

In memory of T. A. Stephenson

Synthesis and Study of Monomeric and Dimeric Amidine Complexes of Nickel(II) and Platinum(II). Crystal Structure of Bis(*N,N'*-diphenylbenzamidino)platinum(II), [Pt{PhNC(Ph)NPh}₂][†]

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Amidino-complexes, $[\{M[R'NC(R)NR']_2\}_n]$ ($M = Ni$ or Pt , $R, R' =$ allyl or aryl), have been synthesised from $NiCl_2 \cdot 0.3C_4H_{10}O_2$ or $[Pt(PhCN)_2Cl_2]$. The nickel complexes are dimeric in the solid state, but monomeric with chelating amidino-groups in solution. In contrast, for the platinum complexes, monomeric structures are indicated both in the solid state and solution. This is confirmed by the *X*-ray crystal structure determination of $[Pt\{PhNC(Ph)NPh\}_2]$ [space group $C2/c$; unit-cell dimensions $a = 25.413(7)$, $b = 6.031(2)$, $c = 20.586(3)$ Å, $\beta = 109.89(2)^\circ$, and $Z = 4$], which shows both amidino-groups to have electron delocalisation [C–N 1.334(7), 1.340(7) Å] and to be symmetrically σ, σ -bonded through nitrogen atoms [Pt–N 2.040(5) and 2.025(5) Å]. The NCN skeletal angle [$106.7(5)^\circ$] is similar to the angle in other related complexes. ^{13}C n.m.r. studies of selected nickel and platinum complexes in solution are reported, and using the skeletal NCN ^{13}C n.m.r. signal as the criterion of bond type, bidentate chelate and not bridging amidino-groups are shown to occur in solution, indicating monomeric species. Interestingly two sets of signals of equal intensity, but differing by only 1 p.p.m. are observed for $[Ni_2\{PhNC(Ph)NPh\}_4]$ at 25 °C; amidino-structural types in solution are discussed.

Bis(amidino)-complexes of palladium have recently been reported,¹ together with the *X*-ray crystal structure of $[Pd\{p-MeC_6H_4NC(Me)NC_6H_4Me-p\}_2]$. Interestingly the acetamidino-complexes are found to be monomeric in the solid and vapour states (by mass spectrometry) as well as in solution (by n.m.r.), whereas the benzamidino-complexes are dimeric in the solid and vapour, but monomeric in solution (cryoscopy). At low temperature ($-80^\circ C$) the presence of a second species having bridging amidino-groups, detected by ^{13}C (and ^{19}F) n.m.r. spectroscopy, was interpreted as arising from a monomer \rightleftharpoons dimer equilibrium in solution. The ^{13}C n.m.r. signal arising from the skeletal NCN group has been used as a criterion of bonding, signals at 166–175 p.p.m. being assigned to a chelate group, and signals at 159–167 p.p.m. to a bridging group. This same criterion is applied in the present work which is concerned with related complexes of platinum and nickel. Similarities exist between the chemistry of amidino-complexes of palladium and that of platinum and nickel, but notable differences are also evident. The *X*-ray crystal structure of $[Pt\{PhNC(Ph)NPh\}_2]$, reported here, illustrates a close similarity with the acetamidino-palladium complex.¹

In contrast the bis(amidino)-complex of copper(II), $[Cu_2\{PhNC(Ph)NPh\}_4]$,² and the bis(triazenido)-complexes of nickel(II), palladium(II), and copper(II)³ are dimeric with chromium(II)/copper(II) acetate-type structures.⁴ Also the bis(formamidino)-palladium(II) complexes are reported⁵ to be dimeric. Thus the presence of a substituent on the middle atom of the NXN skeleton ($X = N$ or CR), and the nature of this substituent have a distinct effect on the chemistry of the ligand group.

Results and Discussion

Related routes to those used for the synthesis of amidino-palladium complexes, $[\{Pd[R'NC(R)NR']_2\}_n]$,¹ have been used to synthesise the analogous complexes of platinum(II) and nickel(II). Yellow platinum complexes were obtained from $[Pt(PhCN)_2Cl_2]$ in diethyl ether solutions as solids having short period stability to air/moisture, but in solution the complexes were very sensitive. The monoglyme (1,2-dimethoxyethane) adduct, $NiCl_2 \cdot 0.3C_4H_{10}O_2$, was used to prepare the dark green nickel complexes which were especially sensitive to traces of air/moisture as solids as well as in solution. Stability to air/moisture of these $[\{M[R'NC(R)NR']_2\}_n]$ complexes was in the order $Pt > Pd > Ni$. Interestingly, the colours of the nickel complexes differ significantly from that of the closely related triazenido-complex $[Ni_2(PhNNPh)_4]$ ³ which is red and has a chromium(II) acetate-type dimeric structure⁴ based on square-planar co-ordination of nickel. The green colour of the amidino-complexes is more in keeping with the spectral properties of tetrahedral nickel(II) complexes, e.g. $[Ni(PPh_3)_2Cl_2]$,⁶ but such a geometry requires the d^8 complex to be paramagnetic. According to our n.m.r. studies, all the nickel complexes studied here are diamagnetic, so a local square-planar geometry is indicated. Mass spectral data also indicate dimeric structures, so a structural analogy with the nickel triazenido-complex possibly exists.

The mass spectral data (Table 1) clearly show the nickel complexes to be dimeric in the vapour state, similar to the benzamidino-palladium complexes,¹ and that the platinum complexes are monomeric. As described previously for the palladium complexes, two fragmentation routes are found, the most favoured involving loss of whole amidino-groups (see ref. 1, figure 2), and the least favoured route involving fragmentation of the ligand whilst it is co-ordinated to the metal. Interestingly, though the platinum complexes produce predominantly ions derived from a mononuclear complex,

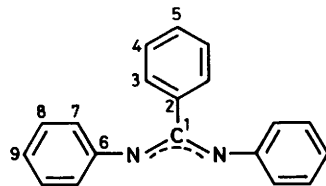
[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Mass spectral fragments^a for $[\{M[R'NC(R)NR']_2\}_n]$ (M = Ni or Pt) complexes

Ion	Amidino-ligand (L) ^b											
	dfpba		dippba		dmmba		dpba		dtba		dpaa	
	Ni	Pt	Ni	Pt	Ni	Pt	Ni	Pt	Ni	Pt	Ni	Pt
$[M_2L_4]^+$	—	—	—	—	—	—	1 202	—	—	—	954	—
$[M_2L_3]^+$	1 039	—	—	—	—	—	931	—	1 015	—	—	—
$[M_2L_2]^+$	732	—	828	—	—	—	660	—	716	—	536	—
$[M_2L]^+$	—	—	—	—	—	—	389	—	—	—	—	—
$[ML_2]^+$	673	809	769	905	489	601	737	657	793	477	613	
$[ML]^+$	366	502	414	550	342	330	466	358	494	268	404	
L^+	307	307	355	355	147	271	271	299	299	209	209	
$R'NCR^+$	198	198	222	222	118	180	180	194	194	118	118	
RCN^+	103	103	103	103	103	103	—	103	103	103	103	
R'^+	95	95	119	119	—	77	—	91	—	—	77	
Metastable peaks	m^* 127.7 (307 → 198)	m^* 127.7 (307 → 198)	m^* 138.8 (355 → 222)	m^* 138.8 (355 → 222)	m^* 50.2 (118 → 77)				m^* 125.8 (299 → 194)		m^* 50.2 (118 → 77)	
	m^* 60.8 (95 → 76)	m^* 60.8 (95 → 76)		m^* 63.8 (222 → 119)				m^* 42.7 (194 → 91)				
				m^* 57.5 (103 → 77)								
				m^* 39.8 (355 → 119)								

^a m/z Values. ^b Hdfpba = di(*p*-fluorophenyl)benzamidine, Hdippba = di(*p*-isopropylphenyl)benzamidine, Hdmba = dimethylbenzamidine, Hdpba = diphenylbenzamidine, Hdtba = di-*p*-tolylbenzamidine, Hdpaa = diphenylacetamidine.

Table 2. ¹³C N.m.r. data^a for $[\{M[R'NC(R)NR']_2\}_n]$ (M = Ni or Pt) complexes

Ligand	Metal	$\theta_c/^\circ\text{C}$	Solvent	C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	C ⁷	C ⁸	C ⁹	CH	CH ₃	Notes
dpaa	Pt	25	(CD ₃) ₂ CO						132.6	127.9	129.6	121.6	17.5		Peak at 153.1 p.p.m. assigned to free ligand
dmmba	Pt	25	CDCl ₃	167.6	132.9	128.5	129.3	132.3					30.3		No significant change at -80 °C
dpba	Pt	25	CDCl ₃	—	135.0	128.2	129.2	127.0	143.4	123.0	128.5	122.2			Peak at 154.1 p.p.m. assigned to free ligand
	Ni	25	C ₆ D ₆	174.1	132.2	—	129.4	126.8	145.8	123.1	—	122.3			Two species in solution in approximately similar amounts
				173.1	131.5	—	129.3	—	145.0	123.0	—	121.5			
dtba	Pt	25	CDCl ₃	—	132.3	128.1	129.0	126.8	140.8	124.7	128.5	130.1			
dfpba	Pt	25	CDCl ₃	—	130.1	128.5	128.9	129.5	139.1	126.0	114.9	159.0			$J(\text{C}^8-\text{F})$ 22, $J(\text{C}^9-\text{F})$ 242
	Ni	25	CDCl ₃	171.6	130.9	128.5	130.9	131.7	147.5	127.3	114.9	159.2			$J(\text{C}^8-\text{F})$ 23, $J(\text{C}^9-\text{F})$ 243
dippba	Pt	25	CDCl ₃	—	132.0	128.0	129.0	129.4	143.3	124.7	125.8	140.8	33.3	23.9	

^a Values in p.p.m. relative to SiMe₄, J values in Hz. Assignments are based on distortionless enhancement by polarisation transfer experiments.

peaks of higher mass correspond to fragments which may arise from units having more than two amidino-groups bound to the metal, e.g. $[\text{Pt}(\text{L})_2\text{PhCN}]^+$, $[\text{Pt}(\text{L})_2\text{MeNC}(\text{Ph})\text{N}]^+$, and $[\text{Pt}(\text{L})_2\text{Me}]^+$ (L = amidino-group). These may arise through thermolysis or by fragmentation of dinuclear or oligomeric complexes in which amidino-groups bridge metal atoms.

In a previous paper¹ we attempted to differentiate between bidentate chelate and bridging amidino-groups using the ¹³C signal for the NCN skeletal carbon atom as the criterion of bonding mode. Signals in the region 166–175 p.p.m. were assigned to chelate groups and in the region 159–167 p.p.m. to bridging groups. Unfortunately the C¹ signal could not be detected for the majority of complexes (Table 2), and for $[\{\text{Pt}[\text{MeNC}(\text{Ph})\text{NMe}]_2\}_n]$, the C¹ signal at 167.6 p.p.m. falls in the area of overlap between the two characteristic regions

making an assignment on this basis uncertain. However, for the two nickel complexes studied, C¹ signals at 174.1 and 171.6 p.p.m. suggest the presence of chelate groups in solution. Interestingly, for $[\{\text{Ni}[\text{PhNC}(\text{Ph})\text{NPh}]_2\}_n]$ two sets of ¹³C n.m.r. signals of the same intensity are observed at 25 °C, but the difference between pairs of signals, Δ , is only ca. 1 p.p.m. This difference is much smaller than that for the C¹ signals for the two forms of $[\{\text{Pd}[p\text{-FC}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{F-}p]_2\}_n]$, i.e. $\Delta =$ ca. 10 p.p.m. for which a chelated monomer \rightleftharpoons bridged dimer equilibrium was suggested to occur in solution. For the nickel complex, both solution forms appear to have chelate groups, and this type of monomer–dimer equilibrium is ruled out. Clearly the differences in the two C¹ carbon environments are slight and could arise from small differences in the bonding modes of the two amidino-groups in the complex. For example,

for monomeric complexes, one group may be delocalised and σ,σ -symmetrically bound, *e.g.* $[\text{Pd}\{p\text{-MeC}_6\text{H}_4\text{NC}(\text{Me})\text{NC}_6\text{H}_4\text{Me-}p\}_2]$,¹ and the other either σ,σ -unsymmetrically attached, *e.g.* numerous tantalum complexes,⁷ or σ,π -unsymmetrically attached, the localised C–N π system being used to

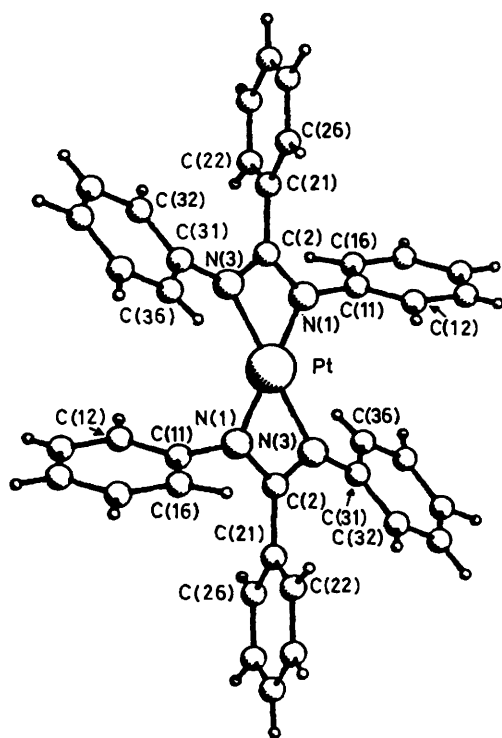


Figure 1. Perspective drawing of $[\text{Pt}\{\text{PhNC}(\text{Ph})\text{NPh}\}_2]$ showing the numbering system used

bond. Both these possibilities appear unlikely in solution on the basis of the strong preference shown for co-ordination through the nitrogen donor atoms, and for symmetrical σ,σ -bonding. This has also been shown to occur in the solid state for $[\text{Pd}\{p\text{-MeC}_6\text{H}_4\text{NC}(\text{Me})\text{NC}_6\text{H}_4\text{Me-}p\}_2]$ ¹ and $[\text{Pt}\{\text{PhNC}(\text{Ph})\text{NPh}\}_2]$ (see below). Two other unlikely structures have the second amidino-group bound either in the π -allyl mode or in the *ortho*-metallated mode. Neither of these forms is consistent with only small changes in the ^{13}C n.m.r. spectrum from that of the usual σ,σ -form. Structures having just two of the four bridging amidino-groups *cf.* $[\text{Pd}_2(\text{C}_3\text{H}_5)_2(\text{O}_2\text{CMe})_2]$ ⁸ appear to be ruled out by the position of the C^1 signal, and structures involving tetrahedral and octahedral co-ordination of the nickel are ruled out also by the absence of paramagnetic broadening of the signals expected for d^8 complexes. The molecular structures of some related platinum complexes, *e.g.* $[\text{Pt}_2(\text{S}_2\text{CC}_6\text{H}_4\text{-Pr}^i\text{-}p)_4]$ ⁹ and $[\text{Pt}_2(\text{S}_2\text{C}_2\text{H}_2)_4]$,¹⁰ consist of two essentially planar PtS_4 units, eclipsed and joined by metal–metal bonding (Pt–Pt 2.748 Å). The nickel complex could conceivably adopt a related structure, and in solution be present as a mixture of monomers and stacked dimers. Differences from the platinum complex $[\text{Pt}_2(\text{S}_2\text{C}_2\text{H}_2)_4]$, however, would arise because the latter complex, though dimeric in the solid state, is monomeric in solution and in the vapour state. For the nickel system, the metal–metal interaction would be required to be stronger, especially for dimers to persist in the vapour phase, and in solution. Clearly further studies are required to determine the cause of the two sets of ^{13}C signals.

In contrast to the ^{19}F n.m.r. spectrum of $[\text{Pd}_2\{p\text{-FC}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{F-}p\}_4]$,¹ the spectrum for the corresponding platinum complex showed no fluxional changes, and a single signal (120.5 p.p.m. relative to CFCl_3) was observed over the temperature range 25–40 °C.

The data collected point to the amidino-nickel complexes being dimeric in the solid state, but monomeric with chelating amidino-groups in solution. In contrast, for the amidino-platinum complexes, monomeric structures are indicated for

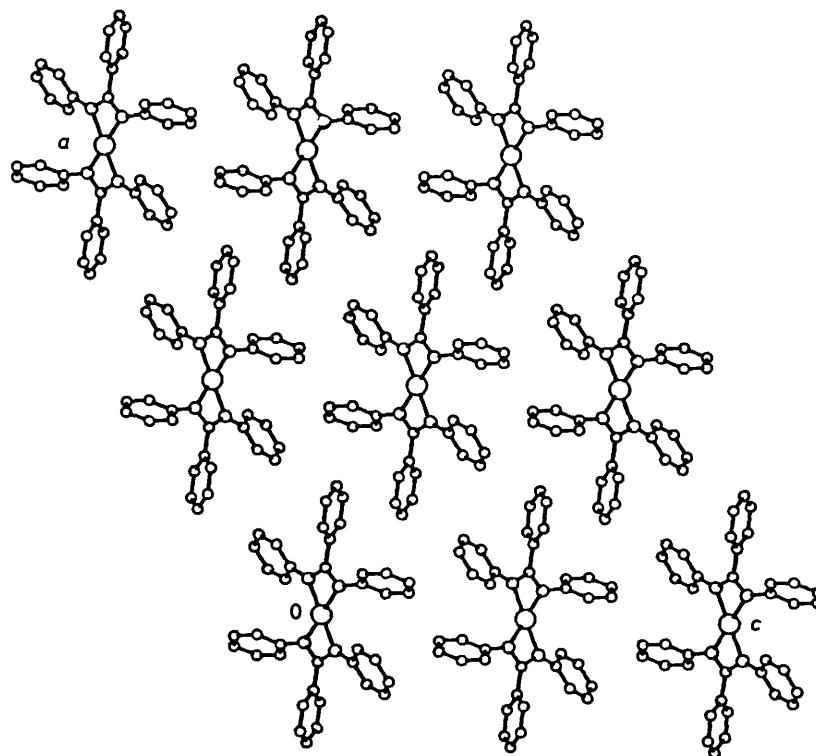


Figure 2. Packing diagram of $[\text{Pt}\{\text{PhNC}(\text{Ph})\text{NPh}\}_2]$ viewed along b

Table 3. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Pt-N(1)	2.040(5)	C(21)-C(22)	1.389(8)
Pt-C(2)	2.523(6)	C(21)-C(26)	1.386(8)
Pt-N(3)	2.025(5)	C(22)-C(23)	1.371(9)
N(1)-C(11)	1.406(7)	C(23)-C(24)	1.382(9)
N(1)-C(2)	1.334(7)	C(24)-C(25)	1.365(10)
C(11)-C(12)	1.372(9)	C(25)-C(26)	1.384(9)
C(11)-C(16)	1.391(8)	N(3)-C(31)	1.387(7)
C(12)-C(13)	1.373(11)	C(31)-C(32)	1.381(9)
C(13)-C(14)	1.357(12)	C(31)-C(36)	1.401(9)
C(14)-C(15)	1.357(12)	C(32)-C(33)	1.384(10)
C(15)-C(16)	1.380(10)	C(33)-C(34)	1.392(11)
C(2)-C(21)	1.493(8)	C(34)-C(35)	1.375(11)
C(2)-N(3)	1.340(7)	C(35)-C(36)	1.383(10)
N(1)-Pt-C(2)	31.80(19)	C(2)-C(21)-C(22)	121.3(5)
N(1)-Pt-N(3)	63.68(18)	C(2)-C(21)-C(26)	119.6(5)
C(2)-Pt-N(3)	31.94(19)	C(22)-C(21)-C(26)	119.1(5)
Pt-N(1)-C(11)	134.7(4)	C(21)-C(22)-C(23)	120.1(6)
Pt-N(1)-C(2)	94.5(4)	C(22)-C(23)-C(24)	120.7(6)
C(11)-N(1)-C(2)	127.5(5)	C(23)-C(24)-C(25)	119.4(6)
N(1)-C(11)-C(12)	120.1(5)	C(24)-C(25)-C(26)	120.6(6)
N(1)-C(11)-C(16)	121.4(5)	C(21)-C(26)-C(25)	120.0(6)
C(12)-C(11)-C(16)	118.3(6)	Pt-N(3)-C(2)	95.0(3)
C(11)-C(12)-C(13)	121.1(7)	Pt-N(3)-C(31)	135.4(4)
C(12)-C(13)-C(14)	120.6(8)	C(2)-N(3)-C(31)	129.3(5)
C(13)-C(14)-C(15)	119.1(8)	N(3)-C(31)-C(32)	124.7(5)
C(14)-C(15)-C(16)	121.8(7)	N(3)-C(31)-C(36)	116.7(5)
C(11)-C(16)-C(15)	119.1(6)	C(32)-C(31)-C(36)	118.6(6)
Pt-C(2)-N(1)	53.7(3)	C(31)-C(32)-C(33)	120.7(6)
Pt-C(2)-C(21)	174.3(4)	C(32)-C(33)-C(34)	120.2(7)
Pt-C(2)-N(3)	53.1(3)	C(33)-C(34)-C(35)	119.6(7)
N(1)-C(2)-C(21)	126.7(5)	C(34)-C(35)-C(36)	120.3(7)
N(1)-C(2)-N(3)	106.7(5)	C(31)-C(36)-C(35)	120.6(6)
C(21)-C(2)-N(3)	126.5(5)		

both solid and solution forms. The monomeric form in the solid state is confirmed by an *X*-ray crystallographic study of [Pt{PhNC(Ph)NPh}₂], which gave a similar structure (Figure 1) to that of [Pd{*p*-MeC₆H₄NC(Me)NC₆H₄Me-*p*]₂.¹ The amidino-groups chelate to the platinum with Pt-N distances [Table 3, 2.040(5) and 2.025(5) Å] typical of σ-bonding only between the metal and nitrogen. The C-N bond lengths (1.33 and 1.34 Å) are intermediate between the typical C-N (1.47 Å) and C=N (1.27 Å) covalent distances, indicating delocalisation in the NCN skeleton. A similar value is found for the palladium complex (1.332 Å).¹ The N-C(phenyl) bond lengths [1.387(7) and 1.406(7) Å] indicate a degree of conjugation between the phenyl rings and the N-C-N system. This is also found for the skeletal carbon substituent also, the N₂C-C(aryl) distance [1.493(8) Å] being intermediate between C-C (1.54 Å) and C=C (1.34 Å) covalent distances. Thus the whole benzamidino-ligand may be regarded as delocalised.

The NCN bite angle [Table 3, 106.7(5)°] is of the same magnitude as for other chelate amidino-complexes,^{1,11} but considerably smaller than NCN for bridging groups, e.g. [Mo₂{PhNC(Ph)NPh}₄] (117°).¹¹ Also unlike many related complexes, e.g. [Pt₂(S₂CC₆H₄Prⁱ-*p*)₄],⁸ the molecules of the amidino-complex are not stacked on top of each other (see Figure 2), the closest Pt-Pt contact, ca. 6 Å, for the amidino-complex, indicating no metal-metal interaction. Not surprisingly, dinuclear Pt₂ species are absent in the mass spectrum. Also solid-state conductivity studies of [Pt{*p*-RC₆H₄NC(Ph)NC₆H₄R-*p*]₂ (R = Me or F) showed the complexes to be semiconductors, with conductivities similar to that of bis(dimethylglyoximate)nickel(II).¹²

Binary triazenido-complexes, [M(RNNR)₂]_n invariably adopt the chromium(II) acetate-type structure⁴ having four

bridging ligands and short metal-metal distances. This mode of bonding is adopted also by the diphenylbenzamidino-group in [Cu₂{PhNC(Ph)NPh}₄]⁻ and [Mo₂{PhNC(Ph)NPh}₄],¹³ but in contrast to [Pd₂(PhNNNPh)₄] the amidino-complex [Pd{*p*-MeC₆H₄NC(Me)NC₆H₄Me-*p*]₂ is monomeric. Interestingly, the formamidino-complex [Pd₂{*p*-MeC₆H₄NCHNC₆H₄Me-*p*]₄, which differs only slightly from the previous complex, is dimeric.¹⁴ Thus the nature of the central atom group of the NXN skeleton (X = N or CR), and in the case of carbon, the identity of group R, has a profound effect on the structural type adopted, and on the chemistry of the resulting complexes. In general, bridge bonding modes are commonly adopted by triazenido- and formamidino-groups, and complexes tend to be dimeric, whereas for acetamidino-groups, the chelate form is usual and monomeric complexes result. Benzamidino-groups are often intermediate, both bridging and bidentate modes being both adopted, and monomeric ⇌ dimeric equilibria often exist in solution.¹

Thermogravimetric Analysis of Amidino-platinum Complexes.—The thermograms obtained over the temperature range 20–1 000 °C for samples under nitrogen are given in Figure 3. Transitions are generally ill defined, and many steps cannot be assigned to likely stages of thermal decomposition. The final residues were shown by atomic absorption analysis to be platinum metal, and weight losses from complexes corresponded closely to full loss of the amidino-ligands to leave pure metal. The solvated complexes all lost solvent at low temperatures in ill defined stages corresponding only approximately to the theoretical percentage weight losses. For example for [Pt(dmba)₂]-PhMe, found 12%, theoretical weight loss 15.8%; for [Pt(dpaa)₂]-CH₂Cl₂, found 11%, theoretical 12%.

The penultimate transition may, in all cases, except [Pt(dpaa)₂], be attributed to decomposition to form [Pt(N-R)] species, e.g. [Pt(dfpba)₂], where R = C₆H₄F, weight loss = 66% (theory 62.4%); [Pt(dippba)₂] 64% (theory 63.2%); [Pt(dmba)₂] 62% (theory 61.4%); [Pt(dpba)₂] 63% (theory, 61.9%); [Pt(dtba)₂] 61% (theory 62.2%). In the case of [Pt(dpaa)₂], the weight loss of 43% may be attributed to the loss of CH₂Cl₂ plus one ligand group leaving a residue of [Pt(dpaa)] [57% (theory 58%)].

Infrared Spectra.—Similar spectra are observed for the three series of complexes [M{R'NC(R)NR'}₂]_n (M = Ni, Pd, or Pt), the ligand absorptions arising from either bidentate or bridging modes of bonding. The i.r. data do not allow these two modes to be distinguished. In general the ν_{asym}(NCN) frequencies for the nickel and platinum complexes are comparable, and slightly higher than those of the palladium complexes. The dimethylbenzamidino complexes are exceptions in that ν_{asym}(NCN) frequencies are identical.

Attempts have been made to assign ν(M-N) frequencies, and weak intensity absorptions at ca. 270 cm⁻¹, observed for a number of complexes appear the prime candidate. Details are as follows: [Ni₂(dpba)₄] 270, [Ni₂(dippba)₄] 280, [Pd₂(dpba)₄] 260, [Pd₂(dtba)₄] 255, [Pd₂(dfpba)₄] 262, [Pt(dmba)₂] 270, [Pt(dippba)₂] 268, and [Pt(dfpba)₂] 270 cm⁻¹ (KBr disc, Nujol mull).

The nickel complexes show the presence of decomposition products in their spectra because of their sensitivity to aerial oxidation or hydrolysis. Free or co-ordinated amidines are indicated by the appearance of ν(N-H) stretching frequencies *etc.*, and brown colourations develop in originally green mulls after a few minutes for many of the complexes.

Experimental

N,N'-Diphenyl-, -di-*p*-tolyl-, -di(*p*-isopropylphenyl)-, -di(*p*-fluorophenyl)-, and -dimethyl-benzamidino and *N,N'*-diphenyl-

acetamide were prepared by published procedures and lithio-derivatives obtained by the method described previously.¹⁵ The complex $[\text{PtCl}_2(\text{PhCN})_2]$ was prepared from a solution of platinum(II) chloride in benzonitrile,¹⁶ and $\text{NiCl}_2 \cdot 0.3\text{C}_4\text{H}_{10}\text{O}_2$ from treatment of hydrated nickel(II) chloride with triethyl orthoformate $[\text{HC}(\text{OEt})_3]$ in monoglyme.¹⁷ Hydrocarbon solvents and diethyl ether were dried over extruded sodium, and tetrahydrofuran (thf) and monoglyme freshly distilled under nitrogen from lithium aluminium hydride. All solvents were subjected to a vacuum to remove dissolved air, stored under nitrogen, and transferred by syringe against a counterflow of nitrogen. All reactions were performed with rigorous exclusion of oxygen.

Spectra.—Infrared spectra in the range 4000–250 cm^{-1} were recorded using Perkin-Elmer 457 and 577 spectrophotometers and ^1H n.m.r. spectra at 60 MHz using a Varian 360L spectrometer. A Bruker HX90E spectrometer modified for Fourier-transform operation using a Nicolet B.N.C. 12 computer was used for ^1H , ^{19}F , and ^{13}C n.m.r. studies. Facilities at the University of Edinburgh (Bruker WH360) were also used for ^{13}C n.m.r. studies. SiMe_4 was used as an internal reference for ^1H and ^{13}C n.m.r. and CFCl_3 for ^{19}F n.m.r. experiments. Mass spectra were obtained using either an upgraded A.E.I. MS9 or VG 7070E instrument operating at 70 eV (1.12×10^{-17} J) and accelerating potentials of 8 and 6 kV respectively. Samples were inserted directly into ion sources at temperatures up to 250 °C.

Analyses.—Carbon, hydrogen, and nitrogen contents of the complexes were determined using a Perkin-Elmer 240 elemental analyser, and nickel and platinum contents by atomic absorption spectrometry using a Perkin-Elmer 403 instrument.

Thermal Analysis.—Thermogravimetric analyses were undertaken using Stanton Redcroft TG750 and 760 instruments (heating rate 10°min^{-1}). Air-sensitive samples were loaded into platinum crucibles in a nitrogen-filled glove-box, and taken to the instrument in a nitrogen-filled container. During transference of the crucible to the instrument some exposure to air occurred, and consequently the error normally associated with this technique is extended to $\pm 3\%$.

Reactions of $[\text{Pt}(\text{PhCN})_2\text{Cl}_2]$.—(a) *With $p\text{-FC}_6\text{H}_4\text{N}(\text{Li})\text{C}(\text{Ph})\text{NC}_6\text{H}_4\text{F}$.* The compound $p\text{-FC}_6\text{H}_4\text{NHC}(\text{Ph})\text{NC}_6\text{H}_4\text{F}$ (Hdfpba, 1.54 g, 5 mmol), dissolved in diethyl ether (50 cm^3), was cooled to 0 °C and *n*-butyl-lithium (50 cm^3 , 1 mol dm^{-3} solution in hexane) added. After warming to ambient temperature the yellow-green solution was stirred for 30 min to ensure complete reaction. The solution was then frozen to -196°C , solid $[\text{Pt}(\text{PhCN})_2\text{Cl}_2]$ (1.18 g, 2.5 mmol) added, and the mixture allowed to reach room temperature slowly whilst being vigorously stirred. After 30 min the solution was dark yellow-green, and after 1 h it became golden yellow. After 16 h the reaction mixture was filtered yielding a bright yellow solid and a dark brown filtrate. The solid was washed with dichloromethane and the extracts added to the filtrate. Evaporation of the latter to dryness, and recrystallisation of the brown solid residue from dichloromethane yielded a yellow powder identified as $[\text{Pt}\{p\text{-FC}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{F}\}_2]$ [m.p. 238 °C (decomp.), yield 64%] [Found: C, 56.6; H, 3.95; F, 9.20; N, 7.25; Pt, 23.8%; *M* (cryoscopy in C_6H_6), 667. $\text{C}_{38}\text{H}_{26}\text{F}_4\text{N}_4\text{Pt}$ requires C, 56.4; H, 3.20; F, 9.40; N, 6.90; Pt, 24.1%; *M*, 809]. N.m.r. (CDCl_3): ^1H , 7.6, 7.0, 6.4 p.p.m. (vbr); ^{19}F , -120.2 p.p.m. (s) (CFCl_3 reference). Mass spectrum: the parent ion $[\text{Pt}(\text{PhCN})_2]^+$ was observed at m/z 809, with fragmentation occurring predominantly by loss of whole ligand groups (Table

1). Low-intensity peaks corresponding to $[\text{Pt}(\text{PhCN})_2\text{Cl}_2]^+$, $[\text{Pt}(\text{PhCN})\text{Cl}_2]^+$, and $[\text{Pt}(\text{PhCN})\text{Cl}]^+$ were observed at m/z 912, 714, and 611 respectively. The positive ion fast-atom bombardment mass spectrum of the complex in a 2,4-diphenylphenol matrix showed a weak parent ion at m/z 810 corresponding to $[M + 1]^+$ and numerous fragment ions indicating a complex breakdown pattern. Peaks at m/z 503, 309, 198, and 195 correspond to $[\text{Pt}(\text{PhCN})_2]^+$, $[\text{PhCN}]^+$, $[\text{C}_6\text{H}_4\text{NC}(\text{Ph})\text{N}]^+$, and $^{195}\text{Pt}^+$ respectively.

(b) *With $p\text{-Pr}^i\text{C}_6\text{H}_4\text{N}(\text{Li})\text{C}(\text{Ph})\text{NC}_6\text{H}_4\text{Pr}^i$.* The lithiation of $p\text{-Pr}^i\text{C}_6\text{H}_4\text{NHC}(\text{Ph})\text{NC}_6\text{H}_4\text{Pr}^i$ (Hdippba) (1.78 g, 5 mmol) in diethyl ether (30 cm^3) and its reaction with $[\text{Pt}(\text{PhCN})_2\text{Cl}_2]$ (1.180 g, 2.5 mmol) were carried out as described above. The product, $[\text{Pt}\{p\text{-Pr}^i\text{C}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{Pr}^i\}_2]$, was obtained as a yellow powder (decomp. 118°C , yield 80%) (Found: C, 75.2; H, 7.00; N, 6.55; Pt, 12.8. $\text{C}_{50}\text{H}_{54}\text{N}_4\text{Pt}$ requires C, 73.5; H, 6.60; N, 6.85; Pt, 13.0%). ^1H N.m.r. (CDCl_3): 7.1–6.4 (26) (vbr); 2.7 (4) (vbr); 1.20, 1.19, 1.10 p.p.m. (24) (br m). Mass spectrum: the parent ion was observed at m/z 905, fragmentation occurring predominantly by loss of ligand groups (Table 1). Low intensity peaks at m/z 1008, 816, 709, and 461 assigned to $[\text{Pt}(\text{dippba})_2\text{PhCN}]^+$, $[\text{Pt}(\text{dippba})(\text{NC}_6\text{H}_4\text{Pr}^i)]^+$, $[\text{Pt}(\text{dippba})\text{NCNC}_6\text{H}_4\text{Pr}^i]^+$, and $[\text{Pt}(\text{NC}_6\text{H}_4\text{Pr}^i)]^+$ respectively.

(c) *With $\text{MeN}(\text{Li})\text{C}(\text{Ph})\text{NMe}$.*—The lithiation of $\text{MeNHC}(\text{Ph})\text{NMe}$ (Hdmba) (0.74 g, 5 mmol) in diethyl ether (100 cm^3) and its reaction with $[\text{Pt}(\text{PhCN})_2\text{Cl}_2]$ were carried out as described above. The yellow product, $[\text{Pt}\{\text{MeNC}(\text{Ph})\text{NMe}\}_2]$, was recrystallised from dichloromethane as golden yellow plates. Further recrystallisation from toluene–dichloromethane mixtures yielded the solvate $[\text{Pt}\{\text{MeNC}(\text{Ph})\text{NMe}\}_2] \cdot \text{PhMe}$ (decomp. 116°C , yield 15%) (Found: C, 52.2; H, 5.80; N, 9.70; Pt, 30.1. $\text{C}_{25}\text{H}_{29}\text{N}_4\text{Pt}$ requires C, 51.6; H, 5.15; N, 9.65; Pt, 33.6%). ^1H N.m.r. (CDCl_3): 7.5 (10), 2.9 p.p.m. (12) (br). Mass spectrum: weak peaks were observed at m/z 621, 518, 503, 474, 382, and 313, corresponding to $[\text{Pt}(\text{dmba})_2\text{MeNC}(\text{Ph})\text{N}]^+$, $[\text{Pt}(\text{dmba})_2\text{NMe}]^+$, $[\text{Pt}(\text{dmba})_2\text{N}]^+$, $[\text{Pt}(\text{dmba})\text{NC}(\text{Ph})\text{NMe}]^+$, $[\text{Pt}(\text{dmba})\text{NCN}]^+$, and $[\text{PtC}(\text{Ph})\text{NMe}]^+$ respectively. A strong peak was observed at m/z 489 corresponding to $[\text{Pt}(\text{dmba})_2]^+$, fragmentation occurring predominantly by loss of ligand groups (Table 1).

(d) *With $\text{PhN}(\text{Li})\text{C}(\text{Ph})\text{NPh}$.*—The lithiation of $\text{PhNHC}(\text{Ph})\text{NPh}$ (Hdpba, 0.68 g, 2.5 mmol) in diethyl ether (50 cm^3), and its reaction with $[\text{Pt}(\text{PhCN})_2\text{Cl}_2]$ (0.59 g, 1.25 mmol) were carried out as described above. The product, $[\text{Pt}\{\text{PhNC}(\text{Ph})\text{NPh}\}_2]$, was obtained as a yellow solid which was recrystallised from dichloromethane to give yellow needles (decomp. 177°C , yield 51%) (Found: C, 61.8; H, 4.55; N, 7.40; Pt, 24.5. $\text{C}_{38}\text{H}_{30}\text{N}_4\text{Pt}$ requires C, 61.9; H, 4.05; N, 7.60; Pt, 26.4%). ^1H n.m.r. (CDCl_3): 7.0, 6.9, 6.8, 6.7 p.p.m. (vbr). Mass spectrum: the parent ion $[\text{Pt}(\text{dpba})_2]^+$ was observed at m/z 737, fragmentation occurring predominantly by loss of ligand groups (Table 1). Fragments relating to the breakdown of the ligand whilst co-ordinated to the metal were found at m/z 660 (weak), 389, and 375, corresponding to $[\text{Pt}(\text{dpba})\text{NC}(\text{Ph})\text{NPh}]^+$, $[\text{PtNC}(\text{Ph})\text{NPh}]^+$, and $[\text{PtC}(\text{Ph})\text{NPh}]^+$ respectively.

(e) *With $p\text{-MeC}_6\text{H}_4\text{N}(\text{Li})\text{C}(\text{Ph})\text{NC}_6\text{H}_4\text{Me}$.* The lithiation of $p\text{-MeC}_6\text{H}_4\text{NHC}(\text{Ph})\text{NC}_6\text{H}_4\text{Me}$ (Hdtba) (0.37 g, 1.25 mmol) in tetrahydrofuran (50 cm^3) and its reactions with $[\text{Pt}(\text{PhCN})_2\text{Cl}_2]$ (0.29 g, 0.63 mmol) were carried out as described above. The product, $[\text{Pt}\{p\text{-MeC}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{Me}\}_2]$, was obtained on recrystallisation from dichloromethane as a yellow powder (decomp. 171°C , yield 38%) (Found: C, 63.7; H, 5.85; N, 6.95; Pt, 23.3. $\text{C}_{42}\text{H}_{38}\text{N}_4\text{Pt}$ requires C, 63.6; H, 4.80; N, 7.05; Pt, 24.6%). ^1H N.m.r. (CDCl_3): 7.2–6.4 (26) (vbr), 2.2 p.p.m. (12) (s). Mass spectrum: the parent ion $[\text{Pt}(\text{dtba})_2]^+$

was observed at m/z 793, fragmentation occurring predominantly by loss of ligand groups (Table 1). Fragments relating to the breakdown of the ligand whilst co-ordinated to the metal were found at m/z 673 and 403 corresponding to $[^{195}\text{Pt}(\text{dtba})\text{C}(\text{Ph})\text{NC}_6\text{H}_4]^+$ and $[^{195}\text{PtNC}(\text{Ph})\text{NC}_6\text{H}_4\text{Me}]^+$ respectively.

(f) *With PhN(Li)C(Me)NPh.* The lithiation of $\text{PhNHC}(\text{Me})\text{NPh}$ (Hdppa) in thf (60 cm³) and its reaction with $[\text{Pt}(\text{PhCN})_2\text{Cl}_2]$ (1.18 g, 2.5 mmol) were carried out as described above. The product, $[\text{Pt}\{\text{PhNC}(\text{Me})\text{NPh}\}_2]$, was obtained on recrystallisation from dichloromethane at -16°C as mustard yellow crystals of the CH_2Cl_2 solvate (decomp. 136°C , yield 23%) (Found: C, 50.4; H, 4.00; N, 8.05; Pt, 29.4. $\text{C}_{28}\text{H}_{26}\text{N}_4\text{Pt}\cdot\text{CH}_2\text{Cl}_2$ requires C, 49.9; H, 4.00; N, 8.00; Pt, 27.9%). ^1H N.m.r. (CDCl_3): 7.00 (20) (br), 1.80 p.p.m. (6) (s) Mass spectrum: the parent ion $[^{195}\text{Pt}(\text{dppa})_2]^+$ was observed at m/z 613, fragmentation occurring predominantly by loss of ligand groups. Fragments relating to the breakdown of the ligand whilst co-ordinated to the metal were found at m/z 459 and 313 corresponding to $[^{195}\text{Pt}(\text{dppa})\text{NC}(\text{Me})\text{N}]^+$ and $[^{195}\text{Pt}(\text{Me})\text{NPh}]^+$ respectively.

(g) *With PhN(Li)CHNPh.* Preliminary results indicate that $[\text{Pt}\{\text{PhNCHNPh}\}_2]$ is formed as described above.

Reactions of $\text{NiCl}_2\cdot 0.3\text{C}_4\text{H}_{10}\text{O}_2$.—With PhN(Li)C(Ph)NPh. The procedure used was essentially the same as that described above for the $[\text{Pt}(\text{PhCN})_2\text{Cl}_2]$ reactions. The lithiation of $\text{PhNHC}(\text{Ph})\text{NPh}$ (Hdpba, 2.72 g, 10 mmol) in monoglyme (100 cm³) was undertaken before the solid nickel chloride solvate (0.78 g, 5 mmol) was added. The initial yellow-green solution became dark green over 14 h. Evaporation of the solvent at ambient temperature, followed by extraction of the residue with toluene (140 cm³) yielded residual nickel chloride and a green solution from which crude solid product was obtained by removal of most of the solvent. The very air-sensitive product was purified by column chromatography (silica Kieselgel 60 Brackman 2-3) in thf using a 15-cm water-cooled column, some unidentified brown decomposition product also being obtained. Green $[\text{Ni}_2\{\text{PhNC}(\text{Ph})\text{NPh}\}_4]$ was finally obtained from evaporation of the eluant to dryness, and crystallisation from dichloromethane (decomp. 134°C , yield 79%) [Found: C, 75.5; H, 5.15; N, 8.50. $(\text{C}_{38}\text{H}_{30}\text{N}_4\text{Ni})_2$ requires C, 75.9; H, 5.00; N, 9.30%]. Mass spectrum: the parent ion $[^{59}\text{Ni}_2(\text{dpba})_4]^+$ was

observed at m/z 1202, fragmentation occurring predominantly by loss of ligand groups (Table 1). Fragments relating to the breakdown of the ligand whilst co-ordinated to the metal were found at m/z 447 and 433 corresponding to $[^{59}\text{Ni}(\text{dpba})\text{N}_2\text{CPh}]^+$ and $[^{59}\text{Ni}(\text{dpba})\text{NCPh}]^+$ respectively.

(b) *With $p\text{-FC}_6\text{H}_4\text{N}(\text{Li})\text{C}(\text{Ph})\text{NC}_6\text{H}_4\text{F-p}$.* The lithiation of $p\text{-FC}_6\text{H}_4\text{NHC}(\text{Ph})\text{NC}_6\text{H}_4\text{F-p}$ (Hdfpba, 4.62 g, 15 mmol) in monoglyme (150 cm³) and its reaction with $\text{NiCl}_2\cdot 0.3\text{C}_4\text{H}_{10}\text{O}_2$ (1.18 g, 7.5 mmol) were undertaken as described above. Green $[\text{Ni}_2\{p\text{-FC}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{F-p}\}_4]$ was isolated as a powder which was recrystallised from tetrahydrofuran to give a 4thf adduct (decomp. 138°C , yield 62%) [Found: C, 68.9; H, 3.85; F, 8.90; N, 6.70. $(\text{C}_{38}\text{H}_{26}\text{N}_4\text{Ni})_2\cdot 4\text{C}_4\text{H}_8\text{O}$ requires C, 67.6; H, 5.15; F, 9.10; N, 6.85%]. N.m.r. (CD_2Cl_2): ^1H , 6.91, 6.59, 6.23 (26) (br m), 3.76 (8) (m, thf solvate), 2.80 (8) p.p.m. (m, thf solvate); ^{19}F , -119.8 p.p.m. (CFCl_3 reference). Mass spectrum: the parent ion was not observed by electron impact studies, the highest ion observed at m/z 1039 corresponding to $[^{59}\text{Ni}_2(\text{dfpba})_3]^+$ (Table 1). Fragments relating to the breakdown of the ligand whilst co-ordinated to the metal were found at m/z 658 and 456 corresponding to $[^{59}\text{Ni}(\text{dfpba})\text{C}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{F}]^+$ and $[^{59}\text{Ni}(\text{dfpba})\text{NC}_6\text{H}_4]^+$ respectively.

(c) *With $[p\text{-Pr}^i\text{C}_6\text{H}_4\text{N}(\text{Li})\text{C}(\text{Ph})\text{NC}_6\text{H}_4\text{Pr}^i\text{-p}]$.* The lithiation of $p\text{-Pr}^i\text{C}_6\text{H}_4\text{NHC}(\text{Ph})\text{NC}_6\text{H}_4\text{Pr}^i\text{-p}$ (Hdippba) (7.12 g, 20 mmol) in monoglyme (100 cm³), and its reaction with $\text{NiCl}_2\cdot 0.3\text{C}_4\text{H}_{10}\text{O}_2$ (1.57 g, 10 mmol) were undertaken as

Table 4. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
Pt	0.25	0.25	0.0
N(1)	0.312 38(17)	0.062 8(8)	-0.013 47(24)
C(11)	0.318 20(20)	-0.061 5(9)	-0.068 4(3)
C(12)	0.298 4(3)	0.020 7(11)	-0.134 5(4)
C(13)	0.301 3(3)	-0.101 7(15)	-0.189 4(4)
C(14)	0.324 2(3)	-0.307 8(12)	-0.179 4(4)
C(15)	0.342 9(3)	-0.393 5(12)	-0.114 6(5)
C(16)	0.339 89(24)	-0.275 5(10)	-0.058 4(3)
C(2)	0.352 88(21)	0.157 2(10)	0.038 5(3)
C(21)	0.414 36(19)	0.121 4(9)	0.056 9(3)
C(22)	0.439 12(23)	-0.078 8(11)	0.084 2(3)
C(23)	0.495 96(24)	-0.104 6(11)	0.102 8(4)
C(24)	0.529 09(24)	0.065 1(11)	0.093 2(3)
C(25)	0.504 94(24)	0.262 0(11)	0.066 2(4)
C(26)	0.447 71(25)	0.291 6(9)	0.047 6(4)
N(3)	0.327 90(18)	0.300 1(7)	0.068 53(24)
C(31)	0.351 62(21)	0.442 3(10)	0.123 8(3)
C(32)	0.398 79(24)	0.395 1(11)	0.179 8(3)
C(33)	0.419 4(3)	0.547 0(14)	0.232 8(4)
C(34)	0.392 5(3)	0.749 4(14)	0.230 4(4)
C(35)	0.344 9(3)	0.796 3(11)	0.175 5(4)
C(36)	0.324 48(24)	0.645 3(11)	0.122 3(3)
H(12)	0.282(3)	0.115(13)	-0.142(4)
H(13)	0.290(3)	-0.046(12)	-0.227(3)
H(14)	0.324 5(22)	-0.390(11)	-0.220(3)
H(15)	0.355 3(24)	-0.519(11)	-0.112(3)
H(16)	0.351 7(23)	-0.338(10)	-0.009(3)
H(22)	0.422(3)	-0.178(10)	0.095(3)
H(23)	0.510(3)	-0.234(9)	0.116(3)
H(24)	0.568 1(23)	0.048(10)	0.108(3)
H(25)	0.526 4(22)	0.371(11)	0.054(3)
H(26)	0.433 6(22)	0.433(11)	0.031(3)
H(32)	0.419(3)	0.271(10)	0.185(3)
H(33)	0.453 1(23)	0.504(10)	0.271(3)
H(34)	0.409 6(22)	0.856(11)	0.273(3)
H(35)	0.321 6(22)	0.933(11)	0.167(3)
H(36)	0.295 5(24)	0.667(11)	0.084(3)

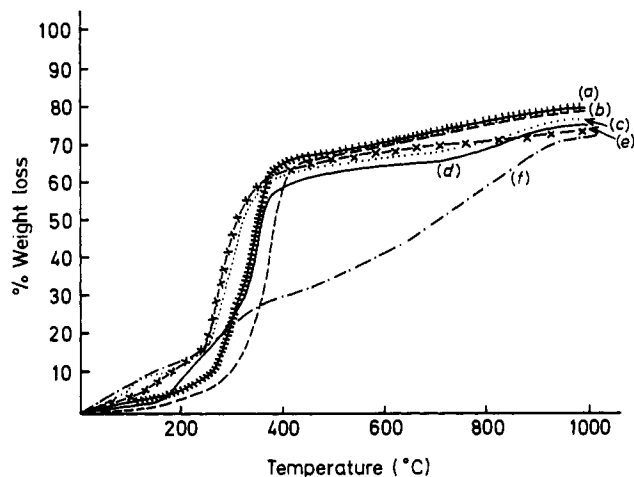


Figure 3. Thermograms for bis(amidino)platinum(II) complexes: (a) $[\text{Pt}\{\text{PhNC}(\text{Ph})\text{NPh}\}_2]$, (b) $[\text{Pt}\{p\text{-Pr}^i\text{C}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{Pr}^i\text{-p}\}_2]$, (c) $[\text{Pt}\{p\text{-FC}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{F-p}\}_2]$, (d) $[\text{Pt}\{p\text{-MeC}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{Me-p}\}_2]$, (e) $[\text{Pt}\{\text{MeNC}(\text{Ph})\text{NMe}\}_2]$, and (f) $[\text{Pt}\{\text{PhNC}(\text{Me})\text{NPh}\}_2]$

described above. The crude green product was extracted with toluene, and the solution cooled to -16°C to produce green $[\text{Ni}_2\{p\text{-Pr}^i\text{C}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{Pr}^i\}_4]$ (decomp. 70°C , yield 89%). In the presence of moisture a metallic grey decomposition product formed. Significant decomposition occurred at -16°C in the solid state under nitrogen and *in vacuo* over several days [Found: C, 78.8; H, 8.05; N, 7.40. $(\text{C}_{50}\text{H}_{54}\text{N}_4\text{Ni})_2$ requires C, 78.1; H, 7.00; N, 7.80%]. Mass spectrum: the parent ion was not observed, the peaks observed at highest mass, m/z 1 021, corresponding to $[\text{Ni}_2(\text{dippba})_2\text{NC}(\text{Ph})\text{NC}_6\text{H}_4]^+$. Fragments relating to the breakdown of the ligand whilst co-ordinated to the metal were found at m/z 918 and 573, corresponding to $[\text{Ni}_2(\text{dippba})_2\text{NC}_6\text{H}_4]^+$ and $[\text{Ni}(\text{dippba})\text{NCNC}_6\text{H}_4\text{Pr}^i]^+$ respectively.

(d) With $p\text{-MeC}_6\text{H}_4\text{N}(\text{Li})\text{C}(\text{Ph})\text{NC}_6\text{H}_4\text{Me}\text{-}p$. The lithiation of $p\text{-MeC}_6\text{H}_4\text{NHC}(\text{Ph})\text{NC}_6\text{H}_4\text{Me}\text{-}p$ (Hdtba) (3.0 g, 10 mmol) in monoglyme (150 cm^3) and its reaction with the nickel chloride solvate (0.783 g, 5 mmol) were undertaken as described above. The crude green solid product was extracted with toluene and yielded green $[\text{Ni}_2\{p\text{-MeC}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{Me}\text{-}p\}_4]$. This complex in the solid state decomposes noticeably at ambient temperature over several days, grey metal particles and brown powder being formed. Attempts to purify the complex in dichloromethane using an alumina column produced green and brown bands, but partial decomposition of the green complex resulted on removal of the solvent *in vacuo* [Found: C, 77.4; H, 6.45; N, 7.95. $(\text{C}_{42}\text{H}_{38}\text{N}_2\text{Ni})_2$ requires C, 76.8; H, 5.80; N, 8.50%]. Mass spectrum: the parent ion was not observed, the highest mass peak being observed at m/z 1 015 corresponding to $[\text{Ni}_2(\text{dtba})_3]^+$ (Table 1). Fragments relating to the breakdown of the ligand whilst co-ordinated to the metal were found at m/z 463 and 448, corresponding to $[\text{Ni}(\text{dtba})\text{NC}_6\text{H}_4\text{Me}]^-$ and $[\text{Ni}(\text{dtba})\text{NC}_6\text{H}_4]^+$ respectively. The brown decomposition product showed only traces of these same ions.

(e) With $\text{PhN}(\text{Li})\text{C}(\text{Me})\text{NPh}$. The lithiation of $\text{PhNHC}(\text{Me})\text{NPh}$ (Hdpaa, 4.2 g, 20 mmol) in monoglyme (150 cm^3) and its reaction with the nickel chloride solvate (1.57 g, 10 mmol) were undertaken as described above. After 18 h much nickel chloride remained in the solid obtained from removal of the solvent *in vacuo* from the reaction mixture. Solvent extraction with toluene gave a dark green solution from which needle crystals of $[\text{Ni}_2\{\text{PhNC}(\text{Me})\text{NPh}\}_4]$ were obtained at -16°C . The needles started to decompose slowly to a light coloured grey-green powder on warming to ambient temperature [Found: C, 75.0; H, 5.75; N, 11.5. $(\text{C}_{28}\text{H}_{26}\text{N}_4\text{Ni})_2$ requires C, 70.5; H, 5.45; N, 11.7%]. The parent ion was observed at m/z 954, fragmentation occurring by loss of whole ligand groups only (Table 1).

*Attempted Reactions of $[\text{Pt}\{\text{PhNC}(\text{Ph})\text{NPh}\}_2]$ with CS_2 , CO , *Synthesis Gas and Sodium, and $[\text{Pt}\{p\text{-FC}_6\text{H}_4\text{NC}(\text{Ph})\text{NC}_6\text{H}_4\text{F}\}_2]$ with PPh_3 .*—No reaction occurred with CS_2 over several days at the reflux temperature, nor with PPh_3 in thf over 6 h at the reflux temperature. Decomposition to the metal occurred in toluene with CO at 240 atm and synthesis gas (CO/H_2) at 160 atm on raising the temperature slowly to 100 and 150°C respectively over many hours. G.l.c. analysis of the final solutions indicated only trace amounts of materials other than toluene.*

X-Ray Crystal Structure of Bis(N,N'-diphenylbenzamidino)platinum(II).—A yellow needle of dimensions $0.6 \times 0.3 \times 0.2$ mm, obtained by recrystallisation from dichloromethane, was mounted in a Lindemann glass capillary and used for determination of unit-cell dimensions and data collection. Cell parameters were based on 20 automatically centred reflections.

All measurements were made using Mo-K_α radiation ($\lambda = 0.710\ 69\ \text{\AA}$).

Crystal data. $\text{C}_{38}\text{H}_{30}\text{N}_4\text{Pt}$, $M = 737.8$, monoclinic, $a = 25.413(7)$, $b = 6.031(2)$, $c = 20.586(3)\ \text{\AA}$, $\beta = 109.89(2)^{\circ}$, $U = 2\ 967\ \text{\AA}^3$, space group $C2/c$ (no. 15), $Z = 4$, $D_c = 1.651\ \text{g cm}^{-3}$, $F(000) = 1\ 456$, $\mu(\text{Mo-K}_\alpha) = 47.8\ \text{cm}^{-1}$.

Data collection and processing. CAD4 diffractometer, $\omega/2\theta$ mode with scan width $1.0 + 0.35 \tan \theta$, scan time up to 1 min, and graphite-monochromatised radiation. Data were collected for the quadrant $-28 \leq h \leq 28$, $0 \leq k \leq 6$, $0 \leq l \leq 21$ to $\theta_{\text{max}} = 22^{\circ}$. No significant drift in intensity was noted during data collection. 1 820 Independent data were measured, of which 1 459 with $F \geq 6\sigma(F)$ were used to solve and refine the structure.

Structure determination and refinement. From the intensity statistics [$F(hkl)$ systematically weak for $h + k = 2n + 1$], a platinum atom was located with C_i symmetry at $\frac{1}{2}, \frac{1}{2}, 0$ and the structure was solved by the DIRDIF¹⁸ procedure, all non-hydrogen atoms being located in the first electron-density map. After application of empirical absorption (DIFABS¹⁹), all hydrogen atoms were located and refined, this being possible because the platinum only contributes to half of the reflections. All non-hydrogen atoms were refined anisotropically to convergence at $R = 0.022$, $R' = 0.028$ for 1 459 data and 241 parameters. Weights of the form $w^{-1} = \sigma^2(F) + 0.000\ 092\ F^2$ were used. All standard crystallographic calculations used SHELX²⁰ and CALC.²¹ Bond lengths and angles for the structure are given in Table 3, and fractional co-ordinates for all atoms are given in Table 4. PLUTO²² was used to produce a perspective drawing of the molecule (Figure 1).

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