The Synthesis, Properties, and Structure of Bis(amidino)-complexes of Palladium. The Crystal Structure of Bis(*N,N'*-di-*p*-tolylacetamidino)-palladium(II)†

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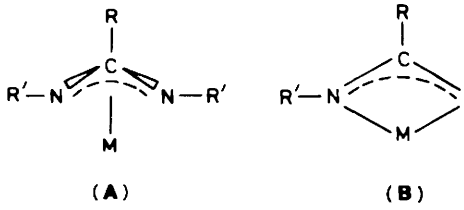
Bis(amidino)palladium complexes [{Pd[R'NC(R)NR']$_2$}$_n$] have been prepared from the reactions of lithioamidines with [PdCl$_2$(PhCN)$_2$]. Mass spectral studies show acetamidino-complexes (R = Me) to be monomeric, but benzamidino-complexes (R = Ph) to be dimeric. In solution the latter complexes are also monomeric (by cryoscopy in C_6H_6), ^{13}C n.m.r. indicating chelate amidino-groups, but at low temperatures (−80 °C) a second species having bridging amidino-groups is detected. ^{19}F N.m.r. studies of [Pd{*p*-FC$_6$H$_4$NC(Ph)NC$_6$H$_4$F-*p*}$_2$] suggest the presence of a species having both bridging and chelate groups. The crystal structure of [Pd{*p*-MeC$_6$H$_4$NC(Me)NC$_6$H$_4$-Me-*p*}$_2$] has been determined: space group *Cmca*, a = 32.089(13), b = 7.049(2), c = 12.282(3) Å; there are four molecules in the unit cell, each with symmetry $C_{2h}(2/m)$. The structure was refined to a discrepancy index, R, of 0.039. The amidino-groups are attached to the square-planar palladium in a symmetrical bidentate σ,σ mode with C–N skeletal distances of 1.322(4) Å, Pd–N distances of 2.038(3) Å, and N–C–N angles of 108.4(3)°.

Reference to the isoelectronic relationship between the amidino-group and the allyl and carboxylato-groups has been made previously,[1,2] and the various modes of bonding of the amidino-group to metals discussed. Monodentate, bidentate, and bridging modes of bonding have been found for the amidino-[1,3] and the isoelectronic triazenido-group RNNNR,[4—7] and chelating groups have invariably adopted σ,σ attachment.[8—13] Spectroscopic studies of complexes such as [M(η^5-C$_5$H$_5$)(CO)$_2${R'NC(R)NR'}][1,14] (M = Mo or W, R' = *p*-tolyl, R = Me or Ph) and [M(CO)$_4${R'NC(R)NR'}][1,15] (M = Mn or Re; R' = *p*-tolyl, R = Me or Ph) indicated symmetrically attached amidino-groups, but it was not possible to distinguish unequivocally between π or σ,σ attachment to the metal (Scheme 1). *X*-Ray crystallographic studies have shown molybdenum complexes,[9,10] *e.g.* [Mo(η^5-C$_5$H$_5$)(CO)$_2${R'NC(R)NR'}] (R = Me, R' = Ph)[9] to adopt the σ,σ mode, the delocalised NCN unit bonding symmetrically to the metal.



(A) (B)

Scheme 1. Symmetrically bonded amidino-groups. (**A**) π attachment; (**B**) σ,σ attachment

In an attempt to explore the isoelectronic relationship with the allyl group and to obtain complexes having π- or σ,π-bonded amidino-groups, bonding modes which have not yet been found, palladium and platinum derivatives seemed to provide a good choice because of the large number of η^3-allyl complexes known.[16] We report here the synthesis of a series of complexes of the type [{Pd[R'NC(R)NR']$_2$}$_n$] (n = 1 or 2) and the *X*-ray crystal structure of [Pd{*p*-MeC$_6$H$_4$NC(Me)NC$_6$H$_4$-Me-*p*}$_2$].[2] The amidine adopts again the symmetrical σ,σ bonding mode.

Results and Discussion

Treatment of [PdCl$_2$(PhCN)$_2$] with lithioamidines [R'N(Li)C(R)NR'] (R = H, Me, or Ph; R' = Me, Ph, or *p*-tolyl) in tetrahydrofuran or monoglyme (1,2-dimethoxyethane) solution affords [{Pd[R'NC(R)NR']$_2$}$_n$] (n = 1 or 2) complexes analogous to the corresponding bis(π-allyl) complexes,[17] but having greater thermal stability and more resistance to aerial oxidation. The amidino-complexes were obtained as high melting, yellow or red crystals, highly soluble in polar solvents, but insoluble or very sparingly soluble in non-polar solvents. They decompose slowly in air, and solutions in organic solvents are very sensitive to aerial oxidation. In chlorinated solvents, over long periods (weeks) under a nitrogen atmosphere, decomposition also occurs.

Notable features of the i.r. spectra of the amidino-complexes are the reduction in the number of absorption bands compared with the parent amidine, and the reduced intensity of many absorptions. The relative simplicity suggests a high degree of symmetry in the complexes. The vibrational spectra of the parent amidines have been studied in detail by Prevorsek,[18] and NCN skeletal stretching vibrational bands described in terms of amidine I to amidine III bands. Absorptions in the 1 640—1 600 cm^{-1} region were assigned to ν_{asym}(NCN) and designated amidine I, and on complexation become weaker in intensity and in some cases become no longer detectable (see Table 1). In the region 1 520—1 390 cm^{-1} a number of bands are reduced considerably in intensity and are assigned to the amidine II band. Also, bands in the 1 400—1 240 cm^{-1} region (amidine III) are affected by co-ordination, either being considerably shifted or reduced in intensity. Though evidence for co-ordination of the amidine is unmistakable, the mode of co-ordination is more difficult to determine. Comparison with spectra of benzamidino-rhenium complexes,[15] known to contain bidentate, chelating

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† *Supplementary data available* (No. SUP 56498, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. A comparison of the i.r. absorptions (1 200—1 700 cm^{-1}) of $[\{Pd[R'NC(Ph)NR']_2\}_n]$ (n = 1 or 2) and the parent amidines $R'NHC(Ph)NR'$[a]

Approximate region for bands[b]	R′ = Me		R′ = Ph		R′ = p-MeC_6H_4		R′ = p-FC_6H_4		R′ = p-$Pr^iC_6H_4$	
	Parent	Complex	Parent	Complex	Parent	Complex	Parent	Complex	Parent	Complex
Amidine I	1 651vs	1 615vs	1 630m(sh)		1 620vs		1 624s		1 620s	1 600m(sh)
			1 621s	1 603m	1 590vs	1 590s	1 615s		1 592vs	1 590m
							1 600vs			
	1 635m(sh)	1 560m(sh)	1 589vs		1 585vs	1 570s	1 590vs	1 580m,br	1 580s	1 570m
			1 575s	1 570s			1 571w			
Amidine II	1 500s	1 500w	1 530vs		1 520vs		1 530vs		1 532vs	1 500s
	1 490m	1 470m	1 490s(sh)		1 500vs	1 500vs	1 495vs	1 490s	1 515s	
			1 470s	1 470m	1 450m				1 460m	
	1 450m		1 440s		1 400m	1 400vw	1 440m	1 430m		
							1 400m		1 418s	1 420w
Amidine III	1 385m		1 330s	1 300w	1 330vs		1 340m		1 380m	1 380vw
	1 370s			1 275w	1 300m(sh)	1 260w	1 290w		1 340s	1 335vw
	1 300m	1 260m	1 240w	1 270w					1 300w	1 302vw
	1 200vw	1 200vw	1 220s	1 210m	1 220vs	1 215m		1 225s	1 278w	1 289vw
									1 230m	1 215w

[a] Nujol or hexachlorobutadiene mulls. [b] Assignments cannot be made with any certainty, but region is indicated where amidine I—III bands are expected.

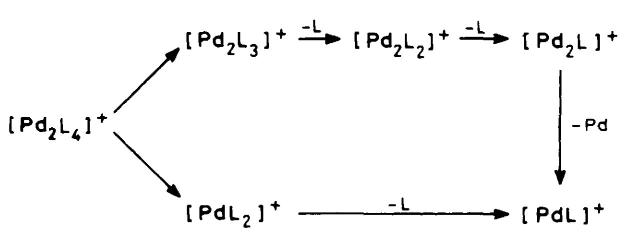
Table 2. Mass spectral fragments for dinuclear benzamidinopalladium complexes $[Pd_2\{R'NC(Ph)NR'\}_4]$

Fragment	Amidino-ligand (m/z)								
	R′ = p-FC_6H_4		p-$Pr^iC_6H_4$		Me		Ph		p-MeC_6H_4
$[Pd_2L_4]^+$	1 440		—		800		1 296		1 408
$[Pd_2L_3]^+$	1 113		1 277	m^* 999.2	—		1 025	m^* 810.7	—
$[Pd_2L_2]^+$	826		922		506		754		810
$[PdL_2]^+$	720		816		400		648	m^* 558.9	704
$[Pd_2L]^+$	—		567		—		482	m^* 219.3	—
$[PdL]^+$	413		461		253		377		405
L^+	307		355		147		271		299
$R'NCPh^+$	198	m^* 127.7	222	m^* 138.8	118		180	m^* 119.6	194
$PhCN^+$	103	m^* 45.8	103	m^* 63.8	103	m^* 50.2	103		103
R'^+	95		119		77		77		91
Ph^+	77	m^* 60.8	77		77		77		77
$C_6H_4^+$	76		76		76		76		

ligands, indicates similar lowering of $\nu_{asym}(NCN)$ frequencies (amidine I) to 1 590—1 606 cm^{-1}, whereas monodentate formamidinopalladium complexes lack this absorption.[19] Consequently a bidentate form of bonding is suggested though it is not possible to differentiate between chelating and bridging modes. Similar difficulties relating to assignment of the bonding mode on the basis of i.r. measurements have been found for 1,3-diaryltriazenido-ligands.[20]

As expected no ν(N–H) stretching frequencies are observed. The ν(M–N) stretching frequencies cannot be assigned with certainty, but weak absorptions at *ca.* 260 cm^{-1} appear prime candidates. Weak absorptions are found for $[Pd_2L_4]$ complexes [L = PhNC(Ph)NPh, p-$FC_6H_4NC(Ph)NC_6H_4F$-p, or p-Me-$C_6H_4NC(Ph)NC_6H_4Me$-p] at 260, 262, and 255 cm^{-1} respectively, similar absorptions being found for nickel and platinum complexes.[21]

The complexes are involatile, but mass spectra were obtained using high source temperatures (200—250 °C). Ions corresponding to a dimeric complex, though detected, gave peaks less intense than those arising from the free amidino-groups, but were identified by the characteristic palladium isotopic pattern. Acetamidino-complexes gave monomeric ions in the vapour state and $[ML_2]^+$ (L = amidino-group), $[ML]^+$, and L^+ were identified. In contrast, the benzamidino-complexes gave dinuclear ions, and two fragmentation pathways are found. The most favoured fragmentation route involves loss of amidino-



Scheme 2. A mass spectral fragmentation route for bis(amidino)-palladium(II) complexes (L = amidino-group)

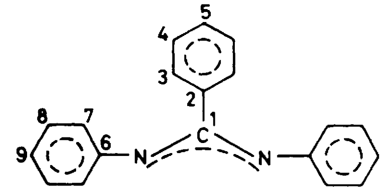
groups as a whole as outlined in Scheme 2. Several of the processes are supported by the presence of metastable peaks (see Table 2). The ligand-ion fragmentation pattern was found to be very similar to that found for the unco-ordinated ligand,[22] and ions relating to the ligand were the most intense in the spectrum. An alternative pathway, found for benzamidino-complexes, when the nitrogen substituents are phenyl, methyl, and *p*-tolyl, involves fragmentation of the ligand whilst it remains co-ordinated to the metal. This less favoured pathway appears to bear no relationship with the substituent groups of the amidine, and only an occasional fragment is detected, *e.g.* $[PdL_2(NCN)]^+$ for R′ = Ph and $[Pd(MeNCN)]^+$ for R′ = Me.

Proton n.m.r. studies of *N,N′*-di-*p*-tolylacetamidino- and *N,N′*-dimethylbenzamidino-complexes in deuteriochloroform and carbon disulphide respectively showed the environments of the N substituents to be indistinguishable, and the amidino-groups to be symmetrically bonded. Between −55 °C and ambient temperature no splitting of the methyl resonances was observed. A bidentate chelate mode of bonding is indicated by the ^{13}C n.m.r. data based upon the skeletal carbon (NCN) signal (C^1) (Table 3), by comparison with data for chelate groups in $[Re(CO)_4\{R'NC(R)NR'\}]$-type complexes[15] and for bridging groups in $[Ag_2\{R'NC(H)NR'\}_2]$.[23] C^1 signals are used as a criterion of bonding mode. For the palladium complexes signals occur in the region 174.4—176.2 p.p.m. compared with 166—175 p.p.m. for bidentate chelate groups and 159—167 p.p.m. for bridging groups. The nitrogen substituent groups produce one set of signals over a wide temperature range, consistent with symmetrically bound amidino-groups. Comparing the aromatic ring-carbon signals with those of the free ligands,[21] the changes are very small indeed except for the *ortho*-carbon of N-substituent rings which moves to higher frequencies (2—5 p.p.m.) and the aromatic carbon attached to the carbon of the NCN skeleton which moves to lower frequencies (0—4 p.p.m.). This is consistent with high electron density on the C^2 carbon.

Low-temperature n.m.r. spectra of both the *N,N′*-di-*p*-fluorophenyl- and *N,N′*-di-*p*-tolyl-benzamidine (Table 3) indicate the presence of another species in solution, albeit in small amount. Also variable-temperature ^{19}F studies of the former complex show a single signal (−120.1 p.p.m.) at 25 and 40 °C but three peaks (−120.1, −121.1, and −121.8 p.p.m. relative to $CFCl_3$) at −40 °C.

The data collected on the complexes reveal differences in the solid, vapour, and solution forms. Mass spectra indicate dimeric benzamidino-complexes, but monomeric *N,N′*-diphenyl- and -di-*p*-tolyl-acetamidino-complexes. *X*-Ray crystallographic studies have confirmed a monomeric structure for the latter complex in the solid. Though dinuclear ions are observed for the *N,N′*-di-*p*-fluorophenylbenzamidino-complex in the mass spectrum, relative molecular mass measurements by cryoscopy in benzene indicate a monomer (found M = 730; monomer and dimer require M = 720 and 1 440 respectively). Thus a dimer ⟷ monomer change may occur for this complex in going from the solid to a solution. The occurrence of such dimer ⟷ monomer changes in solution is also indicated by the n.m.r. data, which are consistent with the presence of one form of the complex (the monomer) being in solution at ambient temperatures, the monomer having bidentate chelate amidino-groups. At low temperatures (−80 °C) a second species is detected for some complexes (Table 3) and is believed to be a

Table 3. ^{13}C N.m.r. data[a] for $[\{Pd[R'NC(Ph)NR']_2\}_n]$ complexes



R′ in R′NC(Ph)NR′	Solvent	θ_c/°C	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	CH_3	C–H (Pr^i)
Ph	$CDCl_3$	25	—	132.0	128.3	129.1	126.1	144.1	124.7	129.0	122.7		
p-MeC_6H_4[b]	CD_2Cl_2	25	174.4	133.0	128.4	129.6	126.2	—	125.4	129.3	132.3	20.8	
		−80	176.2	132.0	128.0	128.8	126.5	144.1	124.6	128.5	131.6	20.2	
p-FC_6H_4[b,c]	CD_2Cl_2	40	176.2	131.2	128.4	129.2	130.1	140.7 (2)	126.0 (7)	115.1 (22)	159.3 (242)		
		25	175.8	130.6	128.2	128.9	129.9	140.0	125.6 (7)	114.9 (22)	158.9 (242)		
		−80	175.3	130.4	127.6	128.4	129.4	139.6	125.0 (7)	114.4 (22)	158.6 (242)		
			165.4	130.1	127.7	128.6	129.4	139.7	124.6	113.7 (22)	157.5 (242)		
p-Pr^i	$CDCl_3$	25	174.8	131.7	127.9	128.9	129.8	142.8	124.4	125.9	141.2	23.9	33.3

[a] Values in p.p.m. relative to $SiMe_4$, J(C–F) values in Hz in parentheses. [b] Spectra obtained at −80 °C indicate the presence of a second species but in small amounts. For R′ = *p*-FC_6H_4, signals are at 165.4, 130.1, . . . p.p.m. for C^1, C^2, . . . *etc.* respectively for the minor species. [c] Assignments are based on distortionless enhancement by polarisation transfer experiments and studies of other systems.[15]

dimeric complex. Detailed studies of the *N,N'*-di-*p*-fluorophenylbenzamidino-complex reveal a new C^1 carbon signal at 165.4 p.p.m. which, using our criterion of bonding mode, we assign to a bridging amidino-group. Dimeric palladium structures, *e.g.* $[\{Pd(R'NNNR')_2\}_2]$, isoelectronic with the amidino-complexes in this work, have been found for 1,3-diaryltriazenido-complexes in the solid,[7] and a similar structure with four bridging groups is thought to be the most likely structure for the benzamidino-complexes in the solid state. Interestingly, monomeric forms of the triazenido-complexes of nickel(II) and palladium(II) occur in benzene solution in equilibrium with dimers/oligomers.[5] The monomeric amidino-complexes are thought to have a similar structure to $[Pd\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}_2]$, for which the crystal structure is reported later.

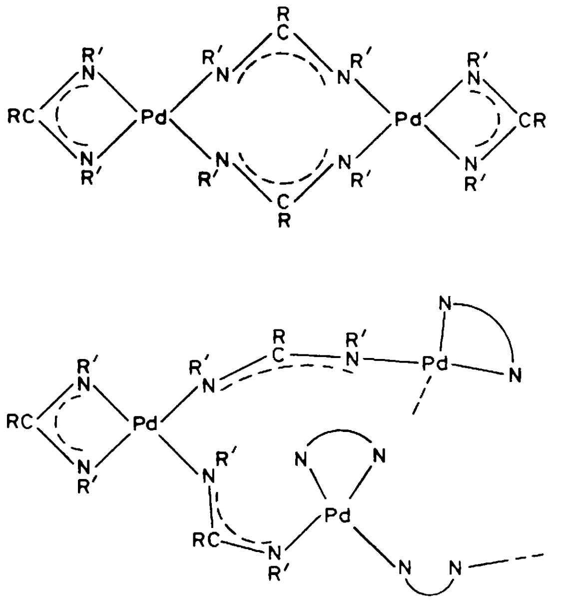


Figure 1. Dimeric and oligomeric structures for $[\{Pd[R'NC(R)NR']_2\}_n]$ complexes having equal numbers of bridging and chelate amidino-groups. N⌒N = amidino-group

The ^{19}F n.m.r. spectrum of the *N,N'*-di-*p*-fluorophenylbenzamidino-complex changes from a single line at ambient temperature to a three-line spectrum at −40 °C, the two new signals appearing to have equal intensity. The corresponding ^{13}C spectrum at −80 °C indicates the presence of more than one species (Table 3), but these data cannot be interpreted simply in terms of a monomer $\rightleftharpoons$ dimer equilibrium in solution, the monomer having two chelate groups and the dimer four bridging groups as indicated earlier. A single ^{19}F signal would be expected for each symmetrically bound amidino-group. In freezing benzene solution the monomer predominates, and in the solid the dimer is indicated by mass spectrometry. The data are consistent with the dimer forming in solution as the temperature is lowered, but the ^{19}F n.m.r. data require the dimer or oligomer to contain $p\text{-}FC_6H_4$ groups in two environments, in equal numbers. Asymmetric chelate groups and monodentate groups are not consistent with the data, particularly ^{13}C data from which bridging groups are indicated by the C^1 (NCN) signal. Consequently dimers (or oligomers) with equal numbers of bridging and chelate groups are thought to occur as illustrated in Figure 1, the structure being intermediate between the monomer and dimer structures already established for these types of complexes.[24] Oligomers based on Pd_3 and Pd_4 rings may also be envisaged but it is thought that dimers are more in keeping with the chemistry previously described for these complexes. Interestingly, Vrieze and co-workers[25] found dimer $\rightleftharpoons$ tetramer equilibria in solution for a number of amidino-silver(I) and -copper(I) complexes.

Crystals of $[Pd\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}_2]$ were found to be orthorhombic with space group *Cmca*. Since the general position in this space group is 16-fold and there are only four molecules in the unit cell, the complex must have $C_{2h}(2/m)$ symmetry and must lie in a special position in the cell with the palladium on the centre of symmetry. It was chosen to be at ½ 0 0 and related positions. The mirror plane is normal to the PdN_4 plane and bisects the N–C–N angles so the two C–N bonds are forced to have the same length [1.322(4) Å] (see Table 4 and Figure 2) consistent with the usual conclusion that bridging and bidentate amidines and triazenes have the π electrons completely delocalised in the three-atom N–C–N or N–N–N skeletal systems. This bond length may be compared with an average value of 1.32 Å for bidentate amidino-groups in general, and of 1.34 and 1.33 Å in the bridging benzamidines

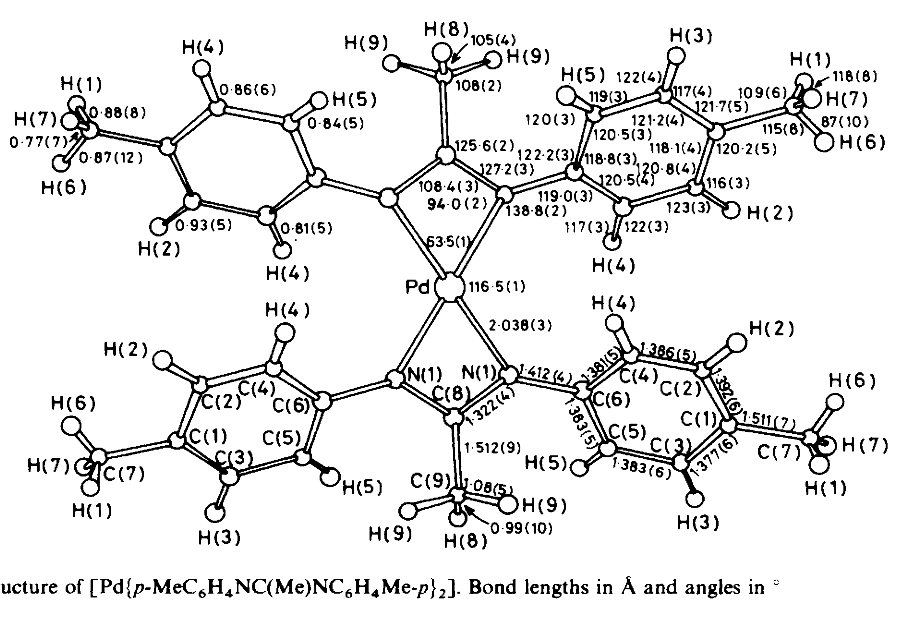


Figure 2. Molecular structure of $[Pd\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}_2]$. Bond lengths in Å and angles in °

Table 4. Comparison of crystallographic data[a] for symmetrically bound acetato- and amidino-groups

	$[Zn(O_2CMe)_2(H_2O)_2]$[43]	$Na[UO_2(O_2CMe)_3]$[44]	$[PdL_2]$[b]	$[TaCl_2(Me)L_2]$[c]	$[TaCl_3L_2]$[d]	$[Mo(\eta^5-C_5H_5)(CO)_2\{PhNC(Me)NPh\}]$[9]	$[Mo(\eta^5-C_5H_5)(CO)_3\{R'NC(Ph)NR''\}]$[e]	$[Re(CO)_2(PPh_3)_2(PhNCHNPh)]$[12]
C–X	1.30, 1.38	1.26, 1.29	1.322(4)	1.37(3), 1.39(3)	1.36(3), 1.36(3)	1.320(4), 1.320(4)	1.310(11), 1.295(11)	1.32(1), 1.34(1)
R–C	1.48	1.52	1.512(9)	1.48(3)	1.54(3)	1.499(5)	1.52(1)	2.22(1),
M–X	2.18, 2.17	2.47, 2.51	2.038(3)	2.160(17), 2.040(17)	2.098(14), 2.193(16)	2.176(3) 2.169(3)	2.175(7), 2.199(6)	2.22(1)
Ligand bite (X–X)	2.21	2.21	2.144(4)	2.20	2.20			
X–C–X	111	121	108.4(3)	106.2(13)	109.4(16)	108.0(3)	112.8(8)	112(1)
X–M–X	61		63.5(1)	61.9(38)	62.4(6)	53.9(1)	59.2(2)	60.0(1)

[a] Distances in Å, angles in °; X refers to co-ordinating atom, oxygen for the acetato-group and nitrogen for the amidino-group; R = skeletal carbon substituent (H, Me, or Ph as appropriate). [b] L = p-$MeC_6H_4NC(Me)NC_6H_4Me$-p. [c] L = $C_6H_{11}NC(Me)NC_6H_{11}$, ref. 8. [d] L = $Pr^i\,NC(Me)NPr^i$, monoclinic; ref. 8. [e] R′ = Ph(Me)CH, R″ = $PhCH_2$; ref. 10.

of $[Mo_2\{PhNC(Ph)NPh\}_4]$[3] and $[Cu_2\{PhNC(Ph)NPh\}_4]$ respectively.[24] Thus the acetamidino-group in this palladium complex is typical of its class. The N–C(phenyl) bond length [1.412(4) Å] indicates a certain degree of conjugation between the phenyl ring and the N–C–N system even though there is a dihedral angle of 42° between their planes. The distance is typical of bidentate *N,N′*-diarylamidino-groups (av. 1.41 Å). The dihedral angle is considerably larger than in the trigonal form of the closely related tris(diphenyltriazenido)cobalt(III),[6,26] where N–C(phenyl) averages 1.407 Å and the average dihedral angle is 12°. The larger angle in the present structure is presumably due to the extra steric hindrance of the methyl group on the central carbon atom. The C–C(methyl) bond length at this point is 1.512(9) Å which compares closely with the average of 1.52 Å found for both bidentate and bridging acetamidino-groups in a range of complexes.[8,9] The C(phenyl)–C(*p*-methyl) bond has virtually the same length, 1.511(7) Å, suggesting similar hybridisation states for C(7) and C(1). These distances compare closely with the average CH_3–C(phenyl) distance of 1.506(2) Å in *p*-tolyl compounds quoted by Domenicano *et al.*,[27] and the angle in the phenyl ring at the point of attachment of the methyl group is the same as the average value of 118.1(1)° quoted in the same reference.

The co-ordination of the nitrogen atoms to the central palladium atom is shown unequivocally to be the σ,σ symmetrically bidentate type. The Pd–N distance [2.038(3) Å] is very similar to that in the orthometallated amidino-complex $[Pd(\eta^5-C_5H_5)\{p\text{-}MeC_6H_3NHC(Me)NC_6H_4Me\text{-}p\}]$[9] (2.040 Å), the triazenido-complex $[Pd_2(PhNNNPh)_4]$ (2.041 Å),[7] and to the lengths of related bonds in other PdN_4 systems. It compares favourably with the corresponding distances in $[Pd(NH_3)_4]^{2+}$ [2.044(3) Å][28] and $[Pd(en)_n]^{2+}$ (en = ethylenediamine) [2.030(6) and 2.043(7) Å][29] for which metal–nitrogen π bonding is absent. Interestingly, Pd–N distances range between 1.86 Å for bis(*N*-ethylsalicylideneiminato)palladium(II)[30] and 2.148 Å for the amine–metal linkage of $[Pd(NCS)(SCN)\{Ph_2P(CH_2)_3NMe_2\}]$;[31] the palladium–nitrogen distances of the present amidino-complex lie towards the middle of this range but towards the top of the range for derivatives having the nitrogen as part of a π system of the ligand. Thus there is no evidence from the crystallographic data for π bonding in the PdN_4 unit.

It is instructive to consider the structures adopted by related palladium complexes having groups isoelectronic with the amidino-group. The acetate group occupies bridging positions in the polynuclear complexes $[Pd_3(MeCOO)_6]$,[32] $[Pd_2(\eta\text{-}C_3H_5)_2(MeCOO)_2]$,[33] and $[Pd_3(MeCOO)_3(Me_2CNO)_3]$,[34] whereas the dithiocarboxylate, dithiocarbamate, dithiodiphosphate, and diselenophosphate complexes are mononuclear[35] and presumably have two bidentate groups co-ordinated to the single palladium ion, as occurs for derivatives of other metals and for $[Pd(S_2CPh)_2]$.[36] The allyl group adopts the π-type mode in $[Pd_2(\eta\text{-}C_3H_5)_2(MeCOO)_2]$,[27] $[Pd(\eta\text{-}C_3H_5)(PPh_3)(SnCl_3)]$,[37] $[Pd(\eta\text{-}C_4H_7)(PPh_3)Cl]$,[38] and $[\{Pd(\eta\text{-}C_3Me_4H)Cl\}_2]$[39] for example, but a bridging position for $[\{Pt(C_3H_5)Cl\}_4]$.[40] Although limited data are available on triazenido-complexes, a preference for bridging rather than bidentate attachment seems apparent, and for $[\{Pd(PhNNNPh)_2\}_2]$ a structure related to that of $[Mo_2\{PhNC(Ph)NPh\}_4]$[3] with four bridging groups has been found.[7] For $[\{Pd(C_3H_7)(p\text{-}MeC_6H_4N_3C_6H_4Me\text{-}p)\}_2]$,[41] it is the triazenido-group and not the allyl group, as in $[\{Pt(C_3H_5)Cl\}_4]$,[40] which bridges the metal atoms. Thus the available data indicate that the acetamidino-group co-ordinates to palladium in a mode which differs markedly from that of the carboxylato-, triazenido-, and allyl groups bonded to palladium, but that a similarity exists with the bonding mode of dithio-groups such as dithiobenzoate. Although not common, the σ,σ bidentate mode occurs for the carboxylato-group in complexes of other metals,[42] and it is relevant to compare the geometry of the amidino-group with those of such bidentate carboxylato-groups.

Bidentate acetate groups occur in $[Zn(O_2CMe)_2(H_2O)_2]$[43] and $Na[UO_2(O_2CMe)_3]$.[44] Although zinc(II) is slightly larger than palladium(II), nevertheless several features of the zinc acetate unit are very similar to those of the palladium amidine unit. For example, the angle at the acetate's skeletal carbon atom is 111° and the co-ordinating atoms are set at a distance of 2.21 Å apart, which are similar to 108.4° and 2.144 Å respectively for the amidino-complex. Other data are given in Table 4 to demonstrate the similarity of the two groups in these complexes. An identical separation between the two co-ordinating atoms of the acetate group occurs for the zinc and uranium complexes, although the metal–oxygen distances for the latter complex are larger than those for the zinc acetate. Other complexes with bidentate amidino-groups bonded to transition metals have comparable C–N distances [1.28(3)—1.39(3) Å] and NCN angles (106.2—113.4°; av. 109.5°) with those for the palladium complex [1.322(4) Å and 108.4(3)° respectively] (selected examples given in Table 4). The similarities between the symmetrical bidentate groups bonding to palladium and other metals are also illustrated in Table 4, and demonstrate that the geometry of the amidino-group appears not to be greatly dependent on the size or oxidation state of the metal.

Experimental

N,N'-Diphenyl-, -di-*p*-tolyl-, -di-*p*-isopropylphenyl-, -di-*p*-fluorophenyl-, and -dimethyl-benzamidine and *N,N'*-diphenyl- and -di-*p*-tolyl-acetamidine and -formamidine were prepared by published procedures and lithio-derivatives were obtained by the method described previously.[1] The complex $[PdCl_2(PhCN)_2]$ was prepared from the commercial metal dichloride by the usual route. Hydrocarbon solvents and diethyl ether were dried over extruded sodium, the tetrahydrofuran (thf) and monoglyme were freshly distilled under nitrogen from lithium aluminium hydride. All solvents were pumped to remove dissolved air, stored under nitrogen, and transferred by syringe against a counter flow of nitrogen. All reactions were performed with exclusion of oxygen.

Spectra.—I.r. spectra in the range 4 000—250 cm^{-1} were recorded on a Perkin-Elmer 457 spectrophotometer and ^1H n.m.r. spectra at 60 MHz with a Varian A56/60D spectrometer. Mass spectra were obtained with an A.E.I. MS9 instrument at 70 eV (1.12×10^{-17} J) and an accelerating potential of 8 kV. Samples were inserted directly into the ion source at temperatures up to 250 °C.

Analyses.—The carbon, hydrogen, and nitrogen contents of the complexes were determined with a Perkin-Elmer 240 elemental analyser, and the palladium content was determined from the weight of the residue. Metal contents were also determined by atomic absorption spectroscopy using a Perkin-Elmer 403 spectrophotometer.

General Preparative Method for Bis(amidino)-complexes.—The lithioamidine was prepared by adding $LiBu^n$ (5 mmol) in hexane (2 mol dm^{-3} solution) by syringe to a frozen solution of the amidine (5 mmol) in diethyl ether or monoglyme (30 cm^3). On allowing the mixture to warm to ambient temperature and stirring at this temperature for 0.5 h, a colourless to pale yellow solution or cloudy suspension of the lithioamidine was obtained, which was used immediately or stored in a frozen condition.

The lithioamidine solution was added by syringe to a frozen solution of $[PdCl_2(PhCN)_2]$ (2.5 mmol) in ether or monoglyme (20 cm^3). On warming, the colour of the solutions deepens considerably, going from yellow-red to dark red. For some reactions, addition of $[PdCl_2(PhCN)_2]$ to a frozen solution of the lithioamidine was preferred. The reaction was continued until no further colour change was detectable (*ca.* 8—12 h). The cloudy precipitate of lithium chloride was removed by filtration, and the solvent evaporated at ambient temperature under reduced pressure. Orange-red or yellow powders were obtained (typically 65—90% yields) which were recrystallised at low temperatures from chloroform or methylene chloride solutions to obtain highly pure crystals but in low final yields (*ca.* 10%). It was noted that, over long periods in both chlorinated solvents and hydrocarbons, decomposition of the product occurred, metal being one of the products.

*Bis(*N,N'*-diphenylacetamidino)palladium*, $[Pd\{PhNC(Me)NPh\}_2]$. Air stable, deep red crystals (decomp. *ca.* 170 °C without melting) (Found: C, 63.9; H, 5.0; N, 10.6; Pd, 20.2. $C_{28}H_{26}N_4Pd$ requires C, 64.1; H, 4.95; N, 10.7; Pd, 20.2%); *m/z* 524 (P^+).

*Bis(*N,N'*-di-*p*-tolylacetamidino)palladium*, $[Pd\{p\text{-}MeC_6H_4NC(Me)NC_6H_4Me\text{-}p\}_2]$. Deep red platelets, air stable for several months (m.p. 195—197 °C, decomp. >200 °C) (Found: C, 66.9; H, 5.60; N, 9.95; Pd, 18.35. $C_{32}H_{34}N_4Pd$ requires C, 66.2; H, 5.85; N, 9.65; Pd, 18.30%); *m/z* 580 (P^+), 237 (L^+). ^1H N.m.r. ($CDCl_3$): 6.75 (8 H, m, C_6H_4), 2.32 (6 H, $p\text{-}CH_3$), and 1.95 p.p.m. (3 H, CH_3–C). On cooling the solution no splitting of CH_3–C or $p\text{-}CH_3$ signals was detected down to −55 °C when the signals broadened due to precipitation of the complex from solution.

Table 5. Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
C(1)	0.340 0(1)	0.332 2(6)	0.131 1(4)
C(2)	0.353 7(1)	0.261 5(7)	0.031 4(3)
C(3)	0.369 4(1)	0.365 8(6)	0.210 7(3)
C(4)	0.395 6(1)	0.227 1(5)	0.012 9(4)
C(5)	0.411 0(1)	0.326 2(6)	0.193 7(3)
C(6)	0.424 5(1)	0.256 1(5)	0.094 5(2)
C(7)	0.294 3(2)	0.372 4(12)	0.149 3(8)
C(8)	0.500 0*	0.303 8(6)	0.105 9(3)
C(9)	0.500 0*	0.500 4(11)	0.155 2(3)
N	0.466 6(1)	0.208 0(4)	0.075 3(2)
Pd	0.500 0*	0.000 0*	0.000 0*
H(1)	0.288(3)	0.486(12)	0.123(7)
H(2)	0.333(2)	0.262(7)	0.480(4)
H(3)	0.361(2)	0.420(8)	0.269(5)
H(4)	0.404(1)	0.315(7)	0.456(4)
H(5)	0.428(1)	0.335(6)	0.246(4)
H(6)	0.277(4)	0.293(17)	0.118(10)
H(7)	0.284(2)	0.342(10)	0.204(6)
H(8)	0.500*	0.490(15)	0.235(8)
H(9)	0.471(1)	0.067(6)	0.364(4)

* Invariant.

*Bis(*N,N'*-di-*p*-tolylbenzamidino)palladium*, $[Pd\{p\text{-}MeC_6H_4NC(Ph)NC_6H_4Me\text{-}p\}_2]$. Blood red solid (decomp. 122 °C), yield 89% (Found: C, 69.2; H, 5.50; N, 7.60; Pd, 15.4. $C_{42}H_{38}N_4Pd$ requires C, 71.6; H, 5.40; N, 7.95; Pd, 15.1%); *m/z* 1 408 (P^+). ^1H N.m.r. ($CDCl_3$): 6.9(13) and 2.2(6) p.p.m., both very broad.

*Bis(*N,N'*-dimethylbenzamidino)palladium*, $[Pd\{MeNC(Ph)NMe\}_2]$. Yellow, air-stable crystals (decomp. >200 °C without melting), yield 23% (Found: C, 54.9; H, 5.15; N, 13.1; Pd, 26.6. $C_{18}H_{22}N_4Pd$ requires C, 54.0; H, 5.50; N, 14.0; Pd, 26.5%); *m/z* 800 (P^+), 147 (L^+), and 506 ($Pd_2L_2^+$). ^1H N.m.r. (CS_2): 7.41 (5 H, br, C_6H_5) and 2.87 p.p.m. (6 H, CH_3).

*Bis(*N,N'*-diphenylbenzamidino)palladium*, $[Pd\{PhNC(Ph)NPh\}_2]$. Deep red, air-stable crystals (decomp. 133 °C without melting), yield 64.2% (Found: C, 71.30; H, 3.90; N, 8.35; Pd, 16.80. $C_{38}H_{30}N_4Pd$ requires C, 70.35; H, 4.60; N, 8.65; Pd, 16.40%); *m/z* 1 296 (P^+). ^1H N.m.r. ($CDCl_3$); 6.8 p.p.m. (vbr).

Bis(N,N'*-di-*p*-fluorophenylbenzamidino)palladium*, $[Pd\{p\text{-}FC_6H_4NC(Ph)NC_6H_4F\text{-}p\}_2]$. Deep red crystals (m.p. 246 °C), yield 79% (Found: C, 65.95; H, 4.30; F, 11.50; N, 7.85; Pd, 16.80. $C_{38}H_{26}F_4N_4Pd$ requires C, 63.30; H, 3.60; F, 10.55; N, 7.75; Pd, 14.75%); *m/z* 1 440 (P^+). N.m.r. ($CDCl_3$): ^1H, 7.0, 6.6, and 6.4 (vbr); ^{19}F, −120.1 p.p.m. (s) ($CFCl_3$ reference).

*Bis(*N,N'*-di-*p*-isopropylphenylbenzamidino)palladium*, $[Pd\{p\text{-}Pr^iC_6H_4NC(Ph)NC_6H_4Pr^i\text{-}p\}_2]$. Blood red crystals (decomp. 118 °C), yield 80% (Found: C, 75.20; H, 7.00; N, 6.55; Pd, 12.80. $C_{50}H_{54}N_4Pd$ requires C, 73.50; H, 6.60; N, 6.85; Pd, 13.00%); *m/z* value for P^+ not observed, highest mass peak at 1 277 $[Pd_2L_3^+]$. ^1H N.m.r. ($CDCl_3$); 6.9, 6.0(13), 2.1(2), 1.2 and 1.1 (12, d), all very broad.

Structure Determination.—*Crystal data.* $C_{32}H_{34}N_4Pd$, M = 581.0, orthorhombic, a = 32.089(13), b = 7.049(2), c = 12.282(3) Å, U = 2 778 $Å^3$, Z = 4, D_c = 1.389 g cm^{-3}, $F(000)$ = 1 200, Mo-K_α (λ = 0.710 69 Å), μ = 6.68 cm^{-1}, space group *Cmca* or *C2cb* (non-standard setting of *Aba*2) from systematic absences, *Cmca* confirmed from interpretation of the Patterson synthesis and refinement of the structure.

After preliminary *X*-ray photography, 2 054 *X*-ray intensities were measured on a Hilger and Watts computer-controlled, four-circle diffractometer. Of these, 1 394 were regarded as significant $[I > 3\sigma(I)]$. The structure was solved by the Patterson, heavy-atom method and was refined by full-matrix least-squares calculations to a final R value of 0.039. Part way through the refinement, all the hydrogen atoms were located in a Fourier difference map. They were then refined with isotropic thermal parameters while the non-hydrogen atoms were assumed to vibrate anisotropically. In the later stages, reflections having $\Delta F > 4$ were not allowed to contribute to the least-squares sums (there were 46 of these in the last cycle) and a weighting scheme of the form $1/w = 1 + [(|F_o| - B)/A]^2$ was applied, with $A = 30$, $B = 60$, and $|F_o|$ on the absolute scale. Final atomic co-ordinates so obtained are given in Table 5 and the bond lengths and angles calculated from them are shown in Figure 2. The X-RAY system[45] of programs was employed.

Acknowledgements

We thank the S.E.R.C. for a studentship (to J. B.), a research grant, and for contributing to the cost of the diffractometer, the Ministry of Higher Education and Scientific Research of Iraq for a maintenance grant (to M. M. M.), and the Director of the Cripps Computing Centre of Nottingham University for computing facilities. We acknowledge the late Professor T. J. King for assistance with the computing.

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Received 2nd *August* 1985; *Paper* 5/1338