on reduction of Re(VII) and on amidine extraction. Eleven different amidines were studied, the most efficient, *N*-(4-methylphenyl)-*N''*-phenylbenzamidine, giving a detection limit of 8 ppb rhenium.

The reaction of $MnCl_2(C_4H_8O)_2$ with sodium bis-trimethylsilylbenzamidine yielded $Mn(amidinato)_2$ [297], characterised by NMR, infrared spectroscopy, and mass spectroscopy as containing two bidentate amidino groups. The 4-trifluorobenzamidinato analogue was also prepared.

8.6 Iron, ruthenium, and osmium

The study of iron amidino complexes has been limited by the unstable nature of the complexes, making characterisation difficult.

(1) $C_5H_5Fe(CO)_2Cl$ + Liamidine → unstable product difficult to characterise [203]

(2) $Fe(CO)_4X_2$ + Liamidine → "$Fe(CO)_4[(NR)_2C(R)]X$"

$$\Big\downarrow{\scriptstyle Al_2O_3\ \text{filtration}}$$

$$Fe(CO)_4\{RN(H)C(R)NR\}\ [113]$$

The above conclusions are based mainly on infrared data, the complexes being air-, moisture- and thermally sensitive.

Iron(III) chloride and iron(II) chloride react with $R'N(Li)C(R)NR'$ ($R = CH_3$, $R' = Ph$) to produce high-spin $Fe\{R'NC(R)NR'\}_3$ and polymeric $[Fe\{R'NC(R)NR'\}_2]_n$, respectively. The complexes failed to react with, or were decomposed by, a number of reducing, electrophilic and nucleophilic reagents. The exception was the blue $Fe\{p\text{-}CH_3C_6H_4NC(CH_3)NC_6H_4CH_3\text{-}p\}_3$ complex which reacted readily with nitric oxide to form a purple addition complex from which the *N*-nitroso compound $\{p\text{-}CH_3C_6H_4NC(CH_3)N(NO)C_6H_4CH_3\text{-}p\}$ was obtained.

Hieber and Kaiser [115] obtained amidine salts from the reaction of the dimers $\{M(NO)_2Br\}_2$ with *N*-phenylbenzamidine ($M = Fe$, Co), formulated as $[(ON)_2M\{H_2NC(Ph)NPh\}]^+Br^-$.

An Fe(III) salt of formamidine has been isolated from the reaction of $FeCl_3$ with S_4N_4, HCl and H_2CCl_2. The complex $[HC(NH_2)_2]_3FeCl_6$ was characterised by X-ray crystallography [126].

Robinson and co-workers [262] found that the reactions of the carbodiimide (i-PrN=C=NPr-i) with $[Ru(X)(CO)(PPh_3)_3]$ ($X = Cl$, Br) complexes in refluxing benzene involved insertion of the carbodiimide into the Ru–H bond and concomitant dehydrogenation of an isopropyl group to yield the complexes $[RuX\{CH_2{=}C(CH_3)N{-}CH{-}NCH(CH_3)_2\}(CO)(PPh_3)_2]$. The chelate nature of the ligand was established by X-ray crystallography. They also noted that $OsH_2(CO)(PPh_3)_3$ reacted with (i-PrN=C=NPr-i) to afford the intermediate $OsH\{(CH_3)_2HCN{-}CH{-}NCH(CH_3)_2\}(CO)(PPh_3)_2$, which on further heating dehydrogenated to yield $[OsH\{CH_2{=}C(CH_3)N{-}CH{-}NCH(CH_3)_2\}(CO)(PPh_3)_2]$. Examples of amidine capping ligands with osmium clusters are also known. Diisopropyl and *N*,*N*′-dibenzyl formamidines react with $Os_3(CO)_{12}$ and $Os_3(CO)_{10}(cyclooctene)_2$ to yield $HOs(CO)_9$(i-PrNCHNPr-i) and $H_2Os_3(CO)_9(C_6H_5CH_2NCHNCH_2C_6H_4)$, respectively [116], the latter containing an ortho-metallated group, (Fig. 8).

Lewis and co-workers [75] reacted $Os_3(CO)_{10}(NCCH_3)_2$ with amidines and formed the complexes $Os_3(\mu\text{-}H)(CO)_{10}\{NHC(CH_3)NH\}$ and $Os_3(\mu\text{-}H)(CO)_{10}(NC_6H_5C(C_6H_5)NH\}$, which were subsequently thermally decarbonylated to the nonacarbonyls, one of which, $Os_3(\mu\text{-}H)(CO)_9(CH_3CN_2H_2)$, exists in tautomeric

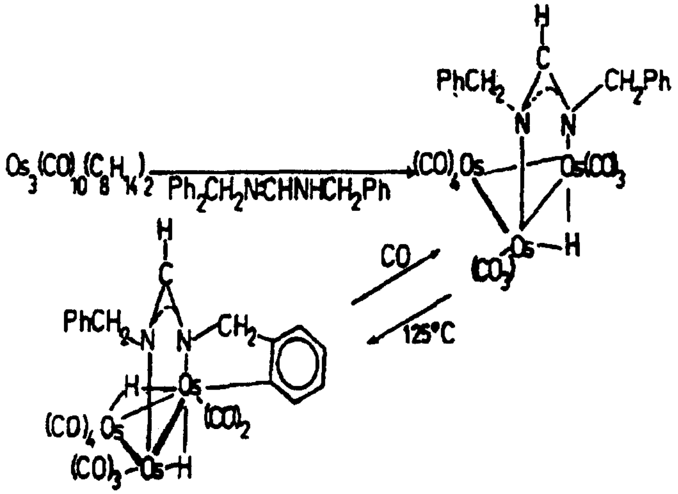
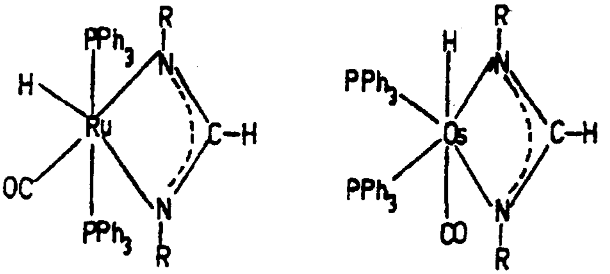


Fig. 8. Reaction of $Os_3(CO)_{10}$ (cyclooctene) with *N*,*N*′-dibenzylformamidine.

forms. $Os_3(\mu\text{-}H)(CO)_9\{NC_6H_5C(C_6H_5)NH\}$, characterised by X-ray crystallography, has the three osmium atoms in an isosceles triangle, one edge of which is bridged by the NH nitrogen atom of the amidino ligand with the second nitrogen bound to the third osmium atom.

Treatment of $[RuH_2(PPh_3)_4]$ and $OsH_4(PPh_3)_3$ with *p*-tolylisocyanate yielded the formamidino compounds $HM\{RNC(H)NR\}(CO)(PPh_3)_2$ [117,118]. The ruthenium complex was found to be the same as that previously synthesised from di-*p*-tolyl carbodiimide [84]. However, the less labile osmium complex, rather than isomerising to the thermodynamically more favoured structure **I**, which is preferred by the ruthenium complex, adopts structure **II** (Fig. 9). The formation of the formamidinato ligand is thought to involve the fragmentation of at least two isocyanates, the overall stoichiometry being

$$RuH_2(PPh_3)_4 + 2RNCO \rightarrow RuH\{RNC(H)NR\}(CO)(PPh_3)_2 + PPh_3 + OPPh_3$$



(I) (II)

Fig. 9. The preferred structures of $HM(PPh_3)_2(CO)\{RNCHNR\}$($M = Ru$, Os; $R = p$-tolyl) complexes.

or

$$OsH_4(PPh_3)_3 + 2RNCO \rightarrow OsH\{RNC(H)NR\}(CO)(PPh_3)_2 + OPPh_3 + H_2$$

Robinson and co-workers [174] have also investigated the reactions of the carbodiimide (i-PrN=C=NPr-i) with several hydrides, which afford products containing the bidentate *N,N'*-di-*p*-tolylformamidinato ligand (L). The hydrides $[MHX(CO)(PPh_3)_3]$ ($M = Ru$, Os; $X = Cl$, Br or $OCOCF_3$), $[MH_2(CO)(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$, $[OsH_4(PPh_3)_3]$, $[IrHCl_2(PPh_3)_3]$, (trans chlorides), and *mer*-$[IrH_3(PPh_3)_3]$ yielded the complexes $[MX(L)(CO)(PPh_3)_2]$, (two isomers), $[MH(L)(CO)(PPh_3)_2]$, $[M(L)_2(PPh_3)_2]$, $[IrCl_2(L)(PPh_3)_2]$ and $[IrH_2(L)(PPh_3)_2]$, respectively. The structure and stereochemistries of the new complexes were determined by ^1H and ^{31}P NMR, and the crystal structure of *trans*-$\{RuH(L)CO(PPh_3)_2$ confirmed the presence of a chelated amidino group.

Osmium pentachloride reacts with trichloroacetonitrile in the presence of chlorine to yield $[Cl_4Os\{NC(CCl_3)N{=}CCl(CCl_3)\}]_2$ [119], which with PPh_4Cl adds a chloride ion to produce $PPh_4[Cl_5Os\{NC(CCl_3)N{=}CCl(CCl_3)\}]$, for which the X-ray crystal structure, shown in Fig. 10, was determined on the CH_2Cl_2 solvate.

Dehnicke and co-workers have reacted *N,N,N'*-tris(trimethylsilyl)benzamidine with $FeCl_3$ in tetrahydrofuran, yielding $[FeCl_4][C_6H_5C(NHSiCH_3)_2]_2$, characterised by X-ray crystallography [273].

As part of an investigation into the activation of CO_2 by transition-metal complexes, Jia and Meek [281] have synthesised two ruthenium amidino complexes by carbodiimide insertion into a ruthenium hydride bond viz. RuH(RNCHNR)(CYTTP), where $R = p\text{-}CH_3C_6H_4$, or C_6H_{11}, $CYTTP = (C_6H_5)_2PCH_2CH_2CH_2P(C_6H_{11})_2)_2$. NMR and infrared spectroscopy, etc. indicated a bidentate amidino ligand.

The complex $Ru_2(CH_3C_6H_4NC(H)NC_6H_4CH_3)_4$ was synthesised by Cotton and Ren [288] from tetrakisacetatodiruthenium and the lithioamidine and was

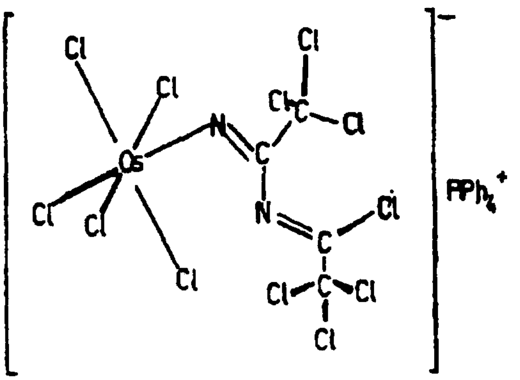


Fig. 10. X-ray crystal structure of $PPh_4^+[Cl_5O_5\{NC(CCl_3)N{=}CCl(CCl_3)\}]$[119].

characterised by X-ray crystallography as having a long Ru–Ru distance (2.474(1) Å) and four bridging ligands. The complex is diamagnetic and molecular orbital calculations confirmed a $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4$ ground state configuration.

Dehnicke and co-workers have extended the chemistry of the silylbenzamidinato ligand by the synthesis of $\{C_6H_5C(NSi(CH_3)_3)_2\}_2FeCl$ [289] from FeOCl and the amidine. The complex, characterised by X-ray crystallography, infrared spectroscopy, and Mössbauer spectroscopy, has an iron atom in a distorted trigonal bipyramidal environment, with the chlorine ligand and two nitrogen atoms of different amidino chelating in equitorial positions. The remaining nitrogen atoms occupy apical positions.

8.7 Cobalt, rhodium, and iridium

Olsen [120] has determined the structure of acetamidinium tetrachlorocobaltate in which each cation is shared by two anions, thus forming an infinite two-dimensional array.

Minghetti et al. [121] have compared the direct addition of two different *N,N'*-diarylformamidines [L = ArNCHNHAr] to metal salts. It was found that when Ar = *p*-nitrophenyl, the amidine was unreactive, the attempted reaction with cadmium bromide, zinc bromide, cobalt chloride, $[(CO)_2RhCl]_2$ and silver fluoroborate yielding no new complexes. However, when Ar = *p*-tolyl, the following were formed: L_2CoCl_2 (blue), $[LH]_2[CoCl_4]$ (turquoise), $(CO)_2RhClL$ (pale yellow), L_2ZnBr_2 (white), L_2CdBr_2 (white), $L_3Cd_2Br_4$ (white), $LHgCl_2$ (yellow), $[L_2Ag]^+BF_4^-$ (white), and L_2AgNO_3 (white). The inactivity of the *p*-nitrophenyl-substituted formamidine was attributed to the electron-withdrawing group in the aromatic ring.

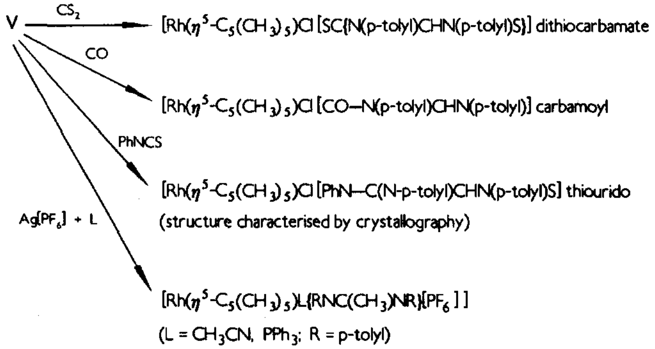
Attempts by Kilner [122] to use the lithio-amidine route to yield cobalt complexes proved unsuccessful and no pure compounds were isolated:

$$CoCl_2 + \text{Liamidine} \xrightarrow{\text{monoglyme}} \text{light blue solid} + LiCl$$

The reaction of $CoCl_2 \cdot 6H_2O$ with acetamidine (1:6 ratio) in methanol yielded $Co(CO_3)(C_2H_6N_2)_4Cl_2 \cdot 2H_2O$, the CO_3 resulting from the reaction of acetamidine with atmospheric carbon dioxide. The structure of the complex was determined by X-ray crystallography [300]. The cobalt ions occur in an octahedral environment, coordinated by a bidentate carbonate group and by the imino nitrogens of the four acetamidines.

Recent work by Sargesson and co-workers [221] concerning the roles of combinations of metal ions in catalytic studies of coordinated organic substrates resulted in the synthesis of $Na[(NH_3)_3Co\{\mu\text{-}OH\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}\{CH_3C(NH)_2\}\}\text{-}Co(NH_3)_3](S_2O_6)_2 \cdot H_2O$, which contains a bridging acetamidine group. The complex was formed by stirring $[(NH_3)_4Co(\mu\text{-}NH_2\mu\text{-}OH)Co(NH_3)_4](CF_3SO_3)_4 \cdot H_2O$ in acetonitrile overnight at room temperature. The complex, characterised by NMR, IR, elemental analysis, and X-ray diffraction, has cobalt atoms bridged by $HNC(CH_3)NH$, NH_2, and OH groups.

$Rh\{\eta^5\text{-}C_5(CH_3)_5\}Cl(RNC(R')NR)$ (**V**), where $R' = H$ or CH_3, was prepared from the reaction of $[Rh_2\{\eta^5\text{-}C_5(CH_3)_5\}_2Cl_4]$ with $[RN(H)C(R')NR]$ in the presence of base, or by reaction with $Ag\{RNC(R')NR\}$ or $K\{RNC(R')NR\}$ [123,124]. The reactions of **V** have been extensively studied.



Piraino et al. [125] synthesised $[Rh(dien)(RNCHNR)]_2$ (dien = cycloocta-1,5-diene (**VI**), norborodiene (**VII**); R = *p*-tolyl). The complexes are dimeric and bridged by the amidino ligand, and react with carbon dioxide, bis(1,2-diphenylphosphino)ethane(dppe), and PPh_3 with displacement of the diene ligand to yield $[Rh(CO)_2\{RNC(H)NR\}]_2$, $[Rh(dppe)_2]^+$ and $[Rh(PPh_3)_2\{RNC(H)NR\}]_2$, respectively. The last complex was only isolated as an O_2 adduct. With HCl or HBF_4(aq.), **VI** and **VII** form the formamidino cation $[p\text{-tolylNHC(H)NH-}p\text{-tolyl}]^+$, and $[Rh(dien)X]_2$, X = Cl, F. $[Rh(C_8H_{12})(RNCHNR)]_2$ reacts with CS_2, SO_2, PhNCS, and PhNCO with diene replacement. However, the only isolated product was $[Rh(CS_2)(RNCHNR)]$, to which a polymeric structure was assigned.

The reaction of $[Rh(CO)_2Cl_2]_2$, with $Li\{RNC(R')NR\}$, where $R' = CH_3$ or H, has been investigated by both Abel and Skitterall [263] and Connelly et al. [127]. The complexes are thought to be binuclear bridged species (Fig. 11). An intermediate, unstable and difficult to isolate, was noted when $R' = H$. It was thought to be $Rh(CO)_3(XC_6H_4)NCHN(C_6H_4X)$ (X = F or Cl), which can easily lose CO to form the bridged dimers. Further, $\{Rh(RNC(CH_3)NR)(CO)_2\}_2$ (**VIII**) underwent the following reactions (R = *p*-tolyl):

$$\begin{tikzcd}
\mathbf{VIII} \arrow[r, "\text{PPh}_3\text{ substitution}"] \arrow[dr, "\text{I}_2\text{ oxidative addition}"'] & {[Rh_2\{RNC(CH_3)NR\}_2(CO)_3(PPh_3)]} \\
& {[\{RhI(RNC(CH_3)NR)(CO)_2\}_2]}
\end{tikzcd}$$

The complex $[Rh(CO)L_2\{RNC(CH_3)NHR\}][BF_4]$ ($L = PPh_3$, R = Ph, or *p*-tolyl) [128] has been prepared from the appropriate diarylacetamidine and $[Rh(CO)L_2\{OC(CH_3)_2\}][BF_4]$.

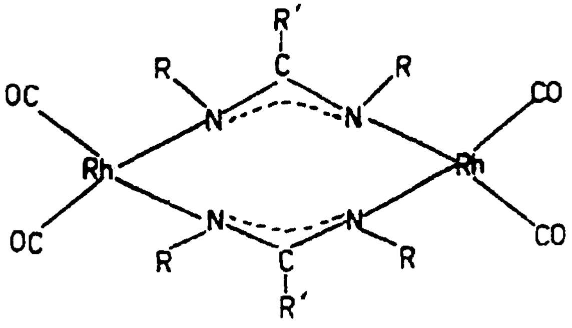


Fig. 11. Structure of $[Rh(CO)_2\{RNC(R')NR\}]_2$ complexes.

This synthetic work has been extended to cyclic voltammetry studies of rhodium amidino complexes [216]. The complex $Rh_2(CO)_4\{C_6H_5NC(C_6H_5)NC_6H_5\}_2$ showed a more restricted redox chemistry than its triazenido analogue, with only one irreversible wave being noted in addition to that for the formation of $[Rh_2(CO)_4\{C_6H_5NC(C_6H_5)NC_6H_5\}_2]^+$. This implies that the amidino ligand is a better σ donor and a worse π acceptor than the analogous triazenido ligand. Further, based on E° values obtained for $[Rh_2(CO)_3(PPh_3)(C_6H_5NC(C_6H_5)NC_6H_5)_2]$, a series of paramagnetic complexes with a $[Rh]_2$ core were prepared by one electron transfer processes, viz.

$$[Rh_2(CO)_3(PPh_3)(C_6H_5NC(C_6H_5)NC_6H_5)_2]$$

$$\downarrow Fe(C_5H_5)_2 \cdot PF_6$$

$$[Rh_2(CO)_3(PPh_3)(C_6H_5NC(C_6H_5)NC_6H_5)_2]PF_6$$

$$\downarrow L$$

$$[Rh_2(CO)_2(PPh_3)(L)(C_6H_5NC(C_6H_5)NC_6H_5)_2]PF_6$$

$$\downarrow NBu_4BH_4$$

$$[Rh_2(CO)_2(PPh_3)(L)(C_6H_5NC(C_6H_5)NC_6H_5)_2]$$

$L = PPh_3$; $AsPh_3$; $P(OPh)_3$.

As part of their studies in asymmetric catalysis, Brunner and Agrifoglio [129] found that $[RhCl(C_8H_{14})_2]_2$, together with the optically active amidines (Fig. 12, (i)–(v)) or their lithium derivatives produce hydrogenation catalysts after activation with molecular hydrogen. At room temperature and 1 bar H_2 pressure, the catalysts hydrogenate the prochiral substrates (Z)-a(N-acetylamino)cinnamic acid, itaconic acid, a-methylcinnamic alcohol, as well as cyclohexene, benzene and toluene. However, the catalytic hydrogenation activity is balanced by low optical induction, only the hydrogenation of a-methylcinnamic alcohol with 1.5–2.0% ee leading to any enhancement.

Piraino et al. [130] have reported the oxidation of $[Rh(C_8H_{12})$-$\{p$-tolylNCHN-p-tolyl$\}$ by $AgNO_3$ which leads to paramagnetic

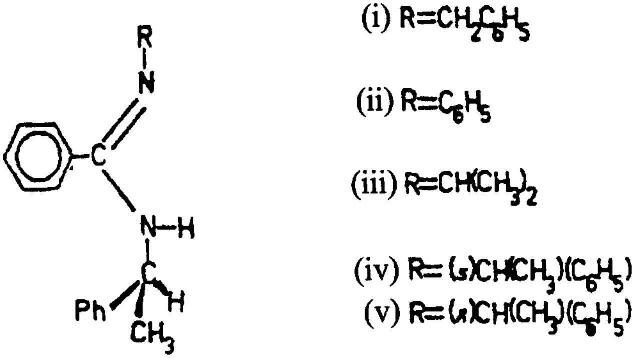


Fig. 12. Asymmetric amidines used in rhodium catalysed hydrogenation reactions [129].

[Rh_2\{*p*-tolylNCHN-*p*-tolyl\}$_3(NO_3)_2$\} (**IX**), characterised by X-ray crystallography [204]. The structure has three bridging formamidino groups about the Rh—Rh (2.485 Å) unit, with an unsymmetrically bound bidentate nitrato group on each metal. The structure has no known amidine analogues, and a formal oxidation state of 2.5 is implied. The complex **IX** undergoes a variety of reactions. With nucleophilic agents, displacement of the nitrato groups occurs leading to [Rh_2\{*p*-tolylNC(H)N-*p*-tolyl]$_3X_2$] ($X = I^-$, SCN^-). The neutral ligands, PPh_3 and pyridine, were found to react slowly with **IX**, yielding triphenylphosphine oxide and pyridine oxide, respectively. There is a corresponding yield of mixed valence formamidino complexes where the oxidation state of the rhodium atoms has been reduced. Further investigation of these complexes, and a further complex obtained using diethylamine [245], showed that an excess of the neutral ligands yields asymmetric Rh_2^{4+} complexes via reductive elimination of one nitrate group. X-ray crystallographic studies of the [$Rh_2Am_3(NO_3)L$] complexes show all the complexes [$L = PPh_3$, pyridine, Et_2NH] to have delocalised σ, σ-bound, bridging amidino-groups, except that one of the three bridging groups in the diethylamine complex is bound in an unusual way, σ,σ-N, N′, with a localised double bond. Related iridium complexes have also been synthesised, and analogous reactions investigated [126–128].

A number of rhodium and iridium complexes of amidines have been prepared by the reactions of [MCl(diene)]$_2$ (M = Rh, Ir; diene = cyclooctadiene(COD), norbornadiene(NBD), and tetrafluorobarrelene(TFBE)) complexes with potassium *N*,*N*′-diphenylbenzamidate, or the parent ligand [139]. The former reactions produced complexes of the type M(RNC(R)NR)(diene), a mononuclear or binuclear arrangement being determined by the dialkene present. All COD complexes are mononuclear, the others binuclear. The latter reaction produced complexes of the form [MCl\{RNC(R′)N(H)R\}(diene)]. Two complexes [$Rh_2(C_6H_5NC(C_6H_5)$-$NC_6H_5)_2$(COD)] and [Rh_2\{($C_6H_5C(NC_6H_5)_2$(TFBE)$_2$] were characterised by X-ray crystallography and found to have bidentate and bridging amidino groups, respectively. The rhodium complexes were found to react with carbon monoxide yielding $[Rh_2\{\mu\text{-}C_6H_5C(NC_6H_5)_2\}_2(CO)_4]$, which underwent a two-centre oxidative addition with iodine, yielding the rhodium(II) complex $[Rh_2\{\mu\text{-}C_6H_5C(NC_6H_5)_2\}\text{-}I_2(CO)_4]$. An "A" frame complex $[Rh_2\{\mu\text{-}C_6H_5C(NC_6H_5)_2\{\mu\text{-dppm}\}_2\text{-}(CO)_2]ClO_4$, (dppm $= (C_6H_5)_2PCH_2P(C_6H_5)_2$) was isolated from the reaction of $[Rh_2Cl_2(\mu\text{-dppm})_2(CO)_2]$, with $AgClO_4$ and $K\{C_6H_5NC(C_6H_5)NC_6H_5\}$.

Connelly et al. [140] found that the oxidation of the acetamidino compound $[Rh_2(CO)_3(PPh_3)(\mu\text{-}C_6H_5NC(CH_3)NC_6H_5\}_2$ provided a route to asymmetric species. The cyclic voltammogram of the above complex shows a reversible one-electron oxidation wave ($E° = 0.20$ V), and a second irreversible process at ca. 1.2 V. Reaction with $[Fe(n\text{-}C_5H_5)_2(PF_6)]$ gave a paramagnetic tricarbonyl $[Rh_2(CO)_3(PPh_3)\{\mu\text{-}C_6H_5NC(CH_3)NC_6H_5\}_2](PF_6)$, found to undergo substitution readily with donor ligands to give $[Rh_2(CO)_2(PPh_3)L(\mu\text{-}C_6H_5NC(CH_3)\text{-}NC_6H_5)_2(PF_6)]$ ($L = PPh_3$, $AsPh_3$ or $P(OPh)_3$). The $E°$ values suggested a facile chemical reduction, and reaction of these donor complexes with $[NBu^n_4][BH_4]$ in dichloromethane gave maroon neutral complexes $[Rh_2(CO)_2(PPh_3)L\text{-}\{\mu\text{-}C_6H_5NC(CH_3)NC_6H_5\}_2]$, which could not be prepared by thermal substitution of the original amidine complexes. The data recorded did not allow a distinction to be made between trapped valence Rh(I)–Rh(II) or delocalised $Rh^{1.5}$ species. Kadish and co-workers [141] prepared $Rh_2(PhNC(Ph)NPh)_4$ from the reaction of $Rh_2(O_2CCCH_3)_4$ with N,N'-diphenylbenzamidine, the structure with four bridging amidino groups being determined by X-ray crystallography. The complex was oxidised and reduced by reversible one-electron transfer processes, which were followed by cyclic voltammetry, and the products characterised by ESR spectroscopy. Bear et al. [205] attempted unsuccessfully to explain the unique Rh(II)–Rh(I) formation in $Rh_2(C_6H_5C(C_6H_5N)_2)_4^+$ by comparing the electrochemical properties and ESR parameters with those of complexes of the type $[Rh_2(O_2CCH_3)_3L]^+$ (L = various naphthylpyridines).

Piraino et al. [210] extended his study of rhodium amidine complexes, synthesising the mixed ligand complex $Rh_2(RNCHNR)_2(O_2CCF_3)_2(H_2O)_2$ from $Rh(C_6H_{12})(p\text{-}CH_3C_6H_4NCHNC_6H_4CH_3\text{-}p)$, and AgO_2CCF_3. The structure of the benzene solvate complex, determined by X-ray crystallography, showed the amidino ligand to be in the unusual cisoid arrangement, which, though not easily explained, may be due to steric factors. The complex forms 1:2 adducts with pyridine, dimethyl sulphoxide, piperidine, and 4-methylimidazole. Electrochemical studies in various solvents showed that the complex could undergo two sequential one-electron, quasi-reversible anodic processes, viz. Rh(II)Rh(II)/Rh(II)Rh(III) and Rh(II)Rh(III)/Rh(III)Rh(III). Of the anodic products, only the mixed Rh(II)Rh(III) derivative was found to be stable. Piraino and co-workers [254] have extended their previous work on $Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)_2(O_2CCF_3)_2(H_2O)_2$ by investigating the reactions of the complex with a number of phosphorus donors, including PPh_3, $P(C_6H_{11})_3$, $PCH_3(C_6H_5)_2$, $P(CH_3)_2C_6H_5$, $P(Bu^t)_3$, $P(Bu^n)_3$, $P(OCH_3)_3$, PPh_2H, and $P(CH_3)_3$. A simple 1:1 reaction yielded adducts of composition

$Rh_2\{CH_3C_6H_4NCHNC_6H_4CH_3\}_2\{O_2CCF_3\}_2L$. 1:1 or 1:2 ratio reactions at higher temperature (308 K) yielded the same adducts except in the cases of $P(OCH_3)_3$ and PPh_2H where there was an indication of dimer decomposition. ^{31}P and ^{19}F NMR studies of the complexes show an isomerisation mechanism in which the axial phosphine moves to an equatorial position with a concomitant change in bonding of a carboxylate from bridging to bidentate (Fig. 13).

Piraino et al. [217] have also investigated the chemistry of amidino complexes containing a Rh_2 core. Heating a mixture of $Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)_2(O_2CCF_3)_2(H_2O)_2$ and $CH_3C_6H_4NHCHNC_6H_4CH_3$ yields green platelets of $Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)_4$. The complex was characterised by X-ray crystallography, and was shown to consist of two rhodium atoms bridged by amidino groups in a "lantern"-type structure. The reaction of $Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)_4$ with carbon monoxide generated a remarkably stable monocarbonyl adduct $Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)_4 \cdot CO$ (^{13}C carbonyl resonance 144.06 ppm. rel. to TMS). Electrochemical studies of $Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)_4$ indicated two reversible redox changes Rh(II)Rh(II)/Rh(II)Rh(III), and Rh(II)Rh(III)/Rh(III)Rh(III). Cotton and Feng [255] applied molecular orbital calculations to the $Rh_2(Am)_4$ complex synthesised by Piraino et al. [217] as part of his study of metal–metal bonded systems. For a model compound with HNC(H)NH as the ligand, it was found that the energy of the metal–metal antibonding δ^* orbital was higher than that of the corresponding

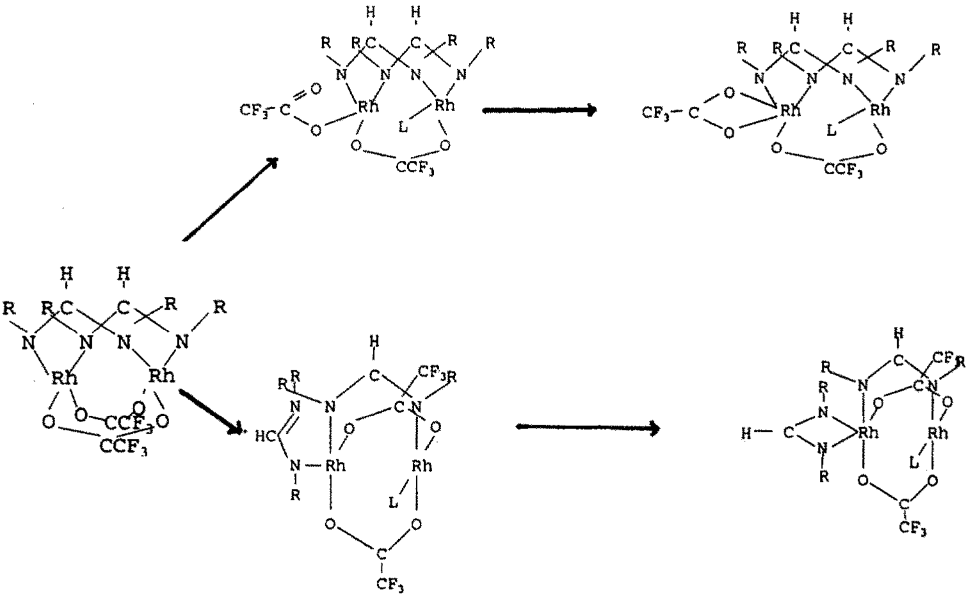


Fig. 13. Suggested structural changes following the coordination of phosphines L to $[Rh_2\{CH_3C_6H_4NCHNC_6H_4CH_3\}_2\{O_2CCF_3\}_2$[254].

antibonding π orbital. This was postulated to be a result of electronic effects from the ligands, i.e. the strong interaction between the orbital of the Rh_2 unit and the p-π ligand orbitals.

Piraino and co-workers [256] have extended studies on rhodium(I) amidino complexes to electrochemical studies of $Rh_2(COD)(CO)_2(Am)_2$ and $Rh_2(CO)_4(Am)_2$ (COD = 1,5-cyclooctadiene, Am = p-$CH_3C_6H_4NCHNC_6H_4CH_3$-p). In all cases, the sequential anodic processes observed, which involve changes in the molecular framework, were preceded by formation of the $[Rh_2L_4]$ monocation. Of note was the stability of the cation in comparison to the carboxylate complex analogues. In a further extension, Piraino and co-workers [257] have studied the effect of solvent–solute interactions on the redox potential of two "lantern" structure amidino complexes, viz. $Rh_2(O_2CCF_3)_2(Am)_2$ (**X**), and $Rh_2(Am)_4$ (**XI**) (Am = p-CH_3-$C_6H_4NCHNC_6H_4CH_3$-p). Attempts were made to correlate a number of empirical solvent parameters to changes in the redox potentials of **X** and **XI**. For **X**, the use of "acidic" parameters yielded a best fit, whereas for **XI**, a mixture of "acidic" and "basic" parameters was required. The conclusion reached was that the main solvent effect originates from coordination of a solvent molecule to the metal as an axial ligand. In the case of **XI**, there is not only a sigma type of interaction, but some pi interaction also.

Further, as part of their work on Rh_2 amidino complexes, Piraino and co-workers [225] have measured UVPES spectra of $Rh_2(Am)_2(O_2CCF_3)_2$ and $Rh_2(Am)_4$ (Am = N,N'-di-p-tolylformamidino). Using first-principle quantum mechanical calculations, a $(\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2})$ description of the electronic configuration of the complex was obtained, which was found to be in agreement with experimental results.

Initial studies of the thermal and photochemical properties of a rhodium(II) amidinate complex have been reported [226].

Preliminary electrochemical data reported by Cotton and Poli [211] for $[Ir\{CH_3\text{-}C_6H_4NC(H)NC_6H_4\text{-}CH_3\}(COD)]_2$ (COD = cyclooctadiene) when compared with those for $[Ir(L)(COD)]_2$ (L = 6-methylhydroxypyridinato, hydroxypyridinato, pyrazoylborato) indicated that the amidino complex was the best candidate for oxidation reactions. Cotton also extended the work of Piraino et al. [210] with rhodium to the iridium system (see Fig. 14).

A pyridine adduct was characterised by X-ray crystallography. One of the iridium atoms in the dimer may be thought to exist in a square-based pyramidal geometry, the coordination positions being occupied by two nitrogen atoms, two C=C bonds of the cyclooctadiene ligand and the second iridium atom. The second iridium may be thought to exist in an octahedral environment with two amidino nitrogen atoms, two trifluoroacetate oxygen atoms, the iridium atom and the pyridine ligand occupying the six positions. The short iridium–iridium distance (2.774 Å) is claimed as the first example of a dative Ir(I)···Ir(III) bond. Cyclic voltammetry studies of the complex and its adduct indicate that they undergo similar reduction

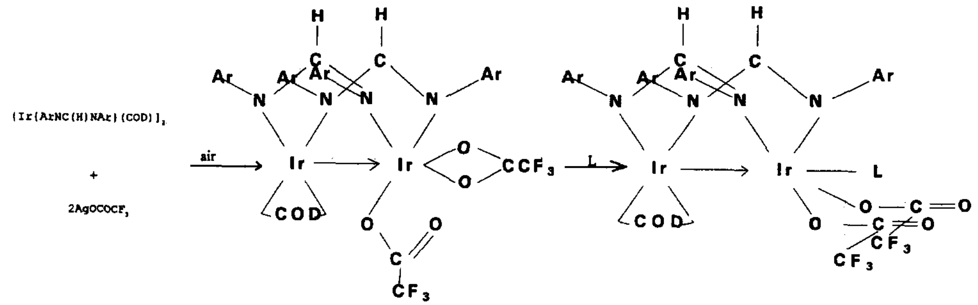


Fig. 14. Amidine = $CH_3C_6H_4NC(H)NC_6H_4CH_3$; COD = cyclooctadiene; L = C_5H_5N, H_2O, CD_3CN, $(CD_3)_2SO$. Formation of amidino/carboxylate complexes of iridium.

processes involving loss of an axial ligand. Further, the ease of exchange of the axially coordinated water in $(COD)Ir(CH_3C_6H_4NCHNC_6H_4\text{-}CH_3)_2\text{-}Ir(OCOCF_3)_2(H_2O)$ with pyridine gave $(COD)Ir(CH_3C_6H_4NCHNC_6H_4CH_3)_2\text{-}Ir(OCOCF_3)_2(C_5H_5N)$, and an unidentified orange powder. In an attempt to identify this unknown, Cotton and Poli [178] investigated its reaction with pyridine in detail. Treating $(COD)Ir(CH_3C_6H_4NCHNC_6H_4CH_3)_2Ir(OCOCF_3)_2(H_2O)$ with pyridine in hexane, and heating to 60°C yielded orange crystals of $[Ir_2(\mu\text{-}NC_5H_4)_2(CH_3C_6H_4NCHNC_6H_4CH_3)_2(NC_5H_5)_4]^+OCOCF_3^- \cdot 3(C_5H_5N)$. The amidino-group bridges the two Ir atoms, and the molecule contains ortho-metallated pyridines. The structure was confirmed by ^{13}C NMR, though it was not possible to differentiate between the "head and tail" configurations of the pyridines. The crystal structure of the complex showed disorder, with neither the trifluoroacetate nor the solvate pyridine molecule being clearly recognised. The closely related dinuclear cation $[Ir_2(\mu\text{-}NC_5H_4)_2(\mu\text{-}CH_3C_6H_4NCHNC_6H_4CH_3)(NC_5H_5)_2\text{-}(CH_3CN)_2]^+[B(C_6H_5)_4]^- \cdot 2CH_3CN \cdot (4.2CH_3CN)$ was prepared by treating the pyridine adduct with excess sodium borohydride in acetonitrile as solvent. The complex was characterised by X-ray crystallography, the amidine again bridging the Ir atoms [178].

Cotton and Poli [229] have extended the study of metal–metal bonded complexes, with the synthesis of $[Ir(Am)(COD)]_2$ and $[Ir_2(\mu\text{-}Am)(\mu\text{-}NH\text{-}p\text{-}C_6H_4CH_3)(COD)_2]$. The former iridium(I) dimers were synthesised by the reaction of $[IrCl(COD)]_2$ with $K\{CH(N\text{-}p\text{-}C_6H_4CH_3)_2\}$ in toluene, and the latter by partial alcoholysis produced by undertaking the same reaction in the presence of *t*-butyl alcohol (Am = $p\text{-}CH_3C_6H_4NCHNC_6H_4CH_3\text{-}p$; COD = cyclooctadiene). The former was characterised by infrared, and NMR spectroscopy as a dinuclear complex with two bridging amidino ligands and two chelating cyclooctadiene ligands, the Ir(I) atoms being presumed to exist in a square planar environment. The latter complex was characterised by X-ray crystallography, the structure again being dinuclear with amidino and *p*-toluido bridges and two chelating cyclooctadiene ligands.

Reversal of the formation reaction of the amidine from amine and orthoformate was put forward as a possible explanation of the partial hydrolysis reaction.

The shortest Ir—Ir bond recorded (2.524 Å) is claimed for a compound synthesised by Cotton and Poli [220]. The reaction of $[(COD)Ir(CH_3C_6H_4NCHNC_6H_4CH_3)_2Ir(OCOCF_3)_2H_2O]$ (COD = cyclooctadiene) with two equivalents of $CH_3C_6H_4NHCHNC_6H_4CH_3$ yielded green crystals of $Ir_2(CH_3C_6H_4NCHNC_6H_4CH_3)_4$. The structure is of the typical "lantern" type of bridged dimetallic amidine complexes.

Bear and co-workers [267] have continued their interest in the amidino–rhodium system by studying the spectro-electrochemistry of $Rh_2(PhNCHNPh)_4CO$ using a thin layer IR transmittance microcell. Monitoring of the CO band in the infrared spectrum showed that, in a mixture of dichloromethane and 0.01 M tetra-*n*-butyl ammonium perchlorate, and under 1 atm CO, the following occurred.

$$Rh_2(Am)_4CO \rightarrow [Rh_2(Am)_4CO]^+ \quad + e^-$$

$$\nu_1(CO) = 2050 \quad \nu_2(CO) = 2100\ cm^{-1}$$

During the electrooxidation, ν_1 decreases whilst ν_2 grows in intensity. Photochemical oxidation studies of $Rh_2(Am)_4$ complexes [270] with organochlorine compounds RCl (when $Am = C_6H_5NC(C_6H_5)NC_6H_5$, $C_6H_5NCHNC_6H_5$; $RCl = CCl_4$, $CHCl_3$, CH_2Cl_2, $C_2H_4Cl_2$, C_6H_5Cl, and C_6H_4ClCN). The complexes achieve a halogen abstraction reaction and one electron transfer after irradiation in the visible region. The amidine complexes are, however, less photochemically active than Rh_2(anilinopyridino)$_4$.

A number of amidine adducts of the type $[(NH_3)_5CoNH{=}C(NH_2)R]^{n+}$ have been prepared [268] from the aqueous recrystallisation of nitrile complexes in ammonia, in the presence of trishydroxymethylaminoethane, $NaClO_4$ or $HClO_4$, ($R = CH_3C_6H_4$, F-C_6H_4, $NO_2C_6H_4$).

Recent work [274] has extended the rich vein of chemistry of $[Rh_2(p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p)_2(O_2CCF_3)_2(H_2O)_2$ [210]. The complex is noted for its very labile trifluoroacetate groups, enabling neutral ligand coordination at the equatorial positions, as well as marked axial activity. Its reaction with 2-(diphenylphosphinopyridine, molar ratios 1:1 and 1:2, yield $Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)(O_2CCF_3)\{C_6H_5\}_2PC_5H_4N)(O_2CCF_3)$ (**A**), and $Rh_2(CH_3C_6H_4NC(H)NC_6H_4CH_3)_2(\{C_6H_5\}_2PC_5H_4N)_2(O_2CCF_3)$ (**B**), respectively. Characterisation was by infrared spectroscopy, NMR, and, in the latter case, X-ray crystallography. The complexes have a "lantern" structure with axial sites occupied by monodentate trifluoroacetate ligands. The two phosphorus ligands in the latter case are in a head-to-tail arrangement, giving a large Rh–Rh distance of 2.5406(6) Å. Reaction of **A** or **B** with halide ions (Br^-, Cl^-, I^-) resulted in partial or total substitution of the trifluoroacetato groups. Conductivity measurements in acetonitrile indicate the presence of $[Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)_2$-

(μ-O_2CCF_3)(μ-P{C_6H_5}$_2C_5H_4N$)$^+$ and $Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)_2$-($\mu$-{$C_6H_5$}$_2PC_5H_4N$)$_2^{2+}$, both of which were isolated as the PF_6 salts. In acetone, a similar reaction yielded [$Rh_2(CH_3C_6H_4NCHNC_6H_4CH_3)_2$($\mu$-P{$C_6H_5$}$_2C_5H_4N$)$_2$-($O_2CCF_3$)$\cdot PF_6$. The formation of the complexes was studied via variable-temperature ^{31}P NMR spectroscopy. The 1:1 mixture in $CDCl_3$ showed formation of a monoaxial adduct with a trace of the bis-axial at 310 K, and this adduct yielded a mixture of equatorial isomers. The 1:2 experiment yielded one equatorial isomer. The experiments were found to be solvent-dependent. Reaction of the complex with 1,2-bis(diphenylphosphino)ethane [294] led under mild conditions to ortho-metallation across the Rh—Rh bond, yielding the first example of a Rh(II)–(II) complex with three different bridging ligands and the first example of an ortho-metallated diphosphine.

A complex previously prepared by Piraino et al. [210], $Rh_2(CH_3C_6H_4NC(H)NC_6H_4CH_3)_2(O_2CCF_3)_2(H_2O)_2$, has recently been evaluated for its anti-tumour properties [282]. The amidine complex was administered in DMSO to rats, and found to exhibit anti-cancer activity against T8 sarcoma of Guerin, and Yoshida ascites sarcoma cells. A comparison with *cis*-$Pt(NH_3)_2Cl_2$ showed that the amidine complex exhibited the same anti-tumour activity but had lower toxicity.

The extensive interest of Bear et al. [283] in the chemistry of rhodium amidinato complexes has continued with a recent study of the effect of axial ligation on the oxidation state and molecular structure of such complexes. $Rh_2(PhNCHNPh)_4$ (**XII**) was synthesised from rhodium acetate by ligand addition. The complex formed was then placed in acetonitrile solution, which after several days of evaporation gave a second crystalline complex $Rh_2(C_6H_5NCHNC_6H_5)_4CH_3CN$ (**XIII**). Complex **XIII** was subjected to bulk hydrolysis in $C_2H_4Cl_2$ containing tetra-*n*-butylammonium chloride, and yielded [$Rh_2(C_6H_5NCHNC_6H_5)_4(CH_3CN)$]$ClO_4$ (**XIV**). All three complexes were characterised by X-ray crystallography, and all have structures containing a Rh—Rh bonded species bridged by amidinato ligands. Interestingly, the M—M bond length was found to be insensitive to changes in formal oxidation states or axial ligation. There were, however, slight changes in Rh—N bond lengths and N—Rh—Rh—N torsion angles. Electrochemical and ESR studies indicated that CN, Cl^- and CH_3CN complexation stabilises higher oxidation states, i.e. Rh_2(amidinato)$_4$ to [Rh_2(amidinato)$_4$]$^-$ occurs at the metal centres and yields stable products. Further, Rh_2(II) was found to be stable to CO but Rh(I)/Rh(II) was not.

Bear and co-workers [287] also reported recently the X-ray crystal structure of the previously synthesised [141] $Rh_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_4$ and made a comparison with the analogous cobalt complex, synthesised from lithiobenzamidine and bis(4-cyclohexylbutyrato)Co(II) in tetrahydrofuran. The structures were found to be similar, differences being attributable to the relative sizes of the metals. Hyperfine splitting in the ESR spectra indicated odd electron density being spread

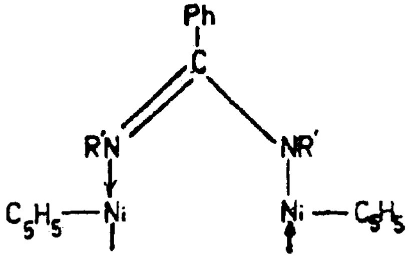


Fig. 15. The proposed structural unit in $(\eta^5\text{-}C_5H_5)Ni\{C_6H_5NC(C_6H_5)NC_6H_5\}_n$.

equally over two cobalt centres in $[Co_2(\text{amidinato})_4]^-$ and $[Co_2(\text{amidinato})_4]^+$. The visible spectra, redox reactions and ESR spectra of the rhodium and cobalt complexes were found to be similar. The cobalt complex showed little tendency to form axial adducts whilst the rhodium complex reacted with CO in dichloromethane, yielding $Rh_2(C_6H_5NC(C_6H_5)NC_6H_5)_4CO$, the complex being characterised by X-ray crystallography. The structure showed that ligation by CO resulted in changed bond distances and angles from the parent complex, primarily around the rhodium ion bound to CO, e.g. Rh–Rh distance increased by 0.046 Å, and the Rh–N bonds by 0.058 and 0.12 Å.

8.8 Platinum, palladium, and nickel

This triad of elements has received extensive attention from a number of workers. Treatment of $[(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl]$ with $C_6H_5N(Li)C(C_6H_5)NC_6H_5$ afforded a brown, insoluble involatile powder [96]. Analytically, data indicated the formulation $[(\eta^5\text{-}C_5H_5)Ni\{C_6H_5NC(C_6H_5)NC_6H_5]$, and its involatility and insolubility indicated a polymer. The infrared spectrum indicates bridging amidino groups. A proposed structure, with retention of an 18-electron configuration for the nickel atom is given in Fig. 15. The complex was found to be very resistant to chemical attack, and it clearly differs fundamentally from the known monomeric allyl derivative $[C_3H_5NiC_5H_5)$ [131].

A nickel *N*,*N'*-dinitrophenylformamidine tetrapyridine adduct was synthesised by Bradley and Wright [132], and tentatively formulated as shown in Fig. 16.

The synthesis of amidines by nucleophillic attack on a nitrile group by secondary amines has been investigated by Paul and Nag [215]. The reaction of $[NiL(NCR)]ClO_4$ (L = methyl-2-(R'CH_2CH_2)NH]cyclopenta-1-enedithiocarboxylate (R' = NH_2, NMe_2, NEt_2; R = CH_3, C_2H_5, C_6H_5) with R_2NH (R = CH_3, C_2H_5, *n*-Pr, NC_4H_8, NC_5H_{10}) yielded complexes of the type $[NiL(NH{=}CR(NR'_2)]ClO_4$. Proton NMR indicated the presence of E/Z isomers.

It was platinum which provided the first known amidine complexes, which were formed to assist in the analysis of amidines. The first complex was prepared in 1865 by Limpricht [133] by the reaction of *N*,*N'*-diphenylbenzamidine hydrochloride

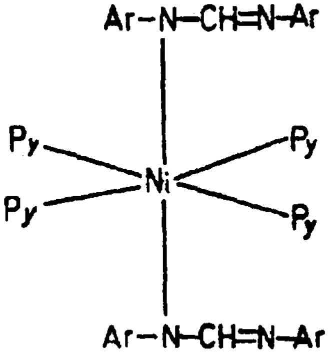


Fig. 16. Suggested structure for bis (*N*,*N*′–dinitrophenyl formamidino) nickel(II)tetrapyridine.

with platinum chloride, yielding a complex, identified by Pinner and Klein [134] as $\{RNC(R')NHR \cdot HCl)_2PtCl_4$. A number of similar platinum complexes followed [135–138,264,265]. Tschugaev and Lebedenski [266] prepared a platinum nitrile complex in which the platinum was thought to bond to four ammonia molecules and two acetonitrile molecules. The anomalous coordination number of the platinum(II) in the complex, supposedly six or five, led to a number of studies [142–144], but it was only when Stephenson [145] determined the structure that the true identity, $Pt(NH_3)_2\{CH_3C(NH_2)NH\}_2Cl_2 \cdot H_2O$, was recognised.

The reaction of amidines (R′N(X)C(R)NR′) (X = H or Li) with platinum or palladium compounds results in the formation of a variety of complexes, their nature depending on the amidine substituents, the metal and the synthetic route used. The reaction of $M(C_6H_5CN)_2Cl_2$ (M = Pt, Pd) with lithioamidines results in the formation of $Pt(Am)_2$, $Pd(Am)_2$, and $Pd_2(Am)_4$ complexes. The structure of $Pt\{C_6H_5NC(C_6H_5)NC_6H_5\}_2$ (XV) has been determined by X-ray crystallography [67] and shown to have a mononuclear structure with symmetrical bidentate ligands (see Fig. 17).

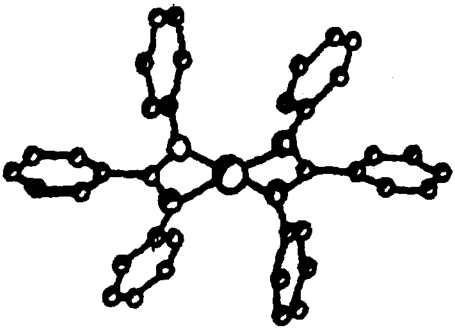


Fig. 17. X-ray crystal structure of $[Pt\{C_6H_5NC(C_6H_5)NC_6H_5\}_2]$ [67].

The palladium complexes have been shown to be dimeric in the case of formamidines ($R = H$) [146] by spectroscopic methods, monomeric and similar to **XV**, in the acetamidine case ($R = CH_3$) [73] by X-ray crystallography, and dimeric in the benzamidine case by spectroscopic methods [73]. Initial NMR studies by Barker and Kilner [147] indicated that, of the two possible dimer structures (Fig. 18), the asymmetric one was correct. Further higher oligomers were indicated in solution. The asymmetric structure was later confirmed by Bear and co-workers [246], the complexes in this case being synthesised from lithioamidine and palladium acetate. Further evidence for the complex solution chemistry for the $Pd_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_4$ complex was shown when, after reflux in methanol, the crystals formed had only bridging amidino groups present. The electrochemistry of the complex was also studied and indicated that the observed Pd(II)–Pd(III) oxidation was metal-centred. NMR (^{19}F) studies have indicated fluxionality when $M = Pd$, $R = C_6H_5$ [147].

Further, treatment of $NiCl_2 \cdot 0.3C_4H_{10}O_2$ with lithio-*N*,*N*′diarylbenz-, acet-, and formamidines results in the formation of $Ni_2(Am)_4$ complexes [67]. These extremely sensitive materials were characterised via elemental analysis, infrared, and mass spectroscopy. Cotton et al. [213] extended this work by reporting the characterisation by X-ray crystallography of two $M_2(Am)_4 \cdot 2H_2O$ complexes ($M = Pd$, Ni; Am = *N*,*N*′-di-*p*-tolylformamidino). The nickel complex was synthesised from $NiBr_2$, and the palladium from $Pd_3(OOCCH_3)_6$ by reaction with lithioformamidine. Recrystallisation in air yielded the aquo adducts. The complexes are isostructural and contain two metal atoms bridged by four amidino groups. No reductive processes were noted during cyclic voltammetry studies, but the complex did undergo oxidation, the final products being identified by controlled potential coulometry as $[M_2(Am)_4]^+$. Reports of formal Ni_2^{5+} species in the literature are rare, the Pd_2^{5+} unit being unknown. This initial work was later extended [214]. The formation of adducts of the palladium complexes with toluene and diethyl ether were described, the work being also extended to oxidation reactions, and molecular orbital calculations. The X-ray structures of $Ni_2(Am)_4 \cdot 2H_2O$, $Pd_2(Am)_4 \cdot 2H_2O$,

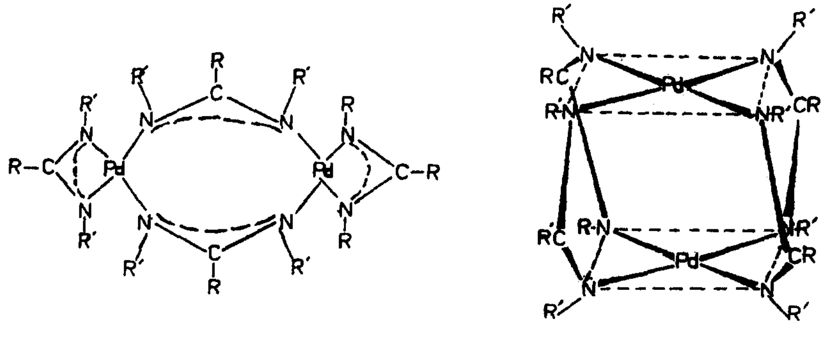


Fig. 18. Dimeric structures for $[Pd\{R'NC(R)NR'\}_2]_2$ complexes.

$Pd_2(Am)_4OC_2H_5$, $Pd_2(Am)_4PF_6$, and $Ni_2(Am)_4 \cdot BF_4$ (Am = *N*,*N*′-di-*p*-tolylformamidino) were all found to be similar, with the metal atoms being bridged by four formamidino ligands. Oxidation of the neutral complexes was achieved via electrochemical and chemical routes.

$$Pd_2(Am)_4 \cdot 2THF + AgPF_6 \xrightarrow{CH_2Cl_2} [Pd_2(Am)_4]PF_6 + Ag$$

$$Ni_2(Am)_4 \cdot 2H_2O + [Ag(CH_3CN)_2]BF_4 \xrightarrow{CH_2Cl_2} [Ni_2(Am)_4]BF_4 + Ag + CH_3CN$$

It was noted that chlorine did not effect oxidation of the complexes and oxidation from Pd_2^{4+} to Pd_2^{5+} and Pd_2^{6+} appears not to be possible, oxidation above Pd_2^{4+} occurring at the ligand. MO calculations showed that, on the basis of the orbitals available and despite the short metal–metal distances present in the complexes, e.g. 2.622(3) Å in $Pd_2(Am)_4 \cdot 2H_2O$, no metal–metal bonding exists.

Treatment of $Pt(C_6H_5CN)_2Cl_2$ with $\{HN(Li)C_6H_5NH\}$ resulted in nucleophillic attack at the nitrile and formation of $Pt\{HNC(C_6H_5)NC(C_6H_5)NH\}_2$, the structure of which was determined by X-ray crystallography (Fig. 19). The palladium analogues were polymeric in nature [83].

With K_2MCl_4 (M = Pt, Pd), *N*,*N*′-diarylamidines form ortho-metallated polymeric complexes (Fig. 20). The chloro-bridges can be cleaved by a variety of reagents, e.g. R′N(Li)C(R)NR′, R′N(Li)NNR′, $AgOOCCH_3$, NaC_5H_5, to form monomeric complexes [73,148].

Dorokhov [237] led one of two groups which have extended Kilner's original work on ortho-metallated amidine complexes with their work on the properties of a cyclopalladated *N*-phenylbenzamidine complex. Synthesis was achieved by two routes, the resultant products differing only in their linking groups. Li_2PdCl_4, sodium

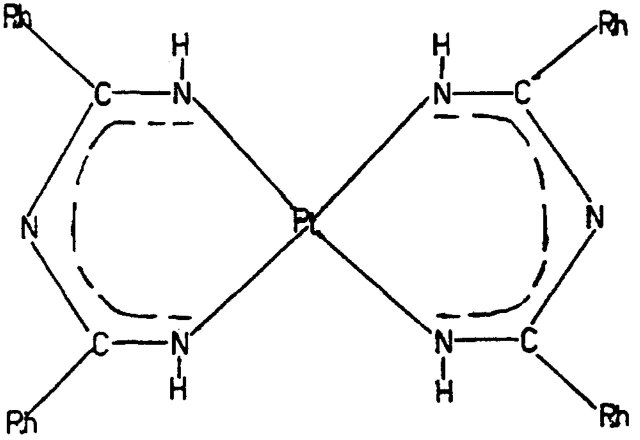


Fig. 19. X-ray crystal structure of $[Pt(HNC(C_6H_5)NC(C_6H_5)NH)_2]$[283].

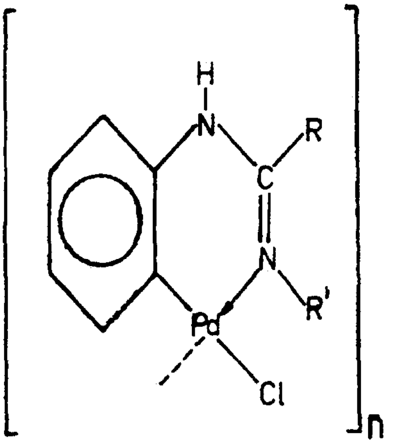


Fig. 20. Six-membered metallocycle formed from *N,N'*-diarylamidines and K_2PdCl_4.

ethanoate, and *N'*-phenylbenzamidine in refluxing methanol/water yielded **XVI**, and Pd(acetate)$_2$, sodium ethanoate, and *N'*-phenylbenzamidine in refluxing acetone yielded **XVII** (see Fig. 21). Reaction with pyridine yielded **XVIII**, with X = Cl or ethanoate, and a **XVII** to **XVI** conversion was found to be possible by stirring **XVII** with lithium chloride in acetone/water. Finally, carbonylation of **XVI** under mild conditions yielded **XIX**.

The second research group was that of Pfeffer and co-workers [233], which extended the chemistry of $\{(Pd\text{-}o\text{-}C_6H_5NHC(CH_3){=}NC_6H_5)Cl\}_n$ (see reaction scheme in Fig. 22). The reaction with pyridine and *t*-butyl isocyanate were used as evidence for **XX** (Fig. 22) existing as a chloro-bridged dimer rather than the polymeric structure postulated by Kilner and co-workers [73]. The complexes were analysed by ^1H NMR spectroscopy and elemental analysis. The pyridine derivative on the basis of elemental analysis and a ν(N—H)str. at ~3000 cm^{-1} in the infrared spectrum was assigned an ionic structure with a pyridinium cation. Complex **XXI** formed in the reaction of **XX** with $C_6H_5C{\equiv}CCOOC_2H_5$ was characterised via X-ray crystallography, the structure showing the result of insertion into the Pd—C carbon bond. $CH_3OCOC{\equiv}CCOOCH_3$ reacts differently producing a five-membered ring, as shown in Fig. 22. Palladium is coordinated in a distorted square-planar arrangement to the nitrogen substituent of the ortho-metallated phenyl ring, a carbon atom derived from the alkyne, chloride and oxygen of a COOR group.

A number of "mixed"-ligand amidine palladium complexes have been prepared and their properties studied. Vrieze and co-workers [149] synthesised both η^3-methylallyldi-*p*-tolylformamidino and acetamidino palladium complexes, $[(\eta^3\text{-}RC_3H_4)Pd(R'NCHNR')]_2$, by two methods, viz. by the reaction of two equivalents of silver amidine with $[(\eta^3\text{-}RC_3H_4)PdCl]_2$, and by the reaction of the amidine, in the presence of KOBu^t, with $[(\eta^3\text{-}RC_3H_4)PdCl]_2$. On the basis of molecular

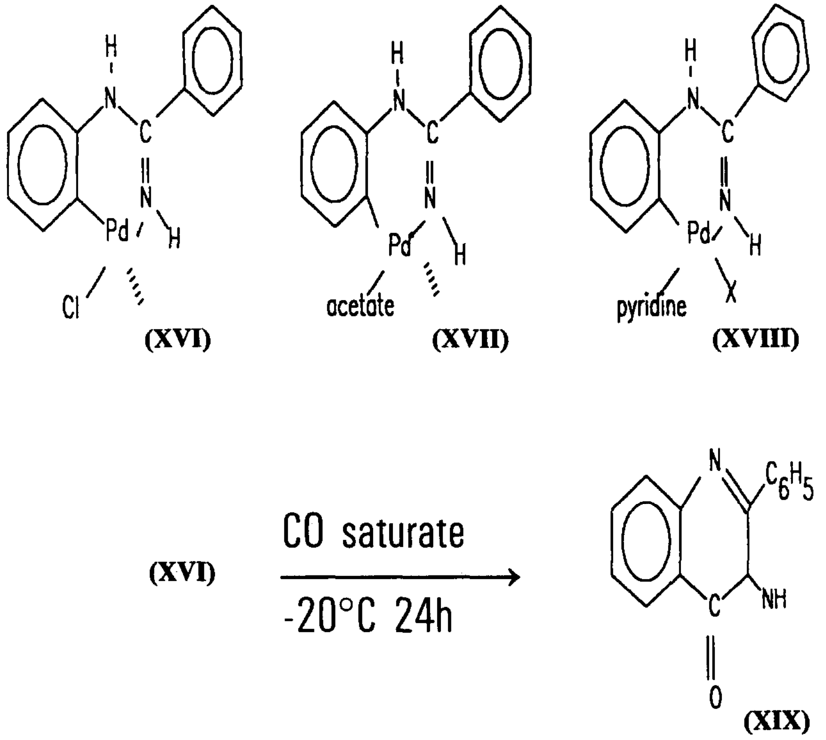


Fig. 21. Ortho-metallated amidino-complexes of palladium.

weight measurements, spectroscopic properties, and by analogy with the crystal structures of triazine complexes, it was concluded that the complexes were dimeric with bridging amidino groups.

Toniolo et al. have undertaken similar studies using the following reactions.

(1) $[Pd(\eta^3\text{-allyl})Cl]_2 + 2Li[RNC(H)NR] \rightarrow$

$[Pd(\eta^3\text{-allyl})\{RNC(H)NR\}]_2 + 2LiCl$ [150]

and

(2) $[Pd(\eta^3\text{-allyl})Cl]_2 + 2[RNHC(H)NR] \rightarrow 2PdCl\{RNC(H)N(H)R\}(\eta^3\text{-allyl})$ [151]

The first reaction produces a mixture of non-interconverting isomers (Fig. 23). The conformer which has equivalent allyl groups was found not to change with changes in temperature, whereas the other conformer at 80–100°C undergoes an intramolecular process which results in the allyl groups becoming equivalent. The presence of bridge splitting ligands such as dimethyl sulphoxide or *N*,*N*′-diarylformamidines, does not affect the process, which occurs without any palladium formamidino bond

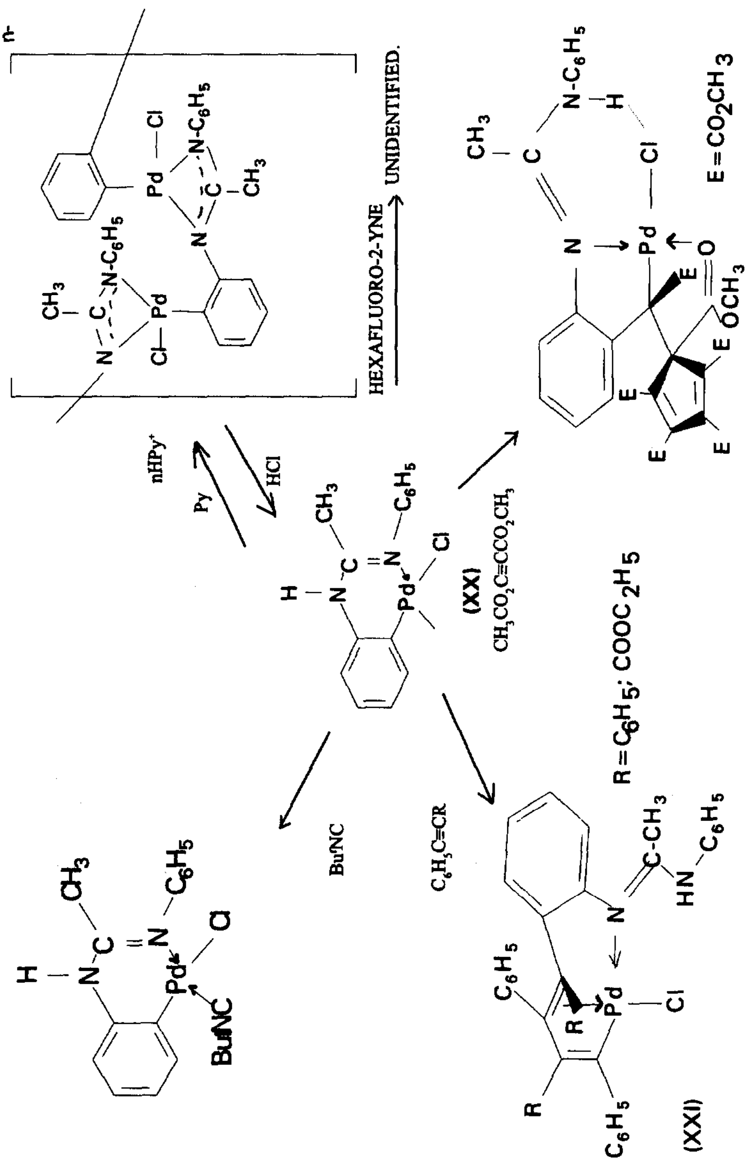


Fig. 22. Reaction chemistry of $[Pd\{o\text{-}C_6H_4NHC(CH_3)NC_6H_5\}Cl]_n$.

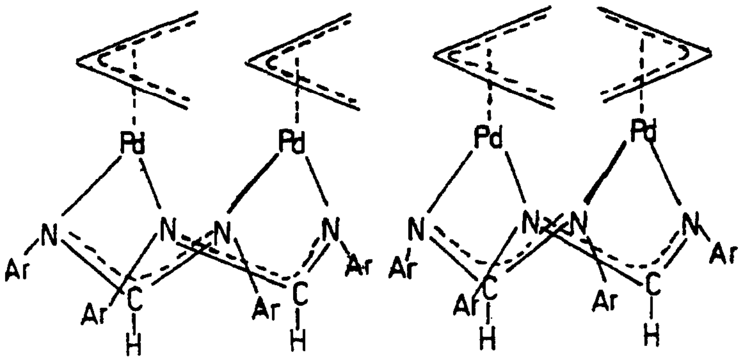


Fig. 23. Isomeric forms of $[Pd(\eta^3\text{-allyl})\{RNCHNR\}]_2$.

breaking, possibly through a broad inversion of the $C_2N_4Pd_2$ ring via a chair conformation.

The second reaction, which involves bridge splitting, gives products which show fluxionality, studied by variable-temperature ^1H and ^{13}C NMR. Two dynamic processes are thought to occur (see Fig. 24(a)). The first process (Fig. 24(a)), operating at room temperature, involves the dissociation of the dimeric amidine complex via cleavage of bridging ligands into monomers followed by recombination. The second process, which has a lower activation energy, was found to be concentration-dependent and involves chloride amidine exchange, thought to be via a penta-coordinated chloro-bridged species, (Fig. 24(b)). Interestingly, the mechanism indicates amino—nitrogen—metal bonding when imino—nitrogen—metal bonding is more likely. For complexes of the type $M(PPh_3)_2Cl\{RNC(H)NR\}$ (where M = Pd, Pt), synthesised by the reaction of $M(PPh_3)_2Cl_2$ with lithioamidines, ^1H NMR variable-temperature studies show a fluxional behaviour which has been interpreted as occurring via a penta-coordinated intermediate with both nitrogen atoms bound to the metal [146,152] (Fig. 24(c)).

Vrieze and co-workers [65] synthesised some monomeric amidine complexes using the route shown in Fig. 25. Similar palladium species have been synthesised, and in solution the neutral palladium species are fluxional, NMR studies indicating that a chelating amidine molecule is involved. Two of the monodentate amidine complexes were characterised by X-ray crystallography, $Pt\{C_6H_3(CH_2NCH_3)_2\}$-$\{CH_3C_6H_4N(H)C(H)NC_6H_4CH_3\}CF_3SO_3$ and $Pt\{C_6H_3(CH_2NCH_3)_2\}\{CH_3C_6$-$H_4N(H)C(H)NC_6H_4CH_3\}$. A recent preliminary communication by van Koten et al. [222] described the formation of copper(I) amidino complexes by the reaction of $[Pt(CH_3C_6H_4NC(H)NC_6H_4CH_3)(C_6H_3\{CH_2N(CH_3)_2\}_2\text{-}2,6)$ with copper chloride.

The mechanism of formation of amidine complexes by the reaction of the dimeric o-cyanobenzyl complex *cis*-$[Pt(o\text{-}CH_2\text{-}C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ with primary anilines has been investigated [153]. The first stage of this two-stage process

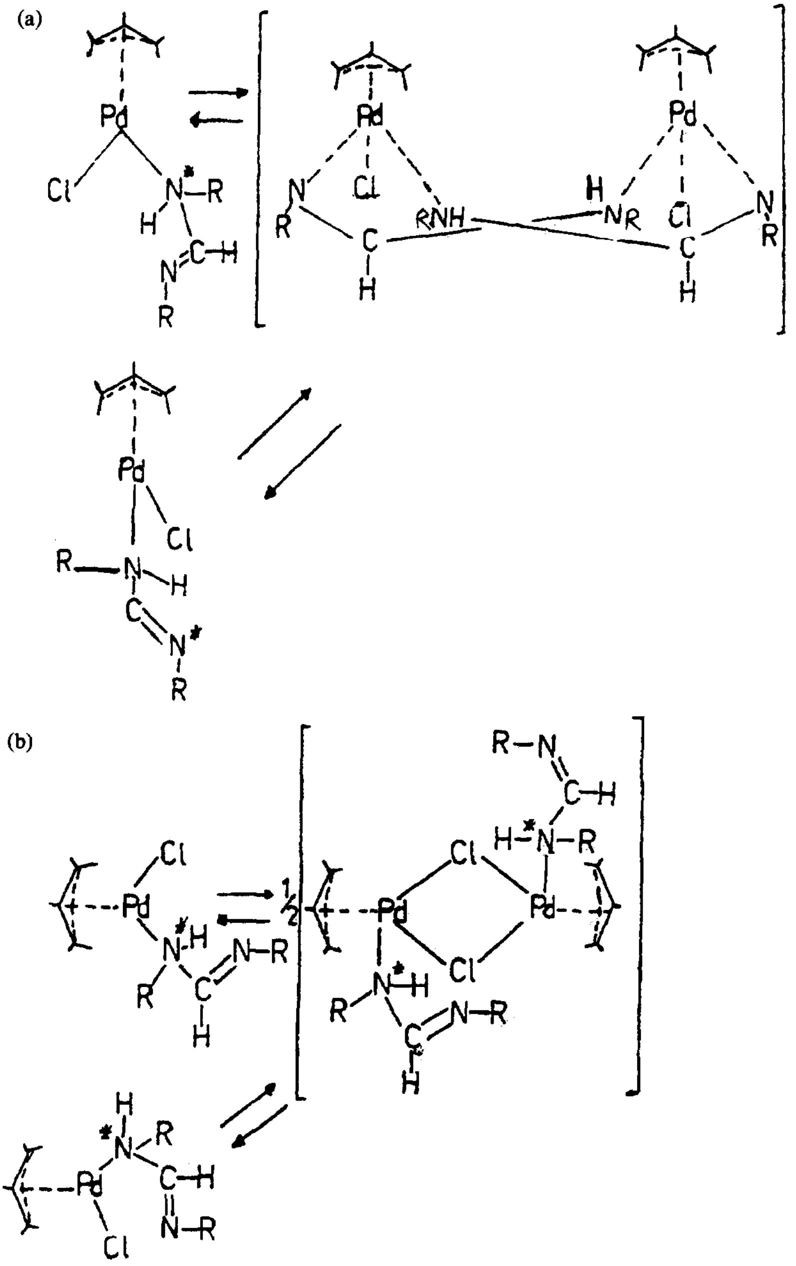


Fig. 24ab. Fluxional changes for [Pd(η^3-allyl){RNCHNHR}Cl].

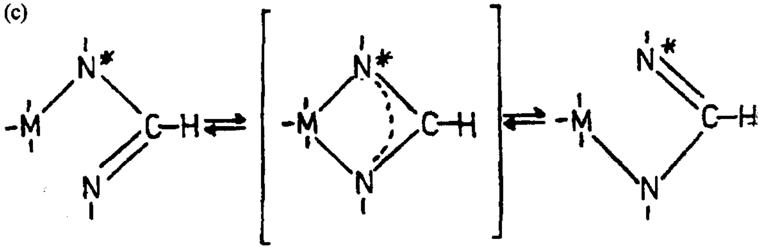


Fig. 24c. Fluxional changes for [Pd(η^3-allyl){RNCHNHR}Cl].

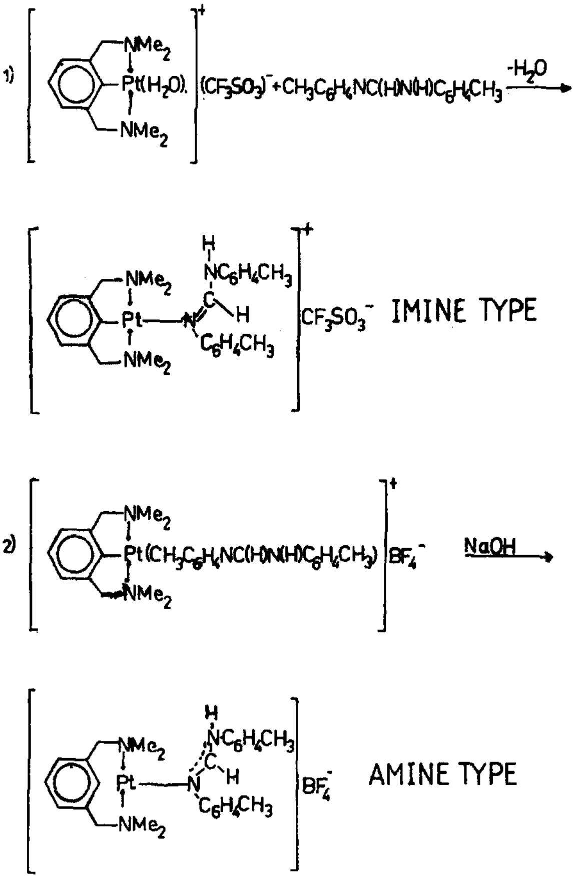


Fig. 25. Synthetic routes to monodentate amidino-complexes.

is thought to involve cleavage of the nitrile bridging group by the entering amine, leading to a labile mononuclear amine complex bearing a pendant CN group. The second slower stage is thought to involve its reaction with the amine, i.e. via nucleophilic attack by the amine nitrogen on the nitrile carbon to yield the platinum(II) amidino species (Fig. 26).

The barrier to haptotropic shifts within the formamidinato ligand in *cis*-$[Pt(PPh_3)_2Cl(HNC(H)NH)]$ has recently been the subject of qualitative extended Huckel MO calculations [219]. The value was similar to those found experimentally for *cis*- and *trans*-$[Pd(PPh_3)_2Cl(p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p)]$, which was obtained from NMR studies [152]. The shift, which has its organic counterpart in tautomerism, may occur in the complexes via a sliding mechanism, monodentate/bidentate interchange, or a Berry pseudo-rotation mechanism.

Further expansion of palladium formamidino chemistry has been undertaken by Uson et al. [250]. Various cis and trans complexes were synthesised, viz.

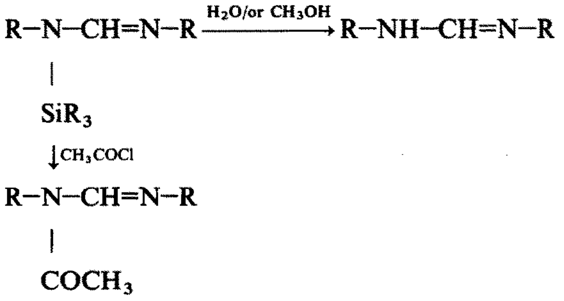
$$(NBu^n_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4] + 2Am\text{—}H \xrightarrow{CH_2Cl_2} cis\text{-}[Pd(C_6F_5)_2(AmH)_2] + 2(NBu^n_4)Br$$

$$[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(C_4H_9S)_2] + 2Am\text{—}H \xrightarrow{CH_2Cl_2} trans\text{-}[Pd(C_6F_5)Cl(AmH)_2] + C_4H_9S$$

$$cis\text{-}[Pd(C_6F_5)_2(AmH)_2 + PPh_3 \xrightarrow{CH_2Cl_2} [cis\text{-}Pd(C_6F_5)_2(AmH)(PPh_3) + Am$$

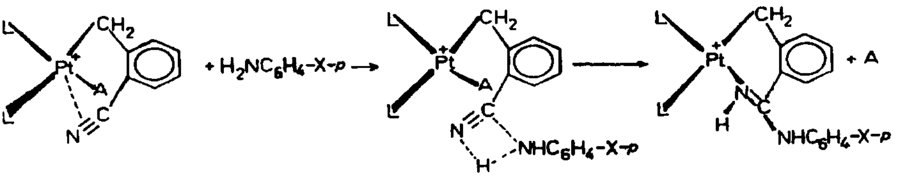
(AmH = di-*N*,*N'*-*p*-tolylformamidine). The complexes were characterised by ^1H and ^{19}F NMR and infrared spectroscopy, the data inferring that the amidino ligand is bonded in a monodentate fashion via its imino nitrogen. Further, $(Bu^n_4N)[Pd(C_6F_5)_2(CH_3C_6H_4NC(H)NC_6H_4CH_3)]$ was synthesised via the reaction of $[Ag(CH_3C_6H_4NC(H)NC_6H_4CH_3]_n$ and $(NBu^n_4)_2[Pd_2(C_6F_5)_4(\mu\text{-}Br_2)]$, and the reactivity of the product investigated (see Fig. 27).

A further reaction of note, which occurs in the presence of catalytic amounts of palladium chloride or tris(triphenylphosphine)chlororhodium, is the hydrosilation of carbodiimides to form *N*-silylformamidines in high yield [154]. The synthetic value of the products was shown by the reaction



$$\begin{array}{l} R\text{—}\underset{\displaystyle SiR_3}{\underset{|}{N}}\text{—}CH{=}N\text{—}R \xrightarrow{H_2O/\text{or } CH_3OH} R\text{—}NH\text{—}CH{=}N\text{—}R \\ \quad\downarrow CH_3COCl \\ R\text{—}\underset{\displaystyle COCH_3}{\underset{|}{N}}\text{—}CH{=}N\text{—}R \end{array}$$

Robson and co-workers [155,156] have used amidines as a bridging ligand in



X = p-OMe; p-Me; H
A = aniline, for example

Fig. 26. Amidine complex generated from a coordinated nitrile.

studies of palladium(II) complexes containing binucleating ligands (see Fig. 28(a) and (b)). The complexes were prepared as part of a synthetic project concerned with the generation of complexes containing a wide range of pairs of "soft" metal centres. Such complexes are of interest because of the possibilities they offer for new types of reaction at bridging sites such as those provided by the amidines.

The synthesis of $[(C_6H_5)_4P][C_6H_5C(NSi(CH_3)_3)_2PdCl_2]$ from $PdCl_2$, $(C_6H_5)_4PCl$, and $C_6H_5C(NHSi(CH_3)_3)N\{Si(CH_3)_3\}_2$, has recently been reported [295]. On reaction with HCl gas in acetonitrile solution, the complex yielded $[(C_6H_5)_4P][C_6H_5C(NH_2)NHPdCl_3]$, confirmed by X-ray crystallography of the acetonitrile solvate. Metal-to-amidine bonding occurs through the imido nitrogen.

In a further extension of the chemistry of the silyl benzamidine ligand, Edelmann [296] reacted $[(\eta^3\text{-}C_3H_5)PdCl]_2$ with $Li[C_6H_5C\{NSi(CH_3)_3\}_2]$ to yield $[C_6H_5C\{NSi(CH_3)_3\}_2Pd(\eta^3\text{-}C_3H_5)]_2$, a dimer which on hydrolysis gave $[C_6H_5C(NH)_2Pd(\eta^3\text{-}C_3H_5)]_2$. Characterisation by X-ray crystallography showed the presence of bridging unsubstituted benzamidinato groups.

8.9 Copper, silver, and gold

Copper and silver, like platinum, were studied in the very early years of transition metal amidine chemistry. Pinner and Klein [134] used silver complexes in a similar manner to those of platinum to analyse amidines, and Bradley et al. isolated a number of them [132,157]. The copper complexes of *N,N'*-di-anthraquinonylformamidine and -benzamidine were tentatively assigned the structure shown in Fig. 29 on the basis of its high solubility, chemical inertness, and the implied high degree of covalency between the copper and nitrogen atoms. The compound was later found to be tetrameric. It was formed from the reactions of cuprous chloride, cupric ethanoate or copper bronze with *N*-1-dianthraquinonylformamidine. The isomeric *N,N'*-1-anthraquinonylformamidines do not yield corresponding copper complexes. A number of green, unstable cupric *N,N'*-diarylformamidines were also synthesised and tentatively assigned the structure shown in Fig. 30 on the basis of molecular weight measurements and chemical reactivity.

Cotton et al. [235] have recently repeated Bradley and Wright's work with

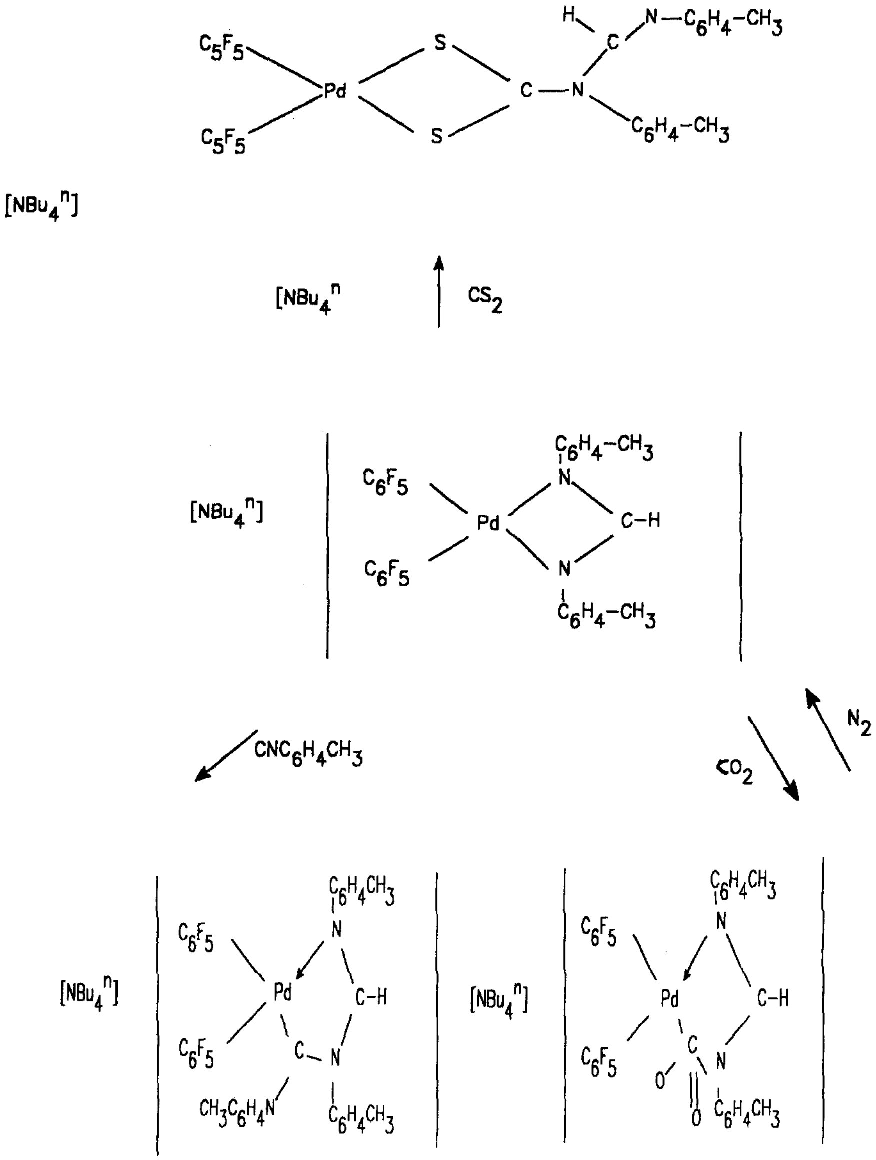


Fig. 27. Reaction chemistry of $[\mathrm{Bu}^n_4\mathrm{N}][\mathrm{Pd}(\mathrm{C_6F_5})_2\{\mathrm{CH_3C_6H_4NCHNC_6H_4CH_3}\}]$.

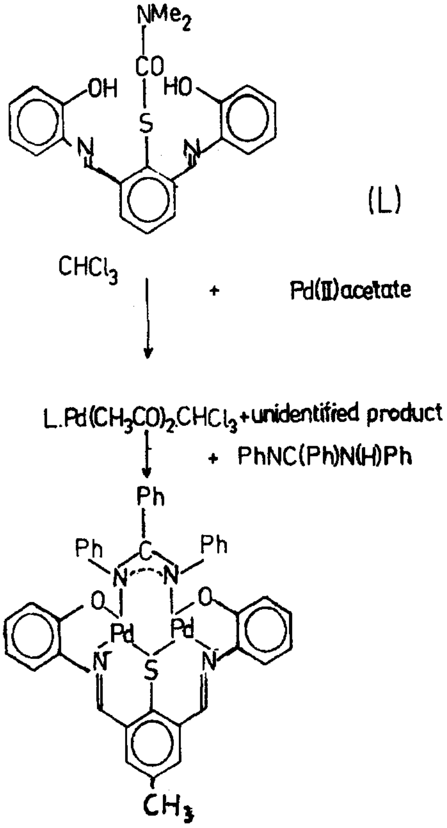


Fig. 28. (a) Preparation of amidino-palladium(II) complexes involving other binucleating ligands.

copper and silver [132] to synthesise $M_2\{p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p\}_2$ ($M = Cu$, Ag). The crystal structures of the two complexes were determined, and because of the M–M distances (Ag–Ag = 2.705(1) Å; Cu–Cu = 2.497 Å) an investigation of the possibility of M–M bonding in the complexes was carried out. Model $M_2(HNC(H)NH)_2$ compounds were used in molecular orbital calculations which indicated no net M–M bond formation. Attempts to produce $Au_2\{p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p\}_2$ analogous to the silver and copper complexes failed. Further attempts by Barker and Kilner [236] to produce gold amidino complexes from the reaction of $AuCl_3$ with lithioamidines has resulted in the production of difficult-to-characterise material.

An acetamidinium tetrachloroaurate complex [120,158,159], analogous to the cobalt complex already mentioned [120], has been synthesised and characterised by X-ray crystallography, optical spectroscopy and EPR spectroscopy. A structural model was proposed in which $CuCl_4^{2-}$ layers were separated by acetamidinium ions, the $CuCl_4^{2-}$ ions alternately occupying tetragonal and tetrahedral sites. This complex

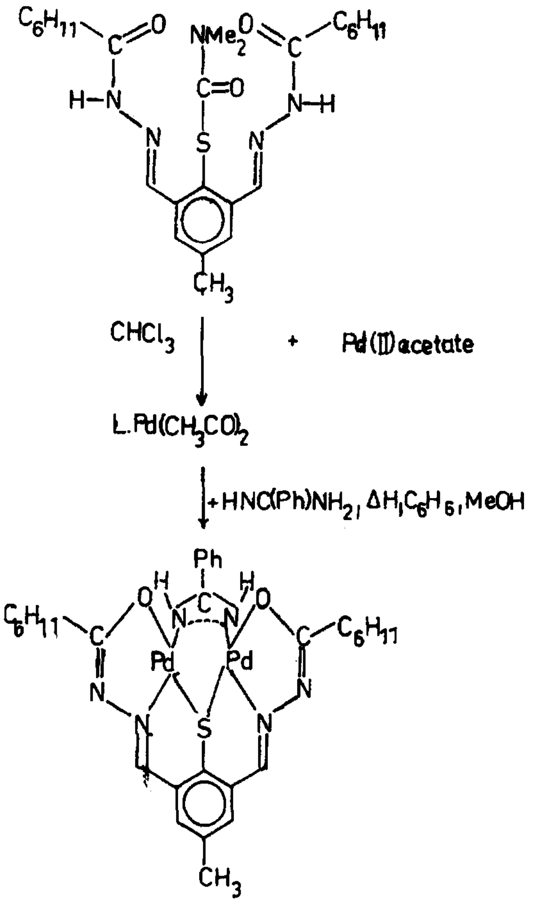


Fig. 28. (b) Preparation of amidino-palladium(II) complexes involving other binucleating ligands.

has also been the subject of a magnetic study [248] and found to be a weak pseudo-one-dimensional anti-ferromagnet, with the unusual property of one-dimensional ordering at 2.5 K, which changes to three-dimensional at 1.8 K. The magnetic data are consistent with the crystal structure, i.e. two types of distorted tetrahedral $CuCl_4$ anion linked by chains of acetamidinium ions.

Carboxylato-analogue copper(I) and copper(II) amidine complexes have been investigated by Kilner et al. [160,161]. Lithioamidines (R'N(Li)C(R)NR', R = H, CH_3, C_6H_5; R' = C_6H_5, p-$CH_3C_6H_4$) react with anhydrous copper(II) chloride to form $[Cu\{R'NC(R)NR'\}_2]_n$ complexes, and with anhydrous copper(I) chloride to form $[Cu\{R'NC(R)NR'\}]_m$. The Cu(II) complexes are air-stable in the solid state and diamagnetic. Experimental data indicated a dimeric structure which was proven by X-ray crystallography [161]. The structure has four bridging amidine groups and a

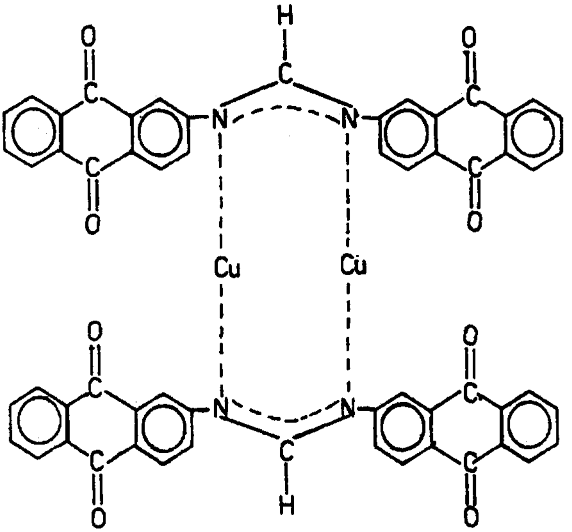


Fig. 29. Structure originally proposed for *N*,*N'*-di-anthraquinonylformamidinocopper(I).

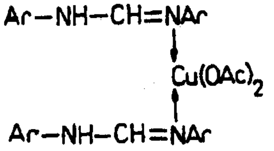


Fig. 30. Proposed structure of $[Cu(CH_3COO)_2(ArNHCHNAr)_2]$.

short Cu–Cu distance (2.46 Å). The Cu(I) complexes are less stable, decomposing rapidly in air when in solution, and reacting in the following manner.

$$Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2 + C_5H_5N \rightarrow Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2 \cdot C_5H_5N$$

$$Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2 + CS_2 \rightarrow Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2CS_2 \rightarrow$$
$$Cu\{C_6H_5NC(CH_3)NC_6H_5\}CS_2$$

Interestingly, thermogravimetric analysis indicates that thermal decomposition does not occur in simple ligand loss steps as might be expected, but involves complex pathways. In solution, the Cu(I) complexes vary in their degree of disproportionation to Cu(0) and Cu(II), stability decreasing from formamidines to acetamidines to benzamidine complexes. Solutions of formamidine complexes show hardly any sign of disproportionation, and a detailed study of dimer–dimer and dimer–tetramer equilibria for these complexes has been carried out by Vrieze and co-workers [162]. Also, initial studies of thermal and photochemical properties of copper(III) amidinates have been reported [226].

A number of copper and silver formamidine complexes $[M\{RNC(H)NR'\}]_n$

(R = *p*-tolyl, R′ = CH_3, C_2H_5, i-propyl, *t*-butyl, C_6H_{11}; $n = 2, 4$) were prepared and studied by ^1H, and ^{13}C NMR, as a function of temperature, concentration, metal atom, and alkyl substituent, and they demonstrated the presence of dimeric and tetrameric isomers (Fig. 31). Only one metal—nitrogen bond in each dimer is required to be broken and two new metal—nitrogen bonds to be formed to give four tetrameric isomers. Conclusions from the study were (i) the size of the alkyl substituents determines the relative ratios of the tetramers, (ii) increasing the temperature causes a corresponding dimer/tetramer ratio increase, (iii) increasing bulk of alkyl substituents causes a corresponding increase in the dimer/tetramer ratio, and (iv) the dimer/tetramer ratio is increased when silver(I) is replaced by copper(I).

A recent spectrophotometric determination of Au(III) involved the formation of yellow $HAuX_4(HA)_2$ salts (X = Cl, Br, I; HA = *N*,*N*′-diphenylbenzamidine) [207].

Studies by Dehnicke and co-workers of the reactions of the trimethylsilylbenzamidinato ligands have been extended to copper [258–261]. Characterisation of two complexes was carried out by X-ray crystallography and infrared spectroscopy. The copper(I) complex $Cu_2[C_6H_5C\{NSi(CH_3)_3\}_2]_2$ was prepared from copper chloride in refluxing acetonitrile. An interesting feature of the white dimeric crystals was a short Cu–Cu distance of 2.42 Å, similar to that reported previously by Kilner and co-workers [160,161] for the copper(II) complex, $Cu_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_4$. Coordination occurred via bridging amidino ligands. Further, copper(II) chloride by the same synthetic route yielded $C_6H_5C(NSi(CH_3)_3)_2CuCl[C_6H_5C(NSi(CH_3)_3)(NHSi(CH_3)_3)]$, which when characterised by X-ray crystallography was found to contain a bidentate chelating and a monodentate amidine ligand in a mononuclear complex. Again, as part of a further study of the chemistry of the *N*,*N*,*N*′-tris(trimethylsilylbenzamidine) ligand, $AuCl_2[C_6H_5C(NSi(CH_3)_3)_2]$ has been prepared by the reaction of *N*,*N*,*N*′-tris(trimethylsilyl)benzamidine [271] with

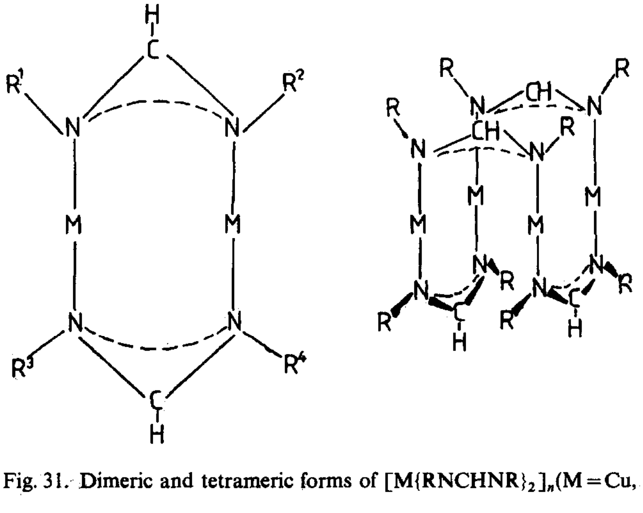


Fig. 31. Dimeric and tetrameric forms of $[M\{RNCHNR\}_2]_n$(M = Cu, Ag; $n = 2,4$).

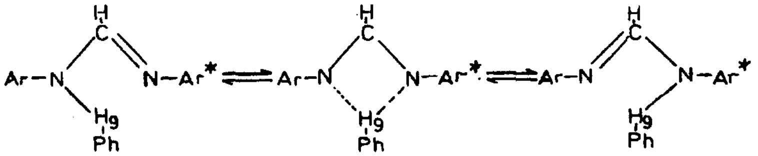


Fig. 32. Fluxional changes for [PhHg(ArNCHNAr)] in solution.

$AuCl_3$ in dichloromethane. Related silver and gold complexes were characterised by X-ray crystallography as square planar, with bridging amidino ligands. Further, $M_2[(C_6H_5C(NSi(CH_3)_3)_2)]_2$, where M = Ag(I), or Au(I), were prepared by reaction of the amidine with either AgO_2CCH_3 or ClAuCO [284]. Both complexes, characterised by X-ray crystallography and infrared spectroscopy, are dinuclear with similar structures to *N*,*N*′-di-*p*-tolylformamidinosilver, previously described by Cotton et al. [235]. Short metal–metal contacts were noted [Ag–Ag 2.652(2) Å, and Au–Au 2.646(2) Å], the two amidino groups bridging the metals.

Hartmann and Strahle [285] has elegantly synthesised a gold(I) *N*,*N*′-diphenylformamidino complex from the sodium salt of the amidine and gold(I) iodide in liquid ammonia. The complex was characterised by X-ray crystallography and found to be tetrameric in the solid state with four gold atoms forming a planar rhombus (Au–Au, 2.597 Å, 3.277 Å). The amidino ligands are bridging, arranged above and below the Au_4 rhombus.

8.10 Zinc, cadmium, and mercury

A number of complexes of the type $MX_2(\text{amidine})_n$, (M = Zn, Cd, Hg; X = Cl, Br) have already been described along with the cobalt analogues [121].

The reaction of equimolar quantities of phenylmercury hydroxide and *N*,*N*′-diarylamidines in ethanol yielded complexes of the type $C_6H_5Hg\{ArNC(H)NAr\}$ [66]. NMR studies indicate that the equilibrium shown in Fig. 32 occurs. Further, an X-ray structure determination of $C_6H_5Hg\{p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p\}$ showed two independent molecules to be present. One complex contains a monodentate amidino ligand (Fig. 33(a)), the

Fig. 33. Structural forms of $[PhHg\{CH_3C_6H_4NCHNC_6H_4CH_3\}]$ determined by X-ray crystallography [66].

other a chelate ligand (Fig. 33(b)), thus providing support for the above equilibrium process.

The exchange mercuration of phenoxy radicals has been studied and it was found that **XXI** (Fig. 34) reacted with the mercury complex **XXII**, to yield **XXIII** and *N*,*N*′-di-*p*-tolylbenzamidine [218].

One of the earliest ortho-metallated complexes known was formed by the reaction of mercury(II) ethanoate with *N*,*N*′-di-*p*-tolylformamidine [132]. The structure (Fig. 35) was assigned on the basis of the reaction of the product with iodine, which gave *N*-(2-iodo-4-methylphenyl)-*N*′-phenylformamidine.

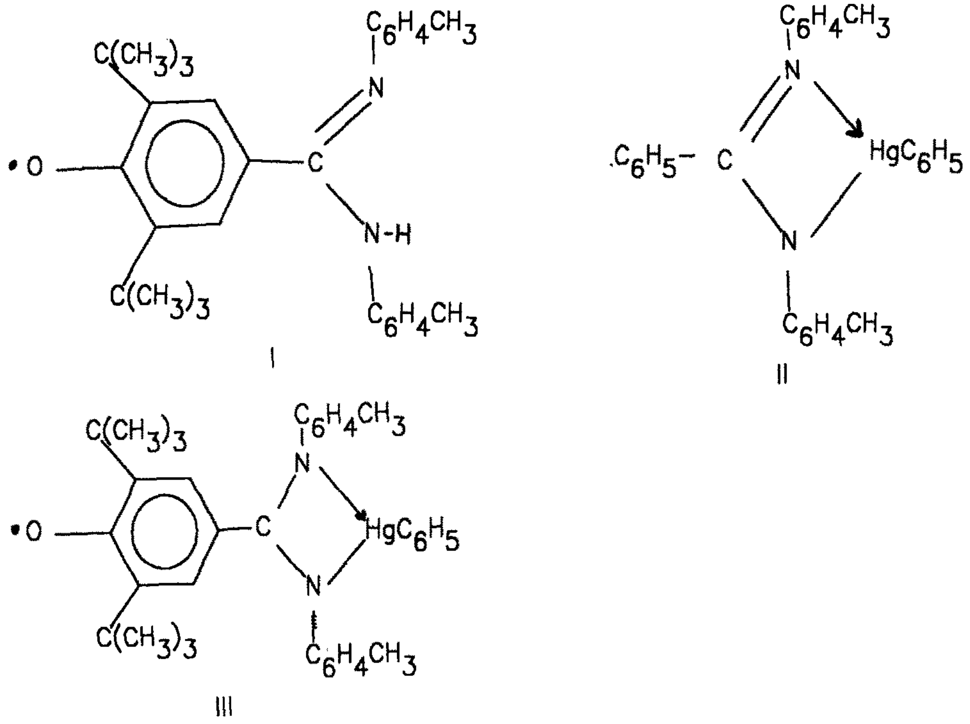


Fig. 34. Exchange mercuration of phenoxy radicals.

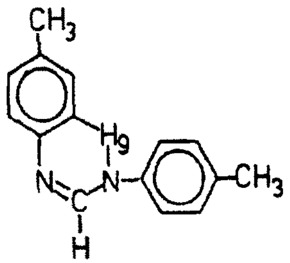


Fig. 35. Structure of the complex derived from mercury(II)ethanoate and *N*,*N*′-di-*p*-tolylformamidine.

As part of the comprehensive coverage of the chemistry of the N,N,N'-tris(trimethylsilyl)benzamidine ligand, Dehnicke and co-workers found its reaction with mercury(II) ethanoate in boiling acetonitrile gave $Hg[C_6H_5C\{NSi(CH_3)_3\}_2]_2$ [291] characterised by X-ray crystallography as having an almost centrosymmetric structure containing two monodentate amidino groups.

Marsh [208] has recently redetermined the X-ray crystal structure of $Zn(C_4H_8N_2O_6)$ and found it to be $[Zn(HCO_2)_3]^-[HC(NH_2)_2]^+$, i.e. formamidinium tris(methanato)zinc(II), and not bis(methanamide)methanatozinc(II). The salt was formed by refluxing $ZnCl_2$ and methanoic acid in methanamide, and then allowing the solution to stand for one week. The formamidinium ions are not coordinated to the zinc atoms but are hydrogen bonded to adjacent methanoate groups.

Barker [147] has recently investigated the reaction of zinc alkyls with amidines and isolated $Zn(Am)_2$ complexes, and further, the reaction of $ZnCl_2$ with $Na[C_6H_5C\{NSi(CH_3)_3\}_2$ was found to yield bis-trimethylsilylzinc(II) [297].

8.11 *Mixed-metal amidine complexes*

Dinuclear complexes containing a metal–metal bond are intermediate between mononuclear complexes and compounds with linear stacks of metals, clusters, and ultimately pure metal. Amidines have proved excellent for linking metals, for example in producing mixed-metal dinuclear compounds, and they have been extensively studied by Vrieze.

Complexes of the type $[(diene)\{RNC(Y)NR'\}_2RhHgCl]$ (diene = 1,5-cyclooctadiene, norbornadiene; $Y = H$; $R = R' = i\text{-}Pr$; $R = CH_3$, i-Pr, $p\text{-}CH_3C_6H_4$; $R' = p\text{-}CH_3C_6H_4$ and $Y = CH_3$; $R = R' = p\text{-}CH_3C_6H_4$), were prepared from the reaction of $[(diene)RhCl]_2$ with $Hg\{RNC(Y)NR'\}_2$ [163]. NMR data indicated that the molecules consist of a rhodium atom coordinated by a bidentate amidino group, HgCl and a nitrogen atom of an amidino group, which bridges the rhodium–mercury bond. ^{13}C NMR studies indicated that, for $R = p\text{-}CH_3C_6H_4$, the complexes are fluxional, involving an interchange of the bridging and chelating amidino groups via monodentate intermediates.

$[(PPh_3)_2(CO)IrCl]$ reacts with $[M\{RNC(H)NR'\}]_n$ ($M = Cu$, Ag; $R = CH_3$, C_2H_5, t-Bu, cyclohexyl; $R' = p\text{-}CH_3C_6H_4$; $n = 2, 4$) to yield $[(PPh_3)_2(CO)IrM\{RNCHNR'\}]$ complexes in which the Ir–M bond is stabilised by a bridging formamidino group [164]. The ease of formation and stability of the complexes were found to be Ir(I) > Rh(I) and Ag(I) > Cu(I), and small R groups > large R groups. The bulk of the substituent R groups on the amidino nitrogen atoms was found to influence which nitrogen bonded to a particular metal. When the NR group was small in bulk, it bonded to either iridium or silver, thus producing two isomers. When R was large in bulk, the NR group only bonded to the silver because of the steric influence of the two phosphine ligands on iridium. The corresponding rhodium compounds could not be isolated.

The complexes [{2,6-((CH$_3$)$_2$NCH$_2$)$_2$C$_6$H$_3$}(*p*-CH$_3$C$_6$H$_4$NCHNR)PtHgXY], (R = CH$_3$, C$_2$H$_5$, i-Pr; X = Cl, Y = Br) were prepared by Vrieze and co-workers [165] by the reaction of [{2,6-((CH$_3$)$_2$NCH$_2$)C$_6$H$_3$)}PtBr] with [Hg(*p*-CH$_3$C$_6$H$_4$NCHNR)Cl], or in lower yield from the exchange reaction of [{2,6-((CH$_3$)$_2$NCH$_2$)$_2$C$_6$H$_3$}(RCO$_2$)PtHg(O$_2$CR)Br] with *p*-CH$_3$C$_6$H$_4$NC(H)NC$_2$H$_5$. One of the complexes [{2,6-((CH$_3$)$_2$NCH$_2$)$_2$C$_6$H$_3$}Pt(μ-{CH$_3$C$_6$H$_4$NC(H)-NC$_3$H$_7^i$})HgBrCl] has been characterised by X-ray crystallography (Fig. 36) [70]. The five-membered ring is thought to act as a stabilising factor. The absence of a subsequent electron transfer reaction may be due to the constraints of the terdentate

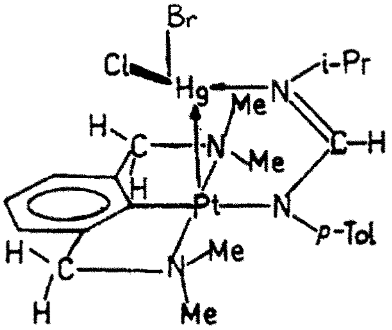


Fig. 36. X-ray crystal structure of [{2,6-((CH$_3$)$_2$NCH$_2$)$_2$C$_6$H$_3$}Pt(μ-{CH$_3$C$_6$H$_4$NCHNC$_3$H$_7^i$})HgBrCl].

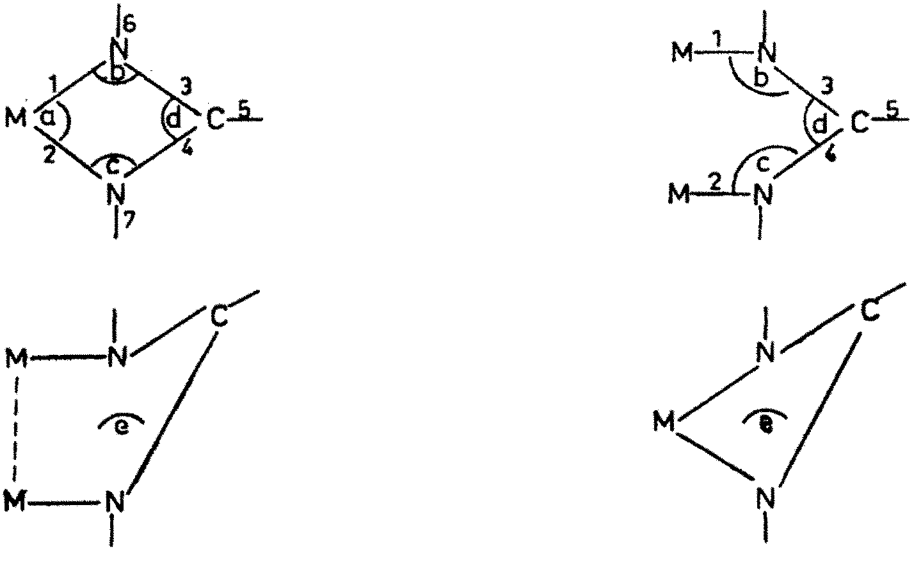


Fig. 37. Key to data in Table 3.

TABLE 3

X-ray structural parameters of amidines and amidino complexes

Compound [Ref.]	Bond length								Bond angles				
	Structure (Fig. 3)	1	2	3	4	5	6	7	A	B	C	D	E
$TiCl_2\{(CH_3)_3SiNCC_6H_5NSi(CH_3)_3\}_2$ [249]	b	2.106(5)	2.066(5)	1.331(8)	1.344(8)	–	–	1.492(9)	64.9(2)	–	–	–	–
$[Ti\{C_6H_5\text{-}C(NSi(CH_3)_3)_2\}Cl_3]_2$ [258]	b	2.072(2)	1.986(2)	1.322(4)	1.351(4)	1.494(4)	1.791(2)	1.787(3)	66.7(1)	87.5(2)	90.3(2)	113.3(2)	–
$[Zr\{C_6H_5\text{-}C(NSi(CH_3)_3)_2\}Cl_3]_2$ [258]	b	2.189(3)	2.140(3)	1.328(5)	1.346(5)	1.496(5)	1.776(5)	1.769(4)	62.8(1)	89.3(2)	90.8(3)	114.9(3)	–
$Zr(C_5H_5)_2Cl\{C_6H_{11}NC(H)NC_6H_{11}\}$	c												
	I	2.252(4)	2.298(4)	1.328(6)	1.309(6)	–	1.477(6)	1.473(6)	58.1(2)	94.8(3)	93.3(3)	113.8(5)	“planar”
Asymmetric unit with two crystallographically dependent molecules [84]	II	2.275(5)	2.310(5)	1.329(8)	1.305(6)	–	1.479(7)	1.472(7)	57.6(2)	94.7(3)	93.8(3)	113.9(5)	“planar”
$V_2\{p\text{-}CH_3C_6H_4NC(H)NC_6H_4\text{-}CH_3\text{-}p\}_4$-$C_6H_5CH_3$ [286]	f	2.092(4)	2.12(4)	–	–	–	–	–	–	–	–	–	“planar”
$V\{p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p\}_2$-$\{C_5H_5N\}_2$ [230]	b	2.175(3)	2.200(4)	1.328(7)	1.323(5)	–	–	–	61.5(1)	92.1(2)	91.2(3)	115.2(4)	“planar”
Two independent molecules in the structure	b	2.189(5)	2.194(4)	1.328(6)	1.325(7)	–	–	–	61.7(2)	91.2(3)	91.2(3)	115.2(4)	“planar”
$V(C_5H_5)\{p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p\}_2$	b	2.110(5)	2.094(5)	1.307(9)	1.313(8)	–	1.417(6)	1.416(7)	62.8(2)	91.6(4)	92.1(4)	113.5(6)	“planar”
[230]		2.107(5)	2.122(6)	1.310(9)	1.313(7)	–	1.424(5)	1.424(7)	62.0(2)	92.6(3)	91.9(4)	112.3(6)	
$TaCH_3Cl_2\{C_3H_7\text{-}N\text{-}C(CH_3)N\text{-}C_3H_7\}_2C_6H_6$	c	2.174(22)	2.073(24)	1.39(4)	1.23(4)	1.56(5)	–	–	59.7(9)	91.3(13)	101.1(20)	107.8(27)	“planar”
(monoclinic) [172]		2.112(20)	2.226(19)	1.43(4)	1.26(4)	1.56(4)	–	–	61.9(8)	93.1(16)	92.9(17)	112.2(25)	
$TaCl_3\{C_3H_7NC(CH_3)NC_3H_7\}_2$ (orthorhombic).	(I)	2.182(20)	2.176(23)	1.35(4)	1.33(3)	1.56(4)	1.45(4)	1.45(3)	61.9(9)	91.9(16)	92.7(17)	113.4(24)	“planar”
	c,b	2.114(19)	2.209(21)	1.30(3)	1.32(3)	1.52(4)	1.38(4)	1.44(5)	58.6(8)	98.3(16)	93.2(16)	109.1(22)	
Two independent molecules opposite	(II)	2.122(18)	2.171(22)	1.27(3)	1.35(3)	1.46(4)	1.51(4)	1.43(3)	59.3(8)	99.9(15)	95.0(16)	106.4(21)	
enantiomorphs (I) and (II) [170]		2.135(18)	2.223(20)	1.41(3)	1.25(3)	1.50(4)	1.54(4)	1.47(4)	59.8(8)	94.8(15)	95.7(17)	109.6(23)	
$TaCl_3\{C_6H_{11}NC(CH_3)NC_6H_{11}\}_2$ (tetragonal)	c,b	2.168(19)	2.159(19)	1.34(4)	1.40(4)	1.51(5)	–	–	61.7(8)	95.7(19)	94.2(15)	108.3(24)	“planar”
[171]		2.089(22)	2.158(23)	1.33(4)	1.33(4)	1.56(5)	–	–	61.6(9)	96.1(18)	93.0(18)	109.2(27)	
$TaCH_3Cl_2\{C_6H_{11}NC\{CH_3)NC_6H_{11}\}_2$ [68]	c,b	2.160(17)	2.149(19)	1.37(3)	1.39(3)	1.48(3)	1.49(3)	1.43(3)	61.9(38)	95.9(12)	95.9(13)	106.2(17)	“planar”
		2.040(17)	2.187(17)	1.40(3)	1.27(3)	1.50(3)	1.53(3)	1.50(3)	60.4(58)	95.6(13)	98.1(12)	105.8(17)	
$TaCl_3\{C_3H_7NC(CH_3)NC_3H_7\}_2$ (monoclinic)	b	2.098(14)	2.193(16)	1.36(3)	1.36(3)	1.54(3)	1.47(3)	1.43(3)	62.4(6)	96.2(11)	92.0(12)	109.4(16)	“planar”
~~[169]~~		2.058(15)	2.180(20)	1.36(3)	1.32(3)	1.55(3)	1.49(3)	1.49(3)	60.1(7)	99.4(14)	95.1(14)	105.4(20)	
$[TaCl_4NC(C_6H_5)N\{Si(CH_3)_3\}_2]_2 \cdot 2CH_2Cl_2$ [269]	a	1.835(8)	–	1.32(1)	1.34(1)	–	1.826(8)	1.50(1)	–	162.7(7)	–	123.3(9)	“non-planar”
		–	–	–	–	–	1.830(8)	–	–	–	–	–	
$Ta(\eta^5\text{-}C_5(CH_3)_5F_3(NSiCH_3)_2C\text{–}C_6H_4OCH_3$ [277]	b	2.187(4)	2.199(4)	1.321(7)	1.327(6)	1.498(7)	1.782(4)	1.764(4)	60.8(1)	92.6(3)	91.9(3)	113.9(4)	–
$TaCl_3(C_6H_{11}NC(CH_3)NC_6H_{11})(C_6H_{11})$-$NC(NHC_6H_{11})O)$ (monoclinic) [171]	b	2.148(19)	2.112(18)	1.30(3)	1.28(3)	1.57(3)	–	–	59.8(8)	92.6(15)	94.8(15)	111.2(18)	“planar”
$Cr_2\{CH_3NC(C_6H_5)NCH_3\}_4$ [90]	f	2.025(5)	2.024(5)	1.332(7)	1.318(7)	1.496(8)	1.471(7)	1.472(7)	–	115.7(4)	115.9(4)	116.6(5)	“planar”
		2.036(4)	2.043(5)	1.351(7)	1.339(7)	1.467(8)	1.458(7)	1.450(7)	–	115.5(3)	115.9(4)	116.1(5)	
$Cr\{C_6H_5C(NSi(CH_3)_3)_2\}_2$ [297]	b	2.100(4)	2.092(4)	1.330(5)	1.334(6)	–	–	–	65.3(1)	89.2(3)	89.1(3)	116.4(4)	–
		2.096(3)	2.095(3)	1.331(7)	1.332(5)	–	–	–	65.4(1)	89.2(2)	89.0(2)	116.4(4)	

TABLE 3 *(continued)*

Compound [Ref.]	Bond length								Bond angles				
	Structure	1	2	3	4	5	6	7	A	B	C	D	E
$Mo_2\{$2,6 xylyl $NC(CH_3)N($2,6 xylyl$)\}_2$-$(CH_3CO_2)_2\cdot 4C_4H_8O$ [91]	f	2.156(5)	2.167(5)	1.337(7)	1.333(7)	1.523(8)	1.443(7)	1.456(7)	–	119.1(4)	118.9(4)	117.5(5)	"planar"
$Mo_2(C_6H_5NC(CH_3)NC_6H_5)_3(CH_3CO_2)$ [91]	f	2.161(5)	2.160(5)	1.342(7)	1.329(7)	1.520(9)	1.425(7)	1.428(7)	–	119.3(4)	119.3(4)	116.1(5)	"planar"
		2.151(5)	2.115(4)	1.321(7)	1.338(7)	1.541(8)	1.441(7)	1.421(8)	–	118.4(4)	119.8(4)	116.1(5)	
		2.140(5)	2.132(5)	1.360(7)	1.340(7)	1.512(8)	1.418(7)	1.418(7)	–	119.6(4)	120.1(4)	115.0(6)	
$Mo(CO)_2\eta$-$C_5H_5(C_6H_5NC(CH)_3NC_6H_5)$ [98]	b	2.176(3)	2.169(3)	1.320(4)	1.320(4)	1.498(5)	1.416(4)	1.407(4)	58.9(1)	96.4(2)	96.7(2)	108.0(3)	"planar"
$Mo(CO)_2(R''$-$C_5H_4)$	(Ia)	2.175(7)	2.199(6)	1.300(11)	1.295(11)	1.52(1)	1.440(4)	1.453(10)	59.2(2)	94.4(5)	93.4(5)	112.8(8)	3.38
$\{(HCC_6H_5R)$-$NC(C_6H_5)N(HCC_6H_5R')\}$ (I), $R'' = R' = H$, $R = CH_3$	(Ib)	2.173(6)	2.190(7)	1.310(10)	1.303(9)	1.50(1)	1.456(9)	1.474(9)	59.0(2)	95.4(5)	94.9(5)	110.5(7)	2.01
(II), $R'' = R' = H$, $R—CH_3$ difference only in the conformation at $CH(CH_3)C_6H_5$ substituent at the benzamidine ligand	(II)	2.149(6)	2.177(6)	1.299(9)	1.291(9)	1.48(1)	1.461(9)	1.460(8)	58.8(2)	96.1(5)	95.0(0)	110.1(7)	1.14
(III), $R'' = H$, $R' = R = CH_3$ differs from I and II in that both nitrogens of the benzamidine ligand bear optically active substituents of composition $(CH—(CH_3)—C_6H_5)$	(III)	2.186(7)	2.134(7)	1.323(9)	1.365(10)	1.48(1)	1.466(10)	1.467(10)	60.7(2)	94.7(6)	95.8(5)	108.5(8)	5.70
(IV), $R'' = R' = R = CH_3$ and it has optically active substituents at both benzamidine ligand nitrogens. Note Ia, Ib – two independent molecules in the asymmetric unit [99]	(IV)	2.187(6)	2.148(5)	1.332(8)	1.310(9)	1.491(8)	1.466(9)	1.478(8)	59.7(2)	94.0(5)	96.2(4)	110.0(7)	2.65
$Mo_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_4$ [69]	f	2.125(9)	2.149(5)	1.32(1)	–	1.56(2)	1.45(1)	1.44(1)	–	118.6(7)	–	118.0(1)	"planar"
		2.163(10)	2.149(5)	1.38(1)	1.33(1)	1.37(2)	1.43(1)	1.44(1)	–	119.9(8)	118.3(4)	114.0(1)	
		2.149(5)	–	1.36(1)	1.33(1)	1.51(1)	1.44(1)	–	–	117.2(5)	–	118.0(1)	
		2.149(5)	–	1.36(1)	–	1.51(1)	1.44(1)	–	–	–	–	118.0(1)	
$MoCl_4\{i$-$(C_3H_7NC(Cl)NC_3H_7$-$i\}$ [111]	b	2.079(4)	2.079(4)	1.319(5)	1.319(5)	–	1.465(7)	1.465(7)	63.0(2)	93.1(3)	93.1(3)	110.8(5)	"planar"
$MoO_2\{(CH_3)_3SiNC(C_6H_5)NSi(CH_3)_3\}_2$ [249]	b	2.105(7)	2.290(8)	1.340(12)	1.327(4)	–	–	1.514(14)	60.8(3)	–	–	–	–
		2.310(7)	2.112(7)	1.307(12)	1.339(12)	–	–	1.505(14)	60.4(3)	–	–	–	–
$\{\eta^5$-$(CH_3)C_5H_4\}Mo(CO)_2\{HCC_6H_5(CH_3)N—C(C_6H_5)NCH_2C_6H_5(CH_3)\}$ [212]	b	2.157(7)	2.170(7)	1.30(1)	1.34(1)	1.47(1)	1.50(1)	1.48(1)	59.3(3)	97.2(6)	95.3(6)	108.1(8)	−0.055
$\{\eta^5$-$(CH_3)C_5H_4\}Mo(CO)_2\{HCC_6H_5CH_3NC(C_6H_5)NCH_2C_6H_5$ [212]	b	2.151(5)	2.192(5)	1.327(8)	1.317(8)	1.479(7)	1.445(7)	1.483(8)	59.5(2)	96.5(4)	94.9(4)	109.2(6)	−0.082
$Mo(\eta^2-(CH_3)_2NCN$-$2,6(CH_3)_2C_6H_3)_4$ [209]	–	2.205(2)	2.181(2)	1.336(7)	–	–	–	–	–	–	–	–	–
		2.278		1.297									
$Mo_2(O_2CC_6H_5)_2\{C_6H_5C(NSi(CH_3)_3)_2)\}_2$ [290]	b	2.151(6)	–	1.335(8)	–	1.53(2)	1.77(1)	–	–	116.6(5)	–	120.3(9)	–
$Mo_2\{CH_3C_6H_4NC(H)NC_6H_4$-$CH_3\}_4PF_6$ [247]	f	2.161(10)	2.149(9)	1.358(15)	1.34(2)	1.435(15)	–	–	–	117.9(8)	118.0(8)	119.0(1)	–
$W_2\{C_6H_5NC(CH_3)NC_6H_5\}_2$-$(C_6N_2OH_7)_2\cdot 2C_4H_8O$ [92]	f	2.11(1)	2.11(1)	1.32(2)	1.40(2)	1.53(2)	1.48(2)	1.40(2)	–	118.1	123.0(1)	115.0(1)	"planar"

$[W_2(CO)_2\{HC(NR)_2\}_2\{RNCHN(R)CH_2\}$; R = 3,5xylyl [72]	f and	2.13(3)	2.12(3)	1.33(5)	1.32(5)	–	1.44(5)	1.42(4)	–	120.0(3)	120.0(2)	124.0(3)	"planar"
		2.13(3)	2.11(3)	1.32(5)	1.34(4)	–	1.42(4)	1.50(5)	–	122.0(2)	123.0(3)	120.0(3)	
	b and	2.26(3)	2.31(3)	1.28(5)	1.28(3)	–	1.43(5)	1.29(4)	57.0(1)	93.0(3)	91.2(2)	119.0(4)	"planar"
	i	1.45(6)	2.20(3)	1.32(5)	1.36(6)	–	1.47(6)	1.41(4)	78.0(1)	107.0(3)	110.0(2)	123.0(4)	"planar"
		$-CH_2-$	–	–	–	–	–	–	–	(N-CH_2-			
		2.26(5)	–	–	–	–	–		–	W)	–	–	
$[W(CO)_5(NH{=}C(C_6H_5)N(CH_3)_2]$ [223]	a	2.243(5)	–	1.303(7)	1.349(7)	1.486(8)	1.464(7)	–	–	135.9(5)	–	123.8(6)	"planar"
		–	–	–	–	–	1.446(7)	–	–	–	–	–	
$W(\eta^5C_5H_5)_2Br(C_2H_6N_2)PF_6$ [292]	salt	2.21(2)	–	1.37(3)	1.27(3)	1.50(3)	–	–	–	–	–	116.2	–
trans-$Tc(P(CH_3)_2C_6H_5)_2(CO)_2\{C_6H_5NC(CH_3)NC_6H_5\}$ [204]	b	2.202(2)	2.203(2)	1.326(3)	1.331(4)	1.502(4)	1.396(4)	1.394(4)	59.0(1)	95.8(2)	95.6(2)	109.4(2)	0.055
$Re_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_2Cl_4(C_4H_8O)$ triclinic [114]	f	2.08(1)	2.09(1)	1.34(2)	1.31(2)	1.48(2)	1.45(2)	1.43(2)	–	121.0(1)	120.0(1)	116.0(2)	"planar"
		2.07(1)	2.06(1)	1.32(2)	1.37(2)	1.50(2)	1.44(2)	1.45(2)	–	121.0(1)	119.0(1)	118.0(1)	
$Re(PPh_3)_2(CO)_2(C_6H_5NC(H)NC_6H_5)$ [173]	b	2.22(1)	2.22(1)	1.32(1)	1.34(1)	–	1.41(2)	1.39(2)	60.0(1)	94.0(1)	94.0(1)	112.0(1)	"nearly planar"
$Re(CO)_4(CH_3CO)_2(C_6H_5C(NH_2)_2)$ [77]	salt	–	–	1.301(7)	1.314(7)	1.488(9)	1.04(10)	1.02(7)	–	–	–	122.8(7)	"amidine planar"
		–	–	–	–	–	0.9(2)	0.95(9)	–	–	–		
$Re_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_2Cl_4$ monoclinic [114]	f	2.06 (2)	2.06(2)	1.34(3)	1.37(3)	1.49(3)	1.44(3)	1.41(3)	–	120.0(2)	120.0(2)	116.0(2)	"planar"
$Re_2(C_6H_5NC(CH_3)C_6H_5)_2Cl_4$ [112]	f	2.08(2)	2.08(2)	1.31(1)	1.37(2)	1.53(3)	1.43(3)	1.43(2)	–	119.8(14)	118.6(14)	118.5(20)	
		2.02(1)	2.07(2)	1.37(2)	1.36(3)	1.51(3)	1.50(2)	1.43(2)	–	121.1(13)	119.7(14)	115.2(18)	
$Re_2(CH_3NC(C_6H_5)NCH_3)_4Cl_2 \cdot CCl_4$ [112]	f	2.055(9)	–	1.32(1)	–	1.56(2)	1.54(2)	–	–	120.4(9)	–	–	–
$[FeCl_4][C_6H_5\text{-}C(NHSi(CH_3)_3]_2]$ [273]	ion	–	–	1.341(9)	1.313(10)	1.496(9)	1.801(7)	1.794(7)	–	–	–	122.4(6)	–
		–	–	–				–	–	–	–	–	
$FeCl[C_6H_5C(NSi(CH_3)_3)_2]_2$ [289]	b	2.109(9)	1.997(8)	1.290(1)	1.360(1)	1.490(1)	1.751(9)	1.757(9)	66.4(3)	86.8(6)	89.7(6)	116.7(9)	–
$FeCl_6\{HC(NH_2)_2\}_3$ [126]	salt	–	–	1.281(9)	1.17(9)	–	–	–	–	–	–	121.0(9)	"planar"
		–	–	–	–	–	–	–	–	–	–	119.0(9)	
$RuCl(PPh_3)_2CO\{CH_2{=}C(CH_3)NC(H)NCH(CH_3)_2\}$ [262]	c	2.048(10)	2.242(10)	1.328(14)	1.300(14)	–	1.406(15)	1.498(14)	61.1(4)	–	–	112.6(10)	"planar"
trans-$RuH(PPh_3)_2CO(CH_3C_6H_4NC(H)NC_6H_4\text{-}CH_3)$ [174]	b	2.183(5)	2.248(5)	1.308(7)	1.315(7)	–	1.418(5)	1.428(6)	59.8(2)	94.3(3)	91.2(4)	114.7(5)	"planar"
$Ru_2\{p\text{-}CH_3C_6H_4NC(H)NC_6H_4\text{-}CH_3\text{-}p\}_4$ [288]	f	2.045(7)	2.041(7)	1.330(11)	1.313(12)	–	–	–	–	119.8(6)	120.3(6)	123.1(8)	"planar"
		2.046(7)	2.019(7)	1.318(12)	1.337(12)	–	–	–	–	120.7(6)	121.5(6)	121.4(8)	
$Os_3(\mu\text{-}H)(CO)_9\{NC_6H_5\text{-}C(C_6H_5)NH\}$, I,II, Independent molecules in the asymmetric unit [75]	kI.	2.198(23) Os(1)–N(1)	2.141(22) Os(3)–N(2)	1.417(39)	1.243(36)	–	–	–	–	–	–	121.7(25)	–
		2.193(23) Os(3)–N(1)	–	–	–	–	–	–	–	–	–	–	
•	II.	2.132(19)	2.174(20)	1.464(37)	1.242(40)	–	–	–	–	–	–	115.3(20)	–
		2.188(20)	–	–	–	–	–	–	–	–	–	–	
$PPh_4[Cl_5Os\{NC(CCl_3)NCCl(CCl_3)\}] \cdot CH_2Cl_2$ [119]	a	1.97(1)	–	1.34(1)	1.35(1)	1.55(1)	–	1.28(1)	–	142.1(8)	–	120.4(10)	–
$Na\{(NH_3)_3Co(\mu\text{-}OH,\mu NH_2,\mu\text{-}CH_3C(NH)_2\}Co(NH_3)_3\}(S_2O_6) \cdot H_2O$ [221]	f	1.907(4)	1.895(3)	1.300(5)	1.318(5)	1.496(6)	–	–	–	128.1(3)	128.0(3)	121.5(4)	"planar"

TABLE 3 *(continued)*

Compound [Ref.]	Bond length								Bond angles				
	Structure	1	2	3	4	5	6	7	A	B	C	D	E
$CoCl_4\{H_3CC(NH_2)_2\}_2$ [120]	salt	–	–	1.3321	1.3214	1.499	–	–	–	–	–	122.0326	central C atom slightly below plane
				1.3300	1.3285							120.6015	
$Co_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_4$ [287]	f	1.953(3)	1.926(3)	1.339(7)	1.346(7)	1.485(8)	1.427(7)	1.408(7)	–	–	–	–	"planar"
		1.944(5)	1.943(5)	1.344(7)	1.332(7)	1.503(5)	1.423(7)	1.427(7)	–	–	–	–	
$\{Co(CO_3)(C_2H_6N_2)_4\}Cl\cdot 2H_2O$ (four independent acetamidinium ions) [300]	salt	1.927(5)	–	1.298(8)	1.348(7)	1.499(6)	–	–	–	–	–	121.9(2)	"planar"
		1.913(6)	–	–	–	–	–	–	–	–	–	–	
		1.942(6)	–	–	–	–	–	–	–	–	–	–	
		1.932(6)	–	–	–	–	–	–	–	–	–	–	
$Rh\{C_6H_5NC(C_6H_5)NC_6H_5\}(C_8H_{12})$ [139]	b	2.106(6)	2.095(6)	1.356(9)	1.331(9)	1.490(8)	1.415(11)	1.411(10)	63.2(2)	92.8(4)	94.0(4)	110.0(6)	"planar"
$Rh_2\{\mu\text{-}C_6H_5NC(C_6H_5)NC_6H_5\}_2(C_{12}F_4H_6)_2$ [139]	f	2.125(4)	2.093(5)	1.350(7)	1.346(7)	1.501(6)	1.442(6)	1.429(5)	–	120.8(4)	126.2(4)	118.1(5)	"non-planar"
		2.086(6)	2.138(4)	1.317(9)	1.339(7)	1.502(7)	1.445(6)	1.431(7)	–	124.2(4)	122.4(4)	120.4(5)	
$Rh_2(CH_3{-}C_6H_4NC(H)NC_6H_4CH_3)\text{-}(O_2CCF_3)\text{-}\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)(C_6H_4)\text{-}\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]CF_3COO$ [294]	f	2.072(6)	2.149(6)	1.31(1)	1.31(1)	1.54(2)	1.41(1)	1.44(1)	–	115.8(5)	–	125.1(7)	–
$Rh_2\{CH_3C_6H_4NC(H)NC_6H_4{-}CH_3\}_3(NO_3)_2$ [130]	f	2.034(15)	2.012(15)	1.339(18)	1.337(20)	–	1.460(23)	1.411(19)	–	121.0(1)	120.0(1)	123.0(1)	6.35 average
		2.047(15)	2.041(14)	1.333(16)	1.280(17)	–	1.413(18)	1.438(16)	–	117.7(9)	120.0(1)	125.0(1)	
		1.985(16)	1.946(18)	1.293(15)	1.361(21)	–	1.437(20)	1.413(18)	–	123.0(1)	121.0(1)	121.0(1)	
$Rh_2\{CH_3\text{-}C_6H_4NC(H)NC_6H_4{-}CH_3\}_4$ [217]	f	2.050(5)	–	1.331(5)	–	–	1.399(6)	–	–	–	–	123.7(8)	"non-planar"
$Rh_2\{p\text{-}CH_3C_6H_4NC(H)NC_6H_4\text{-}CH_3\text{-}p\}_2\{O_2CCF_3\}_2\{H_2O\}_2$ [210]	f	1.996(4)	1.998(4)	1.315(6)	1.305(6)	–	1.420(6)	1.415(6)	–	119.0(3)	118.1(3)	124.5(4)	"planar"
		1.987(3)	1.990(3)	1.303(5)	1.309(6)	–	1.411(6)	1.417(5)	–	118.3(3)	119.4(3)	124.5(4)	
$Rh_2(CH_3\text{-}C_6H_4N\text{-}C(H)\text{-}N\text{-}C_6H_4\text{-}CH_3)_3(NO_3)C_5H_5N$ [245]	f	2.021(7)	2.082(6)	1.341(12)	1.319(11)	1.428(11)	1.436(10)	–	–	118.3(6)	117.1(6)	123.6(8)	"planar"
		2.089(7)	2.010(7)	1.311(11)	1.314(10)	1.440(10)	1.421(11)	–	–	118.3(5)	–	123.2(8)	
		2.060(6)	2.036(6)	1.345(10)	1.299(11)	1.404(11)	1.443(11)	–	–	116.0(5)	120.5(5)	123.0(7)	
$[Rh_2\{CH_3C_6H_4NC(H)NC_6H_4CH_3)_2\{(C_6H_5)_2PC_5H_4N\}_2(O_2CCF_3)_2]$ [274]	f	2.056(5)	2.126(6)	1.314(8)	1.325(6)	1.434(6)	–	–	–	119.3(4)	115.3(4)	123.0(6)	"planar"
		2.139(4)	2.050(4)	1.336(8)	1.314(6)	1.401(8)	–	–	–	112.9(3)	119.0(4)	124.1(5)	
$Rh_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_4CO$ [287]	f	2.056(6)	–	1.302(8)	1.352(8)	1.512(9)	1.405(9)	1.458(9)	–	–	–	–	"planar"
$Rh_2\{C_6H_5NC(H)NC_6H_5\}_4CH_3CN$ [283]	f	2.062(2)	2.066(2)	1.307(2)	1.324(3)	1.420(3)	1.418(3)	–	–	120.0(2)	118.2(2)	122.9(2)	"planar"
$Rh_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_4$ [141,287]	f	2.056(2)	–	1.336(4)	1.322(4)	1.502	1.424(4)	1.421(4)	–	–	–	–	"planar"
		2.044(2)	–	–	–	–	–	–	–	–	–	–	
$Rh_2\{C_6H_5NC(H)NC_6H_5\}_4$ [283]	f	2.057(4)	2.038(4)	1.314(6)	–	1.419(6)	–	–	–	119.9(4)	–	123.7(5)	"planar"
$Rh_2\{C_6H_5NC(H)NC_6H_5\}_4(CH_3CN)(ClO_4)$ [283]	f	2.035(4)	2.025(4)	1.303(5)	1.338(5)	1.456(5)	1.420(5)	–	–	120.4(3)	118.9(3)	123.0(4)	"planar"
$Rh_2(CH_3\text{-}C_6H_4N\text{-}C(H)\text{-}N\text{-}C_6H_4\text{-}CH_3)_3(NO_3)\cdot(C_6H_5)_3P$ [245]	f	2.025(16)	2.074(15)	1.337(19)	1.298(20)	–	–	–	–	119.9(14)	121.9(13)	121.9(18)	"planar"
		1.983(15)	2.025(16)	1.308(22)	1.345(20)	–	–	–	–	123.3(14)	–	120.8(19)	
		2.009(16)	2.035(15)	1.234(21)	1.364(21)	–	–	–	–	124.1(15)	116.7(13)	124.3(20)	

$Ir_2\{p\text{-}CH_3\text{-}C_6H_4NC(H)NC_6H_4\text{-}CH_3\text{-}p\}\text{-}$	f	2.087(7)	2.130(6)	1.322(11)	1.349(10)	–	1.442(10)	1.421(10)	–	124.9(5)	126.3(5)	123.9(7)	"non-
$(\mu\text{-}NH\text{-}p\text{-}C_6H_4\text{-}CH_3)(C_8H_{14})\}_2$ [229]		2.128(7)	2.140(6)										planar"
$\{Ir_2(\mu NC_5H_4)\}_2(\mu\text{-}CH_3\text{–}C_6H_4NC(H)NC_6$	f	2.107(11)	2.097(11)	1.35(2)	1.33(2)	–	–	–	–	120.0(1)	121.2(8)	123.0(1)	–
$H_4\text{–}CH_3)(C_5H_5N)_2(CH_3CN)_2\}\ (BC_6H_5)_4$													
$\cdot 2CH_3CN$ [178]													
$Ir(C_8H_{12})\{CH_3\text{–}C_6H_4NC(H)N$	f	2.003(12)	2.049(12)	1.38(2)	1.29(2)	–	1.44(2)	1.49(2)	–	120.0(1)	125.0(1)	120.0(2)	"planar"
$C_6H_4\text{–}CH_3\}_2Ir(OCOCF_3)_2C_5H_5N$ [211]		2.055(11)	2.081(11)	1.33(2)	1.35(2)	–	1.43(2)	1.40(2)	–	120.0(1)	128.0(1)	124.0(1)	
$Ir_2\{CH_3\text{–}C_6H_4NC(H)\text{-}C_6H_4N\text{-}CH_3\}_4$ [220]	f	2.040(2)	–	1.34(2)	–	–	1.45(4)	–	–	124.0(1)	–	116.0(2)	0.16(2)
$Ni_2\{CH_3\text{–}C_6H_4NC(H)N\text{-}C_6$	f												
$H_4\text{–}CH_3\}_4\cdot H_2O$ [213,222]	room Temp	1.904(5)	–	–	–	–	–	–	–	–	–	–	–
	low Temp	1.898(8)	–	–	–	–	–	–	–	–	–	–	
$Ni_2\{CH_3\text{–}C_6H_4NC(H)N\text{-}C_6H_4CH_3\}_4BF_4$ [213]	f	1.924(8)	1.920(8)	–	–	–	–	–	–	–	–	–	–
$Pd_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_2$	f	2.03(1)	2.05(1)	1.33(2)	1.33(2)	1.54(2)	1.39(2)	1.43(2)	–	124.5(12)	121.3(12)	124.7(11)	"non-
$\{\mu\text{-}C_6H_5NC(C_6H_5)NC_6H_5\}_2$ [246]		2.04(1)	2.00(1)	1.34(2)	1.30(2)	1.31(2)	1.40(2)	1.42(2)	–	127.7(12)	127.7(12)	121.5(16)	planar"
	b	2.00(1)	2.09(1)	1.34(2)	1.31(2)	1.51(2)	1.38(2)	1.42(2)	63.8(5)	94.6(12)	92.0(12)	109.4(16)	–
		2.10(2)	2.03(1)	1.35(2)	1.32(2)	1.31(2)	1.37(2)	1.39(2)	63.9(6)	91.0(12)	94.5(12)	110.0(18)	–
$Pd_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_4$ [246]	f	2.05(1)	2.07(1)	1.31(1)	1.32(1)	1.50(1)	1.42(1)	1.44(1)	–	120.7(9)	120.5(9)	123.4(12)	"non-
		2.05(1)	2.03(1)	1.33(1)	1.33(1)	1.49(1)	1.43(1)	1.43(1)	–	121.3(8)	121.9(4)	122.1(12)	planar"
		2.05(1)	2.06(1)	1.33(1)	1.30(1)	1.53(1)	1.41(1)	1.42(1)	–	119.3(9)	120.4(9)	125.1(12)	–
		2.05(1)	2.04(1)	1.30(1)	1.34(1)	1.52(1)	1.42(1)	1.41(1)	–	121.6(9)	120.7(8)	122.6(12)	–
$Pd_2\{CH_3\text{–}C_6H_4NC(H)NC_6H_4\text{–}CH_3\}_4.O(C_2H_5)_2$	f	Similar to											
[213,222]		H_2O adduct											
$Pd\{C(C_6H_5)=C(COOC_2H_5)$	j	2.182(2)	–	1.304(3)	1.341(3)	–	–	–	–	–		116.5(2)	"planar"
$C(C_6H_5)=C(COOC_2H_5)C_6H_4N=$													
$C(CH_3)NHC_6H_5\}Cl$ [233]													
$Pd\{CH_3\text{–}C_6H_4NC(CH_3)NC_6H_4CH_3\}_2$ [73]	b	2.038(3)	2.038(3)	1.322(4)	1.322(4)	1.512(9)	1.412(4)	1.412(4)	63.5(1)	94.0(2)	94.0(2)	108.4(3)	3.1
$Pd(\eta\text{-}C_5H_5(p\text{-}CH_3C_6H_9))$	j	2.040(6)	1.984(7)	1.285(9)	1.350(9)	1.492(11)	1.516(12)	1.518(15)	91.3(3)	128.2(5)	124.2(6)	122.0(6)	5.2
$N(H)C(CH_3)NC_6H_4\text{–}CH_3)$ [73]													
$[(C_6H_5)_4P]\{C_6H_5C_5(NH_2)(NH)]PdCl_3\}]\text{–}$	a	2.029(8)	–	1.28(2)	1.31(1)	1.50(1)	–	–	–	140.9(6)	–	123.2(8)	–
CH_3CN [295]													
$Pd_2\{CH_3\text{–}C_6H_4NC(H)NC_6H_4\text{–}CH_3\}_4\cdot 2H_2O$	f	2.063(14)	–	–	–	–	–	–	–	–	–	–	–
[213,222]													
$Pd_2\{CH_3\text{–}C_6H_4NC(H)NC_6H_4\text{–}CH_3\}_4\cdot PF_6$	f	2.03(2)	2.05(3)	–	–	–	–	–	–	–	–	–	–
[213,222]													
$[C_6H_5C(NH)_2Pd(\eta^3\text{-}C_3H_5)]_2$ [296]	f	2.077(6)	2.058(7)	1.304(10)	1.308(10)	1.497(10)	0.873(43)	–	–	130.8(5)	–	122.0(7)	–
~~$Pt(NH_3)_2\{CH_3C((NH_2)$~~$NH\}_2Cl_2H_2O$ [145]	salt	1.957	1.957	1.271	1.318	1.533	–	–	–	130.14	–	127.8	0.2
$Pt(C_6H_5N\text{–}C(C_6H_5)NC_6H_5)_2$ [67]	b	2.040(5)	2.025(5)	1.334(7)	1.340(7)	1.493(8)	1.406(7)	1.387(7)	63.68(18)	94.54(4)	95.0(3)	106.7(5)	2.5
$Pt\{C_6H_3(CH_2N(CH_3)_2)_2\}\{CH_3\text{–}C_6H_4\text{–}N\text{-}$	a	2.16(1)	–	1.31(1)	1.35(1)	–	1.45(1)	1.43(1)	–	122.2(7)	–	120.8(9)	–
$(H)C(H)N\text{–}C_6H_4\text{–}CH_3)\}CF_3SO_3$ [65]													

TABLE 3 (*continued*)

Compound [Ref.]	Bond length								Bond angles				
	Structure	1	2	3	4	5	6	7	A	B	C	D	E
Pt{$C_6H_3(CH_2N(CH_3)_2)_2$}-	a	2.132(6)	–	1.345(8)	1.303(7)	–	1.412(7)	1.392(8)	–	118.9(3)	–	121.4(5)	–
{$CH_3C_6H_4NC(H)NC_6H_4$-CH_3} [65]													
{$C_6H_3(CH_2N(CH_3)_2)$}$_2$-	g	2.155(9)	2.16(1)	1.32(1)	1.28(2)	–	1.40(1)	1.53(2)	–	121.8(8)	123.5(8)	125.0(1)	non-planar
Pt(μ-CH_3–$C_6H_4NC(H)N$–C_2H_5]HgBrCl [70]		Pt	Hg										0.15
Pt{($(C_6H_5)_2C_2N_3H_2$)}$_2\cdot 0.75C_6H_5CH_3$				at C1	at C2								
(six-membered ring) [83]	i	1.99(4)	1.90(3)	1.41(6)	1.34(6)	1.47(6)	–	–	87.9(14)	128.0(3)	123.0(3)	125.0(4)	0.02
		1.93(4)	1.96(3)	1.24(6)	1.29(6)	1.57(7)	–	–	89.5(15)	126.0(3)	122.0(3)	130.0(4)	–
				at C3	at C4								
				1.42(5)	1.43(6)	1.58(7)	–	–	–	–	–	133.0(5)	–
				1.37(6)	1.21(6)	1.56(6)	–	–	–	–	–	133.0(4)	–
$Cu_2(C_6H_5NC(C_6H_5)NC_6H_5)_4$ [161]	f	2.019(5)	2.026(5)	1.328(7)	1.334(8)	1.547(7)	1.454(6)	1.439(6)	–	–	–	120.0(5)	"planar"
Cu_2(p-CH_3–C_6H_4N–C(H)–N-	f	1.886(7)	1.859(7)	1.276(11)	1.368(11)	–	1.438(11)	1.426(11)	–	122.8(6)	119.6(6)	122.9(8)	"planar"
C_6H_4–CH_3–p)$_2$ [235]													
{$(C_6H_5)C(NSi(CH_3)_3$}$_2$CuCl-	a	1.999(4)	–	1.304(6)	1.350(6)	1.482(6)	1.780(4)	1.777(4)	–	122.0(3)	–	121.2(4)	–
{$(C_6H_5)C(NSi(CH_3)_3(NHSi(CH_3)_3)$} [261]	and	2.029(4)	1.984(4)	1.334(6)	1.319(6)	1.488(6)	1.730(4)	1.732(4)	67.4(2)	88.0(3)	90.4(3)	114.2(4)	–
	b												
[Cu{$(CH_3)_3SiNC(C_6H_5)NSi(CH_3)_3$}]$_2$ [260]	f	1.890(6)	1.900(5)	1.33(2)	1.321(9)	1.52(2)	1.738(6)	1.750(8)	–	117.5(5)	–	–	"non-
		1.880(6)	1.890(6)	1.34(1)	1.323(9)	1.50(2)	1.747(8)	1.746(6)	–	118.3(6)	–	–	planar"
Ag_2(p-CH_3–C_6H_4N–C(H)–N-	f	2.116(5)	2.094(5)	1.289(7)	1.310(8)	–	1.420(8)	1.448(8)	–	122.5(4)	123.5(4)	124.9(6)	"planar"
C_6H_4–CH_3-p)$_2$ [235]													
$Ag_2[C_6H_5C(NSi(CH_3)_3)_2]_2$ [284]	f	2.128(2)	2.119(2)	1.327(3)	1.329(3)	1.508(3)	1.748(2)	1.751(2)	–	120.0(2)	119.7(2)	125.3(2)	"planar"
		2.129(2)	2.118(2)	1.332(3)	1.321(3)	1.506(3)	1.750(2)	1.751(2)	–	119.9(2)	120.1(2)	125.6(2)	
[Au{$C_6H_5NC(H)NC_6H_5$}]$_4$ [285]	f	2.026(4)	2.008(4)	1.314(6)	1.262(6)	1.404(6)	1.490(7)	–	–	122.6(3)	125.5(4)	128.6(5)	"planar"
		2.000(4)	–	–	–	–	–	–	–	–	–	–	
		2.024(4)	–	–	–	–	–	–	–	–	–	–	
$AuCl_2[C_6H_5C(NSi(CH_3)_3)_2]$ [271]	c	2.016(7)	2.023(6)	1.328(9)	1.32(2)	1.48(2)	1.785(7)	1.787(7)	65.0(3)	92.5(5)	92.5(5)	110.0(7)	–
$Au_2[C_6H_5C(NSi(CH_3)_3)_2]_2$ [284]	f	2.050(7)	2.066(8)	1.30(1)	1.36(1)	1.50(1)	1.804(9)	1.73(1)	–	121.5(6)	117.2(6)	126.3(8)	"planar"
		2.085(7)	2.037(7)	1.29(9)	1.32(2)	1.49(1)	1.784(9)	1.77(1)	–	118.6(6)	121.2(7)	126.2(8)	
{$Zn(HCO_2)_3$}$^-${$HC(NH_2)_2$} [208]	salt	–	–	1.286(4)	–	–	–	–	–	–	–	–	–
HgC_6H_5{$CH_3C_6H_4$–$NC(H)C_6H_4CH_3$}	a (II)	2.13(3)	2.68(2)	1.13(4)	1.30(4)	–	1.54(5)	1.30(4)	49.4(5)	112.0(2)	80.0(1)	117.0(2)	–
two independent molecules [66]	c (III)	2.02(3)	3.19(2)	1.44(4)	1.27(4)	–	1.46(4)	1.51(4)	47.1(5)	121.0(2)	71.0(2)	119.0(2)	
$Hg(C_6H_5C(NSi(CH_3)_2)_2$ [291]	a	2.071(7)	2.721(7)	1.28(1)	1.29(1)	1.50(1)	1.725(7)	1.748(8)	–	105.1(5)	105.0(5)	121.4(7)	–
		2.069(6)	2.717(7)	1.36(1)	1.36(1)	1.48(1)	1.720(8)	1.742(8)	–	–	–	121.4(7)	
$2[H_2NC(CH_3)NH_2]_2CO_3\cdot H_2O$		–	–	1.309(5)	1.315(5)	1.494(5)	0.97	1.10	–	–	–	121.7(3)	–
two independent molecules [188]		–	–	1.307(5)	1.314(5)	1.500(5)	–	–	–	–	–	121.4(3)	

HN(H)C(CH_3)NH [189]	–	–	1.298(1)	1.344(1)	1.502(1)	0.93(2)	0.91(2)	–	–	–	125.5	–
	–	–	–	–	–	–	0.91(2)	–	–	–	–	
[$ClC_6H_4NC(C_6H_5)NC_5H_{10}$] [190]	–	–	1.290(6)	1.365(6)	1.497(7)	1.402(6)	1.468(7)	–	–	–	118.4(4)	–
	–	–	–	–	–	–	1.468(7)	–	–	–	–	
[$H_2NC(C_6H_5)NH_2$]Cl · H_2O [191]	–	–	1.293(7)	1.328(7)	1.471(8)	–	–	–	–	–	121.6(4)	–
[$CH_3OC_6H_4NC(C_6H_5)NC_5H_{10}$] [192]	–	–	1.283(5)	1.372(5)	1.502(6)	1.416(5)	1.467(5)	–	–	–	119.4(3)	–
			–	–	–	–	1.468(5)	–	–	–		
[$C_6H_5N(H)C(C_6H_5)NC_6H_5$]	–	–	1.310(8)	1.369(8)	1.481(8)	1.416(8)	1.403(9)	–	–	–	120.4(5)	–
hydrogen-bonded dimer [193]	–	–	1.295(6)	1.351(7)	1.488(7)	1.412(7)	0.720(49)	–	–	–	122.7(5)	
	–	–	–	–	–	–	1.412(8)	–	–	–	–	
	–	–	–	–	–	–	0.878(54)	–	–	–	–	
[$C_6H_5N(H)C(H)NC_6H_5$]	–	–	1.323(3)	1.311(3)	–	1.408(3)	1.407(3)	–	–	–	122.1(3)	–
hydrogen-bonded dimer [234]	–	–	1.305(3)	1.314(3)	–	1.415(3)	1.412(3)	–	–	–	123.0(2)	
[$O_2NC_6H_4NC(H)NC_5H_{10}$] [251]	–	–	1.302(6)	–	–	1.387(5)	1.467(6)	–	–	–	122.1(4)	–
	–	–	–	–	–	–	1.485(6)	–	–	–	–	

N.B. The structure of $CuCl_4\{H_3(CC(NH_2)_2\}_3$ [120,158,159] has been established, but insufficient data were available for inclusion.

2,6-$((CH_3)_2NCH_2)_2C_6H_3$ ligand, which fixes the N-donor atoms in mutual trans positions. The Pt-to-Hg interaction for the amidino complex is described as a donor type, i.e. (Pt:→Hg), which contrasts with that found for [(2-$((CH_3)_2NCH_2C_6H_4)_2(CH_3CO_2)Pt{-}Hg(O_2CCH_3)$] for which both metals formally provide a bonding electron [166].

The terdentate 2,6-$((CH_3)_2NCH_2)_2C_6H_3$ ligand has also been used to stabilise platinum–silver complexes such as [{2,6-$((CH_3)_2NCH_2)_2C_6H_3$}(*p*-$CH_3C_6H_4$-NCHNR)PtAgBr] (R = CH_3, C_2H_5, i-C_3H_7, $CH_3C_6H_4$), which are formed from the reaction of [{2,6-$((CH_3)_2NCH_2)_2C_6H_3$}PtBr] with [Ag{*p*-$CH_3C_6H_4$NCHNR}]$_n$ [167]. The complexes have been assigned a five-membered chelate ring in which a Pt(II)—Ag(I) bond is bridged by a formamidino ligand. The complex was studied by INEPT ^{109}Ag NMR [168], which supported the proton NMR conclusions that there are two isomers present. The dependence of the isomer ratio on the alkyl substituent was also noted.

9. X-RAY STRUCTURES OF AMIDINE COMPLEXES

The bond lengths and angles reported in Table 3 are based on the key described in Fig. 37. Note that the angle e is a measure of the non-planarity of the amidine–metal ring. In some cases, only a qualitative description can be given. It must also be noted that, although comparisons of distances and angles between the various structures can be useful, crystal packing factors and other crystallographic factors must not be overlooked. Recently, a number of amidine ligand X-ray crystal structures have been reported in the literature, and are listed in Table 3. Data are available on acetamidinium chloride [186], 2,6-dimethylpiperidyl-*N*-phenylacetamidine [187], bis-acetamidinium carbonate monohydrate [188], acetamidine [189], N^2-(*m*-chlorophenyl)-*N*,*N*′-pentamethylenebenzamidine [190], benzamidine hydrochloride monohydrate [191], N^2-(*p*-methoxyphenyl)-*N*,*N*′-pentamethylenebenzamidine [192], *N*,*N*′-diphenylformamidine [234], and N^1,N^1-hexamethylene-N^2-(*p*-nitrophenyl)formamidine [251]. These are, however, only of limited value for direct comparison purposes with those amidino–transition metal complexes for which crystal structures have been determined. Fortunately, the determination of the crystal structure of *N*,*N*′-diphenylbenzamidine [193] allows a comparison to be made between an amidine in its non-coordinated and coordinated forms.

Consideration of the structures of formamidine complexes shows that there is only one example of the bidentate chelate bonded group, in *trans*-bis(triphenylphosphine)-dicarbonyl(*N*,*N*′-diphenylformamidino)rhenium(I) [173]. Interestingly, when data are compared with those of the parent ligand (see Table 4), the formation of the bidentate ligand causes little change in the C–N distances. Delocalised N—C—N systems are indicated for both cases. Further, there is little change in the phenyl-ring C—N bond lengths on complexation, indicating there is little delocalisation of the N—C—N fragments to the rings. Finally, there is a considerable reduction in the

TABLE 4

A comparison of the structural parameters of *N,N'*-diphenylformamidine as a non-complexed ligand and in the bidentate chelate bonding mode

Structural parameter	Ligand	$Re(Am)(CO)_2[(PC_6H_5)_3]_2$
C–N distance (Å)	1.318(3)	1.32(1)
C–N distance (Å)	1.308(3)	1.34(1)
ring C–N distance (Å)	1.41(3)	1.41(3)
ring C–N distance (Å)	1.41(3)	1.39(2)
N–C–N angle (degree)	122.6(3)	112(1)

N–C–N angle (10.6°) on complexation, which is indicative of the strain involved in a bidentate ring complex involving a four-membered ring.

A number of examples exist of the ligand in the bridging bonding mode (see Table 5). The data indicate that slight changes occur in the bond distances and angles when the two bridging hydrogens of the dimeric parent amidine are replaced by transition metals. There is a slight increase in the N–C–N angle, and the C–N bond retains delocalisation.

TABLE 5

A comparison of the structural parameters for the *N,N'*-diphenylformamidine ligand in the non-complexed and bidentate bridging bonding mode

Complex	Ave. C–N (Å)	Ave. ring C–N (Å)	N–C–N	Ref.
Ligand	1.318(3)	1.41(3)	122.6(3)	234
	1.308(3)	1.41(3)		
$Rh_2(Am)(O_2CCF_3)$	1.31(1)	1.41(1)	125.1(7)	294
$\{C_6H_5\}_2P(CH_2)_2PC_6H_5$-$C_6H_4\{C_6H_5\}_2P(CH_2)_2$-$P\{C_6H_5\}_2CF_3COO$	1.31(1)	1.41(1)		
$Rh_2(Am)_4$	1.314(6)	1.419(6)	123.7(5)	283
$Rh_2(Am)_4CH_3CN$	1.307(2)	1.420(3)	122.9(2)	283
	1.324(3)	1.418(3)		
$Rh_2(Am)_4CH_3CNClO_4$	1.303(5)	1.456(5)	123.04	283
	1.338(5)	1.420(5)		
$Rh_2(Am)_2(\{C_6H_5\}_2$-$PC_5H_4N)(O_2CCF_3)_2$	1.314(8)	1.434(6)	124.1(5)	274
	1.325(6)	1.422(9)	123.0(6)	
	1.336(8)	1.401(8)		
	1.314(8)	1.447(7)		
$Au_2(Am)_4$	1.314(6)	1.404(6)	128.6(5)	285
	1.262(6)	1.490(7)		
	1.322(6)	1.480(1)		
	1.333(6)	1.432(6)		

No related comparisons are possible in the acetamidine case because of the lack of structural data on the parent amidine.

The most comprehensive analysis exists for *N,N'*-diphenylbenzamidine [193] (see Table 6). Clearly, on complexation the average C—N bond distance is little changed and delocalisation is retained. The N—C—N angle is very sensitive to the bonding mode adopted. In the bridging case, a reduction of 1.13° (average) is found, whereas for the bidentate mode, a considerable change (12.7° (average)) is involved. The data reflects the relative lack of strain in the five-membered ring compared with the considerable strain involved in the four-membered ring.

A number of more general points become evident from the data. One of the most important structural parameters is the N—C—N "bite" angle. In the chelate complexes, this angle appears to vary with the substituent group on the amidine. For formamidine, an average value of 115° is found, for acetamidine 109°, and for benzamidine 111°. Thus N—C—N angles decrease in the order formamidine > benzamidine > acetamidine. These values may be compared with the average chelate triazene value for the N—N—N angle of 103° [176]. In the bridging case, the N—C—N angle does not depend on the central carbon substituent and varies considerably 115°–125° with an average value of 119°. The large variation is possibly due to the wide degree of metal–metal interactions present in the complexes. As expected, the N—C—N bridge angle is greater than the N—C—N chelate angle, and is similar to that found for bridging triazenes (117°) [176].

In the case of complexes having monodentate amidine groups, average N—C—N angles of 119° in the formamidine case, 123.8° in the acetamidine case, and 121.2° in the benzamidine case are noted. These may be compared with the value of 114° found for the monodentate triazene complex *cis*-$[Pt(1,3\text{-diphenyltriazene})_2(PPh_3)_2]C_6H_6$ [176]. Further, the N—C—N angle for monodentate formamidino complexes only differs by 0–4° from that found for the chelate and bridging formamidino modes. In contrast, the monodentate triazenido complex has a significant difference in the value of its monodentate N—N—N angle (114°) compared with the average values for N—N—N chelate (103°), and bridging N—N—N (117°) angles [176].

The C—N bond distances for both the bidentate chelate (1.33 Å average) and the bridging (1.32 Å) groups are similar. Their values indicate considerable multiple-bond character and lie between the average single and double C—N bond covalent distances of 1.48 Å and 1.24 Å given by Schomaker and Stevenson [177] for a range of C–N distances in organic molecules. The distances also agree well with that for the delocalised C–N unit (1.308 Å) found in the benzamidinium cation [77]. The skeletal C—N bond distance appears to be generally independent of the amidine, and of the metal.

The C–C(5) distance between the amidine fragment and its central carbon atom substituent appears to be independent of the nature of the complex. The average

TABLE 6

A comparison of the structural parameters of the *N*,*N'*-diphenylbenzamidine ligand and its complexes
Am = *N*, *N'*-diphenylbenzamidine; THF = tetrahydrofuran

Complex	C–N (Å)	N–C–N (degree)	Bonding mode	Ref.
Parent	1.416(8)	120.4(5)		193
	1.310(8)	122.7(5)		
	1.351(7)			
	1.295(6)			
$Pt(Am)_2$	1.331(8)	106.7(5)	Bidentate	67
	1.340(8)			
$Cu_2(Am)_4$	1.328(7)	120.0(5)	Bridging	161
	1.334(8)			
$Mo_2(Am)_4$	1.32(1)	118(1)	Bridging	69
	1.38(1)	114(1)		
	1.36(1)	118(1)		
	1.33(1)			
$Re_2(Am)_2Cl_4$ THF	1.34(3)	116(2)	Bridging	114
	1.37(3)			
$Re_2(Am)_2Cl_4$	1.34(2)	116(2)	Bridging	114
	1.32(2)	118(1)		
	1.31(2)			
	1.37(2)			
Rh(Am)(1,5-cyclooctadiene)	1.356(9)	110.0(6)	Bidentate	139
	1.331(9)			
$Rh_2(Am)_2$(tetrafluorobenzo-5,6-bicyclo[2.2.2.]octa-2,5,9-triene)	1.350(7)	118.1(5)	Bridging	139
	1.317(9)	120(5)		
	1.346(7)			
	1.339(7)	118(1)		
$Pd_2(Am)_2(Am)_2$	1.33(1)	124.7(11)	Bridging and bidentate	246
	1.33(2)	121.5(16)		
	1.34(2)			
	1.30(2)			
	1.34(2)	109.4(16)		
	1.31(2)	110.0(18)		
	1.35(2)			
	1.32(2)			
$Pd_2(Am)_4$	1.31(1)	123.4(12)	Bridging	246
	1.32(1)	122.1(12)		
	1.33(1)	125.1(12)		
	1.33(1)	122.6(12)		
	1.33(1)			
	1.30(1)			
	1.30(1)			
	1.34(1)			
$Rh_2(Am)_4$	1.336(4)		Bridging	287
	1.322(4)			
$Rh_2(Am)_4CO$	1.302(8)		Bridging	287
	1.332(8)			
$Co_2(Am)_4$	1.339(7)		Bridging	287
	1.346(7)			

C–C distance found (1.52 Å), compares well with those found in salts of acetamidine (1.53 Å (cobalt), 1.50 Å (platinum) [120,145]), and benzamidine (1.49 Å (rhenium) [77]), and for the free benzamidine ligand (1.48 Å average), representing a normal C–C bond distance.

The M–N–C angle is greater in the bridging complexes (average = 119.6°) than the chelate (average = 94.2°), as expected. Formally, the nitrogen can be regarded as sp^2 hybridised, but the constraints of the ring force a reduction of 25° compared with the idealised angle for the free ligand of 120°. Ring strain is also taken at the metal centre and the angle at the metal is found to be dependent on the nature of the metal, e.g. Ta(V), average 60.6° [68,169–172]; Ru(II), 61.1° [84]; Pt(II), 63.7° [67]; Pd(II), 63.5° [73]. However, the N–C(6,7) substituent distances appear to be independent of the amidine and type of complex (Table 7). The average N–C distance (see Fig. 37, bond distance 5) for the carbon-substituted complexes, i.e. acetamidines and benzamidines (1.48 Å), is close to the pure single bond C–N value of 1.47 Å [79] and indicates that the delocalised NCN π system is not extended to the substituent even when the substituent has a π system of its own.

Considering the M–N bond lengths for the complexes having chelate, σ,σ-bonded complexes, there appears to be two distinct groups. The $Pd\{CH_3C_6H_4NC(CH_3)NC_6H_4CH_3\}_2$ [73] and the $Pt\{C_6H_5NC(C_6H_5)NC_6H_5\}_2$ [67] complexes have an average bond length of 2.038 Å, which compares well with $\{Pd(NH_3)_4\}^{2+}$ [24] (M–N 2.044 Å) [179], and $\{Pd(en)_2\}^{2+}$, (M–N = 2.030 Å and 2.043 Å) [180], and for which metal-to-nitrogen π bonding is absent. The other distinct group consists of a number of molybdenum complexes [98,99] and *trans*-$RuH(PPh_3)_2CO(p\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3\text{-}p)$ [174], for which the M–N bond lengths average 2.23 Å. These latter bond lengths are of similar length to those found in $Mo(CO)_2C_5H_5(C_6H_5NNNC_6H_5)$ (2.15 Å), which contains the related triazenido ligand [176]. A number of factors may explain the data. The palladium and platinum complexes are of a bis-amidino type with no other ligands present on the metal. The other complexes have only one amidine present and a variety of other

TABLE 7

The effect of substituent groups on the *N*-substituent (C)–N bond lengths in R′NC(R)NR′ complexes

Group R′	Ref.	Average C–N	Bonding mode
C_6H_{11}	68	1.48	Chelate
C_3H_7	170	1.47	Chelate
CH_3	90	1.46	Bridge
C_6H_5	67	1.39	Chelate
$CH_3C_6H_4$	73	1.41	Chelate
C_6H_5	69	1.46	Chelate
C_6H_5	193	1.41	Free ligand

ligands which may effect the M–N distance, e.g. there is bond lengthening of the Ru–N bond in the *trans*-RuH(PPh$_3$)CO{*p*-CH$_3$C$_6$H$_4$NC(H)NC$_6$H$_4$CH$_3$-*p*} complex [174] because of the "trans influence" of the hydride ligand in the opposite coordination site. Thus, it appears that the presence of certain groups on the metal other than amidines have the effect of lengthening the M–N bond, though "short" M–N amidine bonding is promoted by symmetric chelation. Another feature of note is that, for molybdenum complexes, C–N bonding is less delocalised than for their palladium counterparts, though there is no evidence for π bonding between the platinum/palladium and the nitrogen atoms. Any π bonding between metals and nitrogen appears unimportant since we have already noted the similarity of C–N bond lengths between complexes which contain no π bonding and the platinum/palladium complexes.

There is also the effect of the size of the central metal on M–N bond distances, particularly differences arising from metals within the same transition-metal group, and the same metal in formally different oxidation states. Two complexes having metals from the same group and in the same formal oxidation state, and amidino groups with the same bonding mode, viz. Pt^{II}{C$_6$H$_5$NC(C$_6$H$_5$)NC$_6$H$_5$)$_2$ [67] and Pd^{II}{*p*-CH$_3$C$_6$H$_4$NC(CH$_3$)NC$_6$H$_4$CH$_3$-*p*}$_2$ [73], have similar M–N bond lengths (2.038 and 2.022 Å), and (2.038 and 2.038 Å), respectively. Inspection of the data in Table 3 shows that, for metals, which range from 1st row to 3rd row metals and oxidation states which range from +V, i.e. tantalum, to +I, i.e. copper, M–N distances occur in the range 1.880(6) to 2.22(1). It is clear that formal oxidation state has little significance in this context and that similar distances are found in related complexes of metals from the same periodic group.

For bridging amidines, the M–N distance average of 2.05 Å is similar to that found for the average M–N bond in bridging triazenes (2.00 Å) [194]. The variation in values is large and appears to be independent of the amidine and other ligands present. Worthy of note are the complexes Cu$_2${C$_6$H$_5$N(C$_6$H$_5$)NC$_6$H$_5$)$_4$ [161] (2.02 Å), Re$_2${C$_6$H$_5$N(CH$_3$)NC$_6$H$_5$}$_2$Cl$_4$ [112] (2.06 Å), and Cr$_2${CH$_3$NC(C$_6$H$_5$)-NCH$_3$}$_4$ [90] (2.03 Å), which all have short M–N distances as well as strong metal–metal interactions.

The general amidine bonding modes were considered in Sect. 2. However, there are a number of less well known modes, as follows.

The insertion products formed when benzonitrile or the methylene group are inserted into the chelate ring give rise to the bonding mode shown by Fig. 3(i). Corresponding changes in the structural parameters occur. The symmetrical PtN$_4$ structure formed in the Pt{HNC(C$_6$H$_5$)NC(C$_6$H$_5$)NH}$_2$ [83] complex involves a six-membered ring with extensive delocalisation and is similar to those in [(PPh$_3$)$_2$Pt{HN$_3$C$_2$(CF$_3$)$_2$}] [198] and [P(OCH$_3$)$_2$(C$_2$H$_5$)Ru{HNC(CF$_3$)NC(CF$_3$)NH}] [199]. As a result, the mean Pt–N distance (1.96 Å) is similar to that found for chelate platinum and palladium bis-amidino complexes but compares more closely with the Pt–N distance in *trans*-{Pt(NH$_3$)$_2$(*N*-methylimidazole)$_2$}Cl$_2$ · 2H$_2$O

[181] (2.01 Å). These values are slightly lower than those normally found for platinum(II) complexes (2.05 Å) [182], and may indicate some multiple bond character. The C—N bond lengths (average 1.34 Å) show considerable π character. They are similar to those found in s-triazine (1.319 Å) [183], which is itself extensively delocalised. The value is also intermediate between the C=N (1.328 Å), and C—N (1.283 Å) distances found for the pseudo-parent benzamidine hydrochloride ligand [191]. The average of the N—C—N angles (127°) indicates an opening up of the angle compared with bridging and chelate N—C—N angles (arising from the six-membered ring), and compared with the benzamidinium ion (121.6°).

In the tungsten–methylene derivative $[W_2(\mu\text{-CO})_2\{\mu\text{-HC}(N\text{-3,5-xylyl})_2\}_2\{\text{HC}(N\text{-3,5-xylyl})_2\}(\text{3,5,-xylyl})\text{NCHN-3,5-xylyl})\text{CH}_2\}$ [72], only one CH_2 group is inserted and the resultant ring is asymmetric. As a result, the M–N distance is larger and the N—C—N angle increased compared with the chelate formamidine in the same complex.

The ortho-metallation mode, Fig. 3 (j), also influences bonding parameters. The π cyclopentadienyl-*N*,*N*-di-*p*-tolylacetamidino-palladium structure [73] has a novel six-membered ring. The Pd–N distance (2.04 Å) is similar to that found for σ,σ-bidentate platinum and palladium bis-amidino complexes. This indicates that there is little π interaction between the ring and the palladium. The Pd–C distance of 1.94 Å can be compared with 1.98 Å in μ-diphenyl acetylene-bis-(μ-pentaphenylcyclopentadienyl)dipalladium(I) [183]. The relevant M–N–C and N–C–N angles in the complex are, as expected, greater than those found for the chelate complexes.

The mixed-metal complex $[\{2,6\text{-}((CH_3)_2NCH_2)_2C_6H_3\}Pt(\mu\text{-}\{CH_3C_6H_4\text{-}NC(H)NC_3H_5\text{-i}\}HgBrCl]$ [70] has an unusual feature in that the M–N distances are very similar, (PtN(1) = 2.155 Å, HgN(2) = 2.156 Å), which contrasts with the differing metal-to-nitrogen bond lengths found in $[(\text{cycloocta-1,5-diene})(p\text{-tolyl-NNNC}_2H_5)_2IrHgCl]$ [184] (Ir—N(1) = 2.10 Å, Hg—N(3) = 2.42 Å), which contains the related triazenido ligand. Also of note is the lack of planarity of the five-membered ring, which may be due to steric effects or the length of the metal—metal bond contained in the ring.

Dehnicke and other workers have produced a large number of complexes using trimethylsilylamidine ligands [249,258,260,261,269,271,273,289,297,298], and X-ray structural data of the many studied allows comparisons to be made between the differently bonded groups. The following average values were noted for benzamidine complexes: M—N = 2.09 Å; C—N = 1.33 Å; C_{skelatal}—C = 1.48 Å; N—M—N = 64.4° (for bidentate and chelate groups), M—N = 2.00 Å; C—N = 1.32 Å; C_{skelatal}—C = 1.48 Å (for bridging groups).

It is clear that a wide variety of amidine bonding modes have now been characterised by X-ray crystallography. However, before more than qualitative comparisons can be undertaken, many more ligand-complex studies need to be undertaken.

10. INDUSTRIAL USE OF METAL AMIDINES

The following section is not meant to be an exhaustive survey of industrial patents involving amidine transition metal compounds, but only an illustration of some of the industrial uses of amidine transition metal systems.

Daugherty and Vaugh [185] used formamidine disulphide hydrochloride to prevent multi-step room temperature etching of copper or copper-alloy printing plates by $FeCl_3$ solutions (16.5–31.5%). The amidine protective coating could be removed from parts of the plates by brushing, allowing one-step etching by the $FeCl_3$ solution without the problem of lateral undercutting.

Lundberg [186] used a mixed copper benzamidine promoter to improve gel times by a factor of 2–3 for elastomer–vinyl–aromatic compositions (butadiene/styrene/divinylbenzene).

Diarylformamidines [175] have also been used as promoters in oxidative poly(phenylene ether) formation. High-molecular-weight poly(phenylene ethers) were prepared by self-condensation of phenols, e.g. 2,6-xylenol, in the presence of amine copper complexes, and *N*,*N*′-diphenylformamidine. Products formed, e.g. poly-2,6,-dimethylphenylene oxide (93% yield), using the formamidine, had an improved intrinsic viscosity.

Finally, the effect of soluble mercury(II), zinc(II), copper(II), and iron(II) compounds and amidines as catalyts for isocyanate polyaddition reactions has been investigated [206]. A number of mixtures were reported to have good catalytic activity.

The review has highlighted that there are large areas of transition-metal amidine chemistry yet to be explored. Interest arises from the synthetic chemistry, the variety of bonding modes, structural aspects, and the reaction chemistry of the complexes. Furthermore, there is an industrial dimension which has yet to be widely explored and exploited.

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