Orthometallated Amidine Complexes of Palladium, Platinum and Nickel(II). Crystal Structure of $[Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p\}(\eta^5\text{-}C_5H_5)]$†

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In aqueous methanol $K_2[MCl_4]$ (M = Pd or Pt) react with formamidines, acetamidines and benzamidines [R′NHC(R)NR′] having aryl substituents to form sparingly soluble orthometallated complexes. *N,N′*-Diaryl-formamidines and -acetamidines form six-membered metallocycles, $[\{M[R'NC(R)NHC_6H_3R'']Cl\}_n]$, whereas for *N,N′*-diarylbenzamidines having both N- and C-aryl substituents five-membered metallocycles $[\{M[R'NC(C_6H_4)NHR']Cl\}_n]$ are also produced. Related complexes form from the reactions of *N*-*p*-tolylacetamide and acetanilide with $K_2[PdCl_4]$. The adducts $[M\{R'NC(R)NHR'\}Cl_2]$ on heating in solution also yield orthometallated complexes. The chloride bridges of the oligomeric/polymeric materials are cleaved to give pyridine and dimethyl sulphoxide adducts, whereas displacement of the chloro-ligand leads to η^5-cyclopentadienyl, acetylacetonato, aceto-, benzamidino-, and allyl complexes, which retain the orthometallated amidino-group. Treatment of the chloride-bridged platinum complexes with CO under pressure causes carbonylation to form $[Pt\{R'NC(R)C_6H_3R''\}(CO)Cl]$, whereas for palladium cleavage of the orthometallated ligand from the metal occurs with formation of the corresponding quinazolin-4-one. The six-membered nature of the metallocycle is confirmed by the crystallographic structure of $[Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\}(\eta^5\text{-}C_5H_5)]$ [a = 9.0267(2), b = 9.8949(8), c = 12.1519(3) Å, α = 89.855(3), β = 121.278(2), γ = 99.199(3)°, space group $P\bar{1}$, Z = 2]. The structure was refined to a discrepancy index R of 0.054 for 2390 reflections. The amidino-group forms a six- rather than a four-membered ring which is also feasible. The ring, which has a shallow boat configuration, contains C–N bonds with different distances [1.285(9), 1.350(9), 1.434(10) Å] indicating little delocalisation of electrons within the ring. The palladium does not lie directly over the centroid of the planar cyclopentadienyl ring but is displaced by 0.25 Å towards one of the ring carbon atoms, though the ring C–C bond distances do not vary significantly from the mean [1.386(17) Å].

A wide variety of complexes of amidines is now known. Mono-, bi-dentate and bridging groups are well established for a variety of metals in a range of different types of complexes,[1] and similarities with isoelectronic 1,3-disubstituted triazines[2] and related ligands,[3] *e.g.* dithiocarboxylate, dithiocarbamate, dithiophosphate and diselenophosphate, have been clearly illustrated. During the early work of Bradley and Wright (1956),[4] exploring the ligand properties of formamidines, *etc.* with metal compounds, the derivative formed from *N,N′*-di-*p*-tolylformamidine and mercury(II) ethanoate was recognised as different from the derivatives of copper, silver and nickel. Treatment of the mercury complex with iodine in ethanol afforded *N*-(2-iodo-4-methylphenyl)-*N′*-4-tolylformamidine **I**, which led the authors to propose the six-membered metallocycle structure **II**.[4] This complex is unusual in that the amidine has lost two hydrogen atoms to become formally a dianion.

Cyclometallation reactions of aromatic compounds having nitrogen, oxygen, sulphur, phosphorus, *etc.* in their side chains are well documented,[5] and show a strong tendency to form five-membered rings. Where a choice of position of attack exists the formation of a five-membered ring is apparently a dominant factor, as shown for the series $C_6H_5(CH_2)_nN(CH_3)_2$,[6] for which metallation occurred only for that compound (n = 1) which was able to form a five-membered ring. Orthometallation of arylamidines was accomplished also by rhenium complexes[7] to form derivatives of the type $[Rh(CO)_3\{R'NC(R)NHC_6H_3R''\}\{R'NC(R)NHR'\}]$, though for benzamidines orthometallation of the skeletal carbon substituent also occurred. In all cases one hydrogen was lost from the amidine, and the resulting ligand **III** is fundamentally different from that postulated for the mercury complex.[4] Interestingly, for the rhenium complexes interchange of the bonding mode, from the orthometallated to the bidentate mode, was achieved by reaction with PPh_3,[7] though the reverse process was not established, even though it may be implicated in the initial attachment of the metal to the amidino-group.

We now report the synthesis and characterisation of a series of orthometallated amidino-complexes of palladium(II),[8] platinum(II) and nickel(II) of the type $[\{M[R'NC(R)NHC_6H_3R'']Cl\}_n]$ **IV**, together with related and representative amide complexes $[\{M[R'C_6H_4NHC(R)O]Cl\}_n]$. A selection of reactions is reported together with the X-ray crystal structure of a representative complex $[Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p\}(\eta^5\text{-}C_5H_5)]$. Also bis(amidine) adducts, $[M\{R'NC(R)NHR'\}_2Cl_2]$ (*cis* and *trans*) have been made.

Results and Discussion

(*a*) *Orthometallate Complexes with Chloro Bridging Atoms.*—Aryl-amidines $R'NHC(R)NR'$ and -amides react with $K_2[MCl_4]$ (M = Pd or Pt) in refluxing aqueous methanol to form grey-green, very sparingly soluble complexes of the type

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† (η-Cyclopentadienyl)[5-methyl-2-(1-*p*-tolylimino-κ*N*-ethylamino)-phenyl-κC^1]palladium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI units employed: eV ≈ 1.60×10^{-19} J, atm = 101 325 Pa.

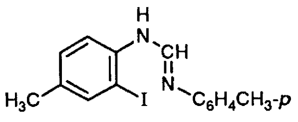
Table 1 Analytical data with calculated values in parentheses for the orthometallated complexes $[\{M[R'NC(R)NHC_6H_3R'']Cl\}_n]$

Complex *							Analysis (%)				
M	R	R′	R″	Colour	M.p./°C	Yield (%)	C	N	H	Cl	M
Pd	C_6H_5	C_6H_4F-*p*	F	Green	228	49.8	50.5	6.20	2.95	8.3	25.0
							(50.8)	(6.25)	(2.90)	(7.90)	(23.7)
Pd	C_6H_5	C_6H_5	H	Green	218(decomp.)	66.8	55.3	7.00	4.15	9.90	26.3
							(55.2)	(6.80)	(3.80)	(8.60)	(25.8)
Pd	C_6H_5	$C_6H_4CH_3$-*p*	CH_3	Green	238	52.0	57.7	6.70	4.25	8.55	26.0
							(57.2)	(6.35)	(4.30)	(8.05)	(24.1)
Pd	C_6H_5	$C_6H_4C_3H_7$-*i*-*p*	C_3H_7-*i*	Green	198(decomp.)	27.9	58.8	5.60	5.85	7.05	20.0
							(60.4)	(5.65)	(5.45)	(7.15)	(21.4)
Pd	CH_3	C_6H_5	H	Green-yellow	252	45.8	47.8	8.10	4.00	9.75	30.0
							(47.9)	(8.00)	(3.70)	(10.1)	(30.3)
Pd	H	C_6H_5	H	Green	232(decomp.)	14.5	45.8	8.25	3.30	11.15	31.8
							(46.3)	(8.30)	(3.25)	(10.5)	(31.6)
Pd	CH_3	$C_6H_4CH_3$-*p*	CH_3	Green	>200(decomp.)		50.2	7.50	4.30	9.60	28.2
							(50.7)	(7.40)	(4.50)	(9.40)	(28.0)
Pt	C_6H_5	C_6H_5	H	Green-brown	208	15.6	46.5	5.35	3.80	6.85	35.9
							(45.5)	(5.60)	(3.00)	(7.05)	(38.9)
Pt	C_6H_5	$C_6H_4C_3H_7$-*i*-*p*	C_3H_7-*i*	Green-brown	189	68.2	51.6	5.30	4.05	5.65	28.0
							(51.2)	(4.80)	(4.75)	(6.05)	(33.3)

Table 2 Mass spectral assignments for $[\{Pd[C_6H_5NC(R)C_6H_4]Cl\}_n]$

	m/*z* (% ion intensity)	
Ion assignment *	R = H	R = CH_3
$[PhCN]^+ + H^+$	104 (25)	—
$[PhNNH]^+$	—	118 (39)
$[PhNC(R)NC_6H_4]^+$	195 (63)	209 (100)
$[PhNC(R)NC_6H_4]^+ + H^+$	198 (13)	210 (19)
$[PhNC(R)NC_6H_4]^+ + 2H^+$	197 (100)	211 (59)
$[PhNCNPd]^+ + H^+$	223 (0.7)	223 (4)
$[Pd(amidine)]^+$	301 (5)	315 (6)
$[Pd(amidine)(tdg)]^+$	423 (24)	437 (35)
$[Pd(amidine)(tdg)(CH_2SCH_2)]^+$	483 (2)	497 (3)

* Ions were verified by computer simulation of isotope patterns; tdg = thiodiglycol.



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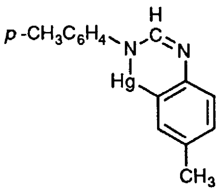

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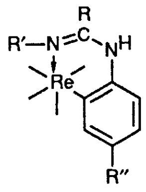

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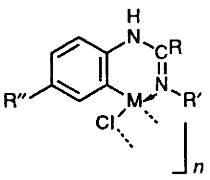

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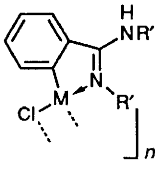

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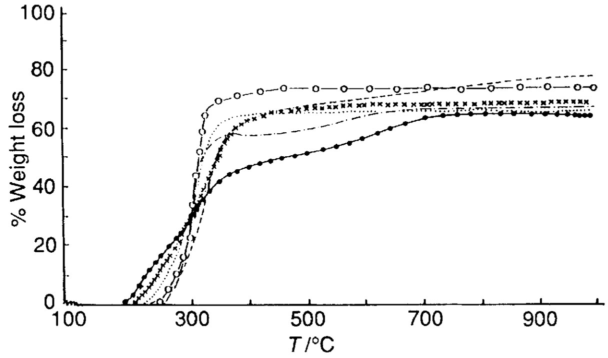


Fig. 1 Thermograms of orthometallated palladium complexes: (○) $[\{Pd[p\text{-}FC_6H_4NC(C_6H_5)NHC_6H_3F\text{-}p]Cl\}_n]$, (– – –) $[\{Pd[p\text{-}i\text{-}C_3H_7C_6H_4NC(C_6H_5)NHC_6H_3C_3H_7\text{-}i\text{-}p]Cl\}_n]$, (× × ×) $[\{Pd[C_6H_5NC(C_6H_5)NHC_6H_4]Cl\}_n]$, (–·–·–) $[\{Pd[C_6H_5NC(CH_3)NHC_6H_4]Cl\}_n]$, (·····) $[\{Pd[C_6H_5NC(C_6H_5)NHC_6H_4]Cl\}_n]$ and (●) $[\{Pd[C_6H_5NCHNHC_6H_4]Cl\}_n]$

$[\{\overline{M[R'NC(R)NHC}_6H_3R'']Cl\}_n]$ and $[\{M[R'C_6H_3NHC(R)O]Cl\}_n]$ respectively. Palladium(II) chloride and $[Pd(C_6H_5CN)_2Cl_2]$ may also be used, and the aqueous methanol may be replaced by monoglyme (1,2-dimethoxyethane), dry methanol, acetonitrile and water though yields are somewhat lower. Acetonitrile was found to cause separation of palladium metal, whilst monoglyme and methanol promote formation of $[Pd\{R'NC(R)NHR'\}_2Cl_2]$ complexes. Use of $[Pd(C_6H_5CN)_2Cl_2]$ gave a high yield of the $[Pd(amidine)_2Cl_2]$ complexes and lower yields of the orthometallated complexes. Not surprisingly, the bis(amidine) adducts $[Pd\{R'NC(R)NHR'\}_2Cl_2]$ when heated in suspension in aqueous methanol lose a molar equivalent of amidinium hydrochloride to form the orthometallated complexes in high yield (*ca.* 80%). Characterisation involved a combination of methods including elemental analysis (see Table 1), thermogravimetric analysis (see Fig. 1), mass spectrometry (see Table 2) and infra-red spectroscopy (see Table 3). The complexes were insoluble in the majority of solvents, involatile, but stable in air. Some solubility in strongly co-ordinating solvents, *e.g.* dimethyl sulphoxide (dmso), pyridine, acetone, *etc.*, was achieved, but these solutions slowly deposited palladium and platinum metal. Nickel complexes were less robust than their palladium and platinum analogues, and readily produced free amidine in solution, from which it proved difficult to separate the complexes.

Table 3 Comparison of IR absorptions of orthometallated complexes[a] and parent amidines $R'NC(R)NHC_6H_4R''$

Amidine				Highest frequency ν(N–C–N)/cm^{-1} (complex)	ν_{asym}(N–C–N)/cm^{-1} (parent amidine)	ν(N–H)/cm^{-1} (complex)
R	R′	R″	M			
C_6H_5	C_6H_4F-*p*	F	Pd	1606	1624	3300
C_6H_5	C_6H_5	H	Pd	1605	1630	3300
			Pt	1605		3290
C_6H_5	$C_6H_4CH_3$-*p*	CH_3	Pd	1605	1620	3300
C_6H_5	$C_6H_4C_3H_7$-*i*-*p*	C_3H_7-*i*	Pd	1610	1620	3300 (3360,[b] 3300[c])
			Pt	1610		3290
CH_3	C_6H_5	H	Pd	1610	1624	3320
			Pt	1605		3480[d]
CH_3	$C_6H_4CH_3$-*p*	CH_3	Ni	1630	1630	3300[d]
			Pd	1612		3340
H	C_6H_5	H	Pd	1630	1670	3280 (3240[b])
			Ni	1670		3300[d]

[a] All spectra were recorded in Nujol or hexachlorobutadiene as mulls, using CsI or KBr plates. [b] Recrystallised from dmso. [c] Recrystallised from pyridine. [d] Not analytically pure.

A diagnostic feature of all the orthometallated amidine complexes is a medium-intensity, sharp ν(N–H) stretching absorption at *ca.* 3300 cm^{-1} (see Table 2), a higher wavenumber than that associated with unco-ordinated amidines (*e.g.* 3230 cm^{-1}). Interestingly crystallisation of $[\{Pd[p\text{-}i\text{-}C_3H_7C_6H_4NHC(C_6H_5)NC_6H_3C_3H_7\text{-}i\text{-}p]Cl\}_n]$ causes a change of ν(N–H) from 3330 cm^{-1} for the product precipitated from the reaction to 3360 cm^{-1} for material recrystallised from dmso. This was thought originally to be due to the breaking down of polymeric material by cleavage of chloride bridges by the donating solvents, and consequent reformation of units having a lower degree of association. This cleavage of chloride bridges to form adducts is a common reaction of such bridged complexes,[9,10] and has been exploited in this work to obtain mass spectra of the materials. Complexes were mulled with thiodiglycol ($HOCH_2CH_2SCH_2CH_2OH$) and studied using the fast atom bombardment (FAB) technique. Pyridine (py) affords yellow and white compounds having the composition [Pd(amidine-H)Cl] and [Pd(amidine-H)Cl(py)] respectively, and a second yellow compound also having the latter composition. The first mentioned yellow and the white compound were thought to be the chloro-bridged dimer and $[Pd\{C_6H_5NC(CH_3)NHC_6H_4\text{-}o\}Cl(py)]$ respectively.[8] However, Pfeffer and co-workers[10] suggest that the original chloro-bridged complexes are not polymers but dimers, implying that in pyridine recrystallisation is one of the processes which has occurred, in addition to adduct formation. The white compound is considered to be a pyridinium salt of a polymeric anion in which an amidino-NCN unit chelates to one metal and bridges to a second metal *via* the *ortho* position of the ring. The second yellow compound is the mononuclear pyridine adduct of the dimer/polymer, resulting from cleavage of the chloro-bridges.

Most of the complexes are highly insoluble, except when adduct formation occurs, and weak solutions only were obtained. Positive and negative ion, electron-impact, and chemical-ionisation mass spectra, produced ions associated with the amidine ligands, but no metal-containing ions. Application of the FAB technique to materials in thiodiglycol however gave fragment ions as shown in Table 2, containing both the metallocycle and co-ordinated mulling agent. No parent ion was detected but the ion of highest mass strongly suggests the process (1). Fragmentation involves complete loss of the mulling agent to give $[Pd\{R''C_6H_4NC(R)NHC_6H_3R''\}]^+$. The most prominent ion in the spectrum is that arising from the free amidine group.

$$[\{Pd[R''C_6H_4NC(R)NHC_6H_3R'']Cl\}_n] + 2n(HOCH_2CH_2)_2S \longrightarrow n[Pd\{R''C_6H_4NC(R)NHC_6H_3R''\}\{(HOCH_2CH_2)_2S\}_2]^+ + nCl^- \quad (1)$$

The low solubility of the complexes prevented the general application of solution-based analytical techniques, so thermogravimetric and electronic spectroscopy for chemical analysis (ESCA) studies were undertaken. The thermograms (Fig. 1) proved to be generally featureless, corresponding to loss of the amidine group to leave a residue containing both palladium and chloride in a 1:1 ratio. An ESCA study[11] of a number of $[\{Pd(\text{amidine-H})Cl\}_n]$ complexes (amidine-H = *N,N′*-di-*p*-fluorophenyl-, *N,N′*-di-*p*-tolyl-, *N,N′*-di-*p*-isopropylphenyl-, *N,N′*-diphenyl-benzamidine, *N,N′*-diphenylacetamidine, or *N,N′*-diphenylformamidine) yielded no further insight into the nature of the materials. The Pd $3d_{\frac{5}{2}}$ core binding energies were consistently of 338.2 eV, and since palladium is one of the elements for which a good correlation between binding energy and oxidation state exists[12] the metal can be assigned an oxidation state of +2. For comparison purposes, corresponding binding energies of 335.7, 336.0, 337.5–339.2 and 340.3 eV are found for the free metal, $[Pd(PPh_3)_4]$, a range of palladium(II) complexes, and $K_2[PdCl_4]$ respectively. No useful conclusions about the bonding of chlorine and nitrogen could be drawn from the Cl($2P_{\frac{3}{2}}$) binding energy of 198.1 eV and N(1s) binding energy of 400.5 eV.

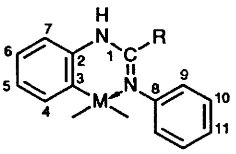
Limited NMR data were obtained for selected complexes mainly in co-ordinating solvents, using long acquisition times (see Tables 4 and 5). Proton NMR spectra showed two notable features, the first being two sets of signals for *para* substituents of the N-aryl groups, as expected for orthometallated structures. Secondly NH signals for the benzamidine complexes occurred at lower frequencies than those for the corresponding formamidine and acetamidine complexes. Further differences are observed in the ^{13}C NMR spectra, which are ascribed to different ring structures for the benzamidine complexes, compared with those of acetamidines and formamidines. The latter amidines may form four- or six-membered metallocycles, whereas benzamidines may also form five-membered rings using the NCN skeletal-carbon substituent. The NMR data are consistent with five-membered metallocycles for benzamidines **V**, but six-membered metallocycles for acetamidines and formamidines **IV**.

The differences are best illustrated by comparing the ^{13}C NMR spectral data for $[\{Pd[C_6H_5NC(CH_3)NHC_6H_4]Cl\}_n]$ in $(CD_3)_2SO$ with those for $[\{Pd[p\text{-}i\text{-}C_3H_7C_6H_4NC(C_6H_5)NHC_6H_3C_3H_7\text{-}i\text{-}p]Cl\}_n]$ in $(CD_3)_2CO$. The NCN skeletal-carbon signal (for C^1, see structures **VI** and **VII**) occurs at a lower frequency for the benzamidine complex (δ 163.5) compared with the acetamidine complex (δ 156.2) and we ascribe the difference to five- and six-

Table 4 Proton NMR data for orthometallated amidines $[\{M[R'NC(R)C_6H_3R'']Cl\}_n]$

Complex							
M	R	R′	R″	NH	C(aryl)H	C(other)H	Solvent
Pd	H	C_6H_5	H	10.1(br)	7.81 (d, MCH), 7.80–7.29 (m, 8 H, aryl)	CH 8.01 (s, 1 H)	$(CD_3)_2CO$
Pd	CH_3	C_6H_5	H	10.17(br)	7.78 (d, MCH), 7.34–7.22 (m, 3 H, metallated ring H), 7.07–6.68 (m, 5 H, aryl ring)	CH_3 1.97 (s, (3 H)	$(CD_3)_2SO$
Pd	C_6H_5	$C_6H_4C_3H_7$-*i*-*p*	C_3H_7-*i*	n.o.	7.43 (d, 1 H, MCH), 7.4–6.47 (m, 12 H, aryl rings)	CH 2.78–2.56 (m, 2 H), CH_3 1.05 (d) and 0.95 (d)	$(CD_3)_2CO$
Pd	C_6H_5	C_6H_5	H	9.14	6.43–5.32 (m, 12 H, aryl rings)	CH_3 1.05 (s) and 1.02 (br s)	$(CD_3)_2SO$
Pd	C_6H_5	C_6H_4F-*p*	F	9.14	6.69–5.68 (m, 12 H, aryl rings)		$(CD_3)_2SO$
Pd	C_6H_5	C_6H_5	H	9.15	6.65–5.71 (m, aryl rings)		$(CD_3)_2SO$
Pd	CH_3	$C_6H_4CH_3$-*p*	CH_3	10.10	7.65 (1 H), 7.02 (m, 4 H), 6.73 (2 H)	1.91 (3 H), 2.16 (3 H), 2.31 (3 H)	$(CD_3)_2SO$
Pt	C_6H_5	C_6H_5	H	9.43	7.39–6.42 (m, aryl rings)		$CDCl_3$
Pt	C_6H_5	$C_6H_4C_3H_7$-*i*-*p*	C_3H_7-*i*	9.36	7.19–6.22 (m, 12 H, aryl rings)	CH 2.63 (m) and 2.80 (m), CH_3 1.16 (d) and 1.01 (d)	$CDCl_3$

d = doublet, m = multiplet, s = singlet, br = broad; δ values relative to $Si(CH_3)_4$; n.o. = not observed.



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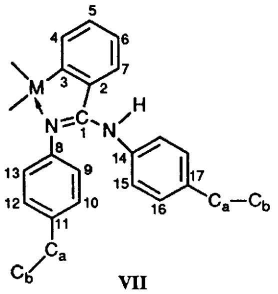
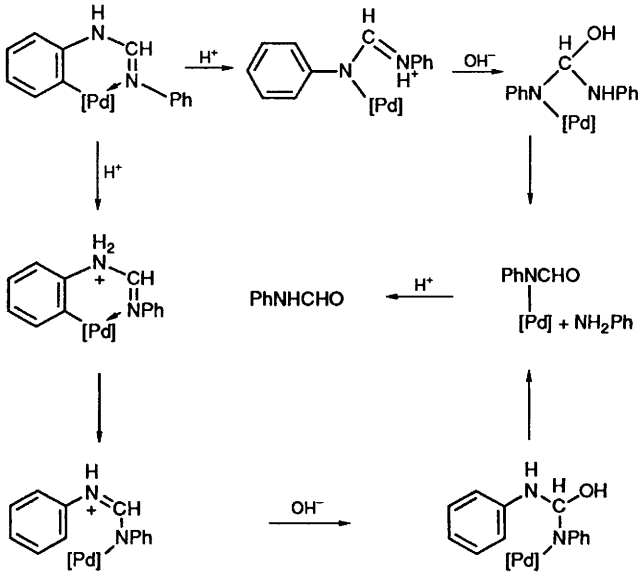


VII

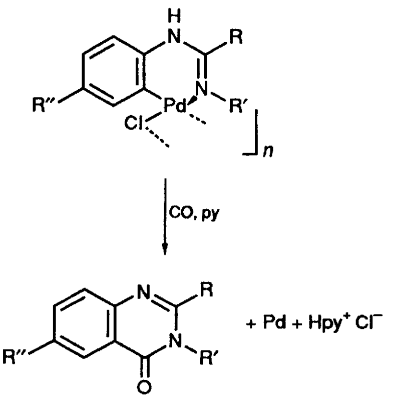
membered ring structures respectively. It is this ring carbon atom (C^1) which will most reflect these differences in the geometry, and the frequency of this signal may provide a diagnostic means of assigning the ring size. The shift to lower frequency for the five-membered ring represents additional delocalisation over C^1 expected for a planar ring system. The signal for the orthometallated carbon (C^3) of the aryl ring moves to lower frequencies compared with normal *ortho*-ring carbons (23 ppm for the acetamidine, 14 ppm for the benzamidine).

(*b*) *Derivatives of the Orthometallated Chloro-bridged Complexes.*—Reference has already been made to chloride-bridge-cleavage reactions taking place when complexes are dissolved in co-ordinating solvents such as dmso and acetone. Though the complexes may be recrystallised from these solvents, careful control of conditions led to the isolation of yellow adducts with dmso and pyridine. Attempts to grow crystals of $[\{\overline{Pd(C_6H_5NHCHNC_6H_4})Cl\}_n]$ in acetone produced $[Pd\{(CH_3)_2C{=}NC_6H_5\}_2Cl_2]$ in small yield by reaction of the solvent with the amidine ligand. This complex was identified by mass spectral and X-ray analysis.[13] *N*-Phenylformamide is a second product. Though strict precautions were taken to avoid air, the most obvious interpretation of these results involves the formation of amine by hydrolysis of the co-ordinated amidine (see Scheme 1). Removal of all traces of water from the acetone was not undertaken and sufficient water may have been present to initiate the process. Reaction of amines with ketones is well known,[14] and may take place also whilst the amine is co-ordinated to the metal.[15] Water is a by-product which would continue the process. Interchange between *N*,*N*′-bidentate and orthometallation bonding modes has been observed for rhenium complexes,[7] and a similar process may be relevant to concomitant formation of *N*-phenylformamide (see Scheme 1).



Scheme 1

Treatment of the orthometallated acetamidine and benzamidine complexes with carbon monoxide at elevated temperatures in the presence of a base to absorb generated hydrogen chloride caused insertion of carbon monoxide, followed by cyclisation to form 4-quinazolinones [equation (2)]. These reactions were undertaken under forcing conditions (150 °C, 130 atm, 6 h), but after this work was completed mild conditions (20 °C, 5 atm, 24 h) were reported to produce the same derivatives in 85% yield.[16]



(2)

Table 5 Carbon-13 NMR data for orthometallated complexes[a]

Complex																						
M	R	R′	R″	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}	C^{16}	C^{17}	C^a	C^b	Solvent
Pd	CH_3	C_6H_5	H[b]	156.2	138.7	151.2	124.8	103.4	127.8	128.8	143.8	131.7	130.6	118.5									$(CD_3)_2SO$
Pd	H	C_6H_5	H				129.9	124.7	130.5			119.9	129.5	124.5									$(CD_3)_2CO$
Pd	C_6H_5	$C_6H_4C_3H_7$-*i*-*p*	C_3H_7-*i*	163.5	138.2	142.5	128.8	129.4	128.3	127.5	146.3	126.9	124.7	131.3	125.3	127.2	146.0	126.7	125.4	131.7	34.7 34.5	24.7 24.4	$(CD_3)_2CO$
Pd	C_6H_5	$C_6H_4CH_3$-*p*	CH_3			142.3												132.8	132.8		24.3		$(CD_3)_2SO$
Pd	C_6H_5	C_6H_4F-*p*	F[c]		132.1							119.1					133.0		118.0		—	—	$(CD_3)_2SO$
Pd	C_6H_5	C_6H_5	H		132.2													119.4	131.8		—	—	$(CD_3)_2SO$
																					CH	CH_3	
Pt	C_6H_5	$C_6H_4C_3H_7$-*i*-*p*	C_3H_7-*i*	164.2	135.2	146.8	128.7	129.0	128.1	—	—	126.1	126.0	132.0	—	127.2	146.3	127.2	125.6	130.5	34.3 34.1	24.6 24.4	$CDCl_3$
Pt	C_6H_5	C_6H_5	H	—	135.7	—	127.2	126.4	127.6	127.8	—	126.7	125.7	124.7	125.6	128.4	—	124.8	129.1	124.4	—	—	$CDCl_3$

[a] All values (δ) relative to $Si(CH_3)_4$. See structures **VI** and **VII** for key to numbering schemes. [b] CH_3 signal at δ 23.2. [c] ^{19}F NMR signals (relative to $CFCl_3$) at δ −117.63 and −120.97.

When analogous platinum complexes were used insertion did not occur and quinazolinones were not formed. Instead carbon monoxide cleaved the chloride bridge(s) to give the carbonyl adducts [$Pt\{R'NC(R)NC_6H_3R''\}(CO)Cl$] [ν(CO) 2095 cm^{-1}]. These complexes may be regarded as precursors to the carbon monoxide insertion products which eventually lead to cyclic products. Two routes are conceivable, each based on the known chemistry of palladium. Route A (Scheme 2) involves insertion into an aryl–palladium bond, followed by rearrangement to form a more stable five membered metallocycle, then nucleophilic attack at the acetyl group, thus forming the quinazolinone cation. Route B involves internucleophilic attack by the imino nitrogen at co-ordinated carbon monoxide to form a strained ring system, which reductively eliminates from the metal prior to cyclisation.

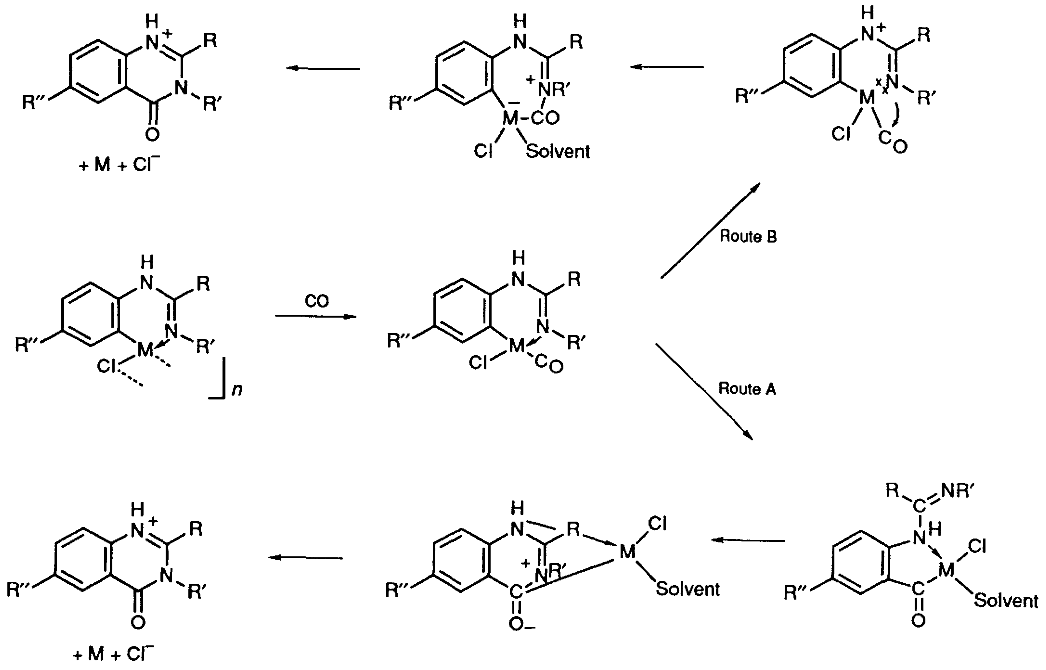
Attempts using aqueous alcohol or toluene solutions of palladium(II) chloride, amidines, and bases, at 150 °C under 100 atm CO, to achieve direct reaction without the separate isolation of the intermediate orthometallated complexes were not successful, and isolated products tended to be the amides R'NHC(R)O. The insertion/cyclisation reaction is similar to the catalytic carbonylations of Schiff bases having C-aryl substituents, to form phthalimidines.[17] These reactions, catalysed for instance by dicobalt octacarbonyl, are thought to involve orthometallation as an intermediate step.

(*c*) *Complexes* [$M(amidine)_2Cl_2$].—Classical bis adducts of the metal chlorides can be formed by the reaction of amidines with MCl_2, $K_2[MCl_4]$ or [$M(C_6H_5CN)_2Cl_2$] complexes in a variety of solvents, but were obtained most conveniently in high yield by the reaction of amidines with [$M(C_6H_5CN)_2Cl_2$] (M = Pd or Pt) in chloroform. The yellow-orange products obtained were mixtures of *cis* and *trans* isomers. For [$Pd\{C_6H_5NC(CH_3)NHC_6H_5\}_2Cl_2$], for example, extraction of the initial product with toluene gave the yellow *trans* form [ν(MCl) 349 cm^{-1}] and the red *cis* form [ν(MCl) 348 and 307 cm^{-1}] by fractional crystallisation. When heated in solution, *e.g.* toluene, methanol, or acetonitrile, these complexes lost HCl and formed a mixture of the orthometallated complex and amidinium hydrochloride. When treated with LiBu^n, complexes of the type [$Pd\{R'NC(R)NR'\}_2$][18] were formed. A similar loss of hydrogen halides was achieved for the related rhenium complexes [$Re\{R'NC(R)NHR'\}(CO)_4X$] (X = Cl or Br).[7] Notable here is the early report by Tschugoev and Lebendinski[19] in 1915 of a complex of platinum, containing an amidine as a two-electron donor, which was formed in the reaction of ammonia with co-ordinated acetonitrile, though the nature of the complex [$Pt(NH_3)_2\{NHC(CH_3)NH_2\}_2]Cl_2 \cdot H_2O$ was only recognised in 1962 when Stephenson[20] determined the crystal structure.

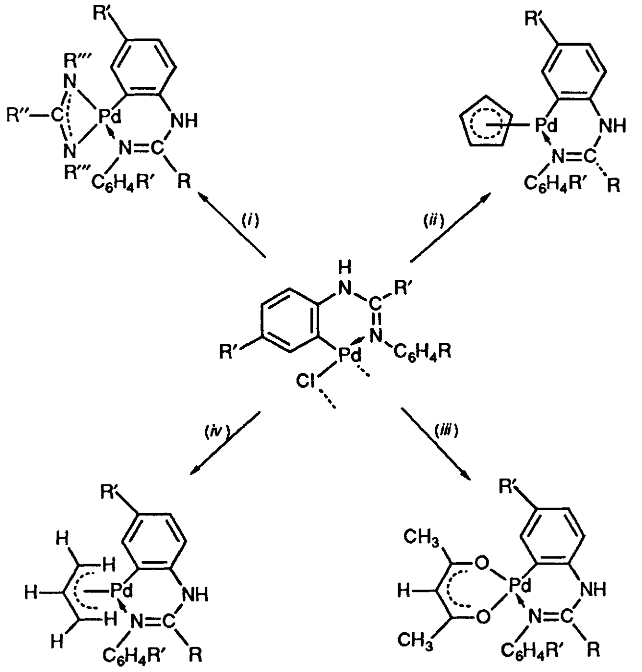
(*d*) *Orthometallated Complexes having Cyclopentadienyl, Carboxylato, Acetylacetonato, Allyl Groups,* etc.—A well-documented reaction of halogeno-bridged complexes of palladium and platinum involves bridge cleavage and metathetical displacement of the halide group.[9] Such reactions were achieved for a representative complex [$\{Pd[p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p]Cl\}_n$]. Treatment of a suspension of this complex in thf or monoglyme with sodium cyclopentadienide, allylmagnesium chloride, *N*-lithiodi-*p*-tolylacetamidine, *N*-lithiodi-*p*-fluorophenylbenzamidine, *N*-lithiodiphenyltriazine, silver ethanoate and thallium(I) acetylacetonate yielded complexes as shown in Scheme 3. Complex **D** is of particular interest because it contains two amidino-groups bonded to the palladium by different bonding modes, one *N,N'*-bidentate and the other orthometallate chelation. The η^5-cyclopentadienyl derivative has been the representative complex studied in the greatest depth. It is monomeric in solution (cryoscopy), in the solid (X-ray analysis) and in the vapour state (mass spectrum), and retention of the orthometallated bonding mode for the amidino-group is demonstrated by ^1H NMR data. This is confirmed by the single-crystal X-ray structure.

(*e*) *Crystal Structure of* [$Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p\}(\eta^5\text{-}C_5H_5)$].—Crystals were found to be triclinic, no symmetry being exhibited on either oscillation or Weissenberg photographs. Two molecules in the unit cell suggested the space group $P\bar{1}$ and this is confirmed by the satisfactory refinement of the structure. The structure determination has established that the complex is a six-membered metallocycle (Fig. 2) with a η^5-cyclopentadienyl group making a dihedral angle of 86° with the metallo-ring system. The Pd–N distance [2.040(6) Å] is close to that of [$Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NC_6H_4CH_3\text{-}p\}_2$] [2.038(3) Å],[18] and to Pd–N distances in [$Pd(NH_3)_4]^{2+}$ [2.044(3) Å][21] and [$Pd(H_2NCH_2CH_2)_2$] [2.030(6) and 2.043(7) Å][22] in which metal–nitrogen π bonding is absent. The palladium–carbon distance [1.984(7) Å] is also typical.[9]

There appears to be no evidence for π interaction between



Scheme 2



Scheme 3 (*i*) LiN(R‴)C(R″)=NR‴; (*ii*) NaC_5H_5; (*iii*) Tl(acac) (acac = acetylacetonate); (*iv*) $Mg(C_3H_5)Cl$

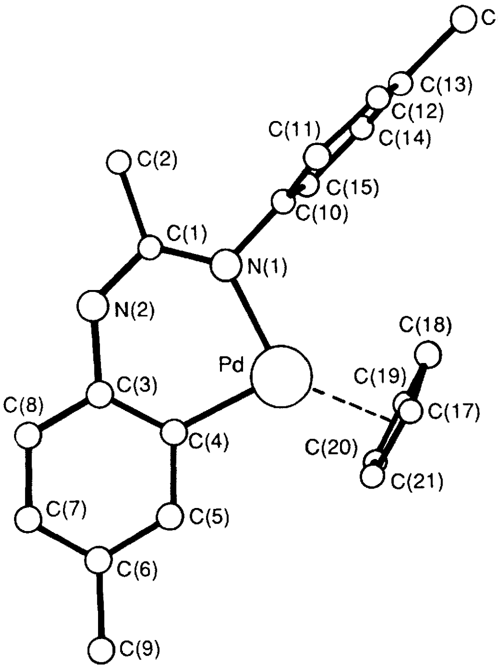


Fig. 2 Molecular structure of $[\overline{\mathrm{Pd}\{p\text{-}\mathrm{CH_3C_6H_4NC(CH_3)NHC}}\mathrm{_6H_3\text{-}CH_3\text{-}}p\}(\eta^5\text{-}\mathrm{C_5H_5})]$

palladium and the rest of the ring in the present compound, although there are six π electrons in the ring available for a quasi-aromatic system, *cf.* tris(pentane-2,4-dionato)chromium(III). The high energy of the $5p_z$ orbital may not allow sufficient overlap with the $2p_z$ orbitals of carbon and nitrogen to permit bonding to occur. Also the low angle at palladium [CPdN 91.3(3)°] in a cycle with normal internal angles of 120° may increase electron–electron repulsion to such an extent as to discourage π bonding. Interestingly the metallocycle is slightly puckered in a shallow boat form which also reduces strain in the ring system, though angles remain greater than 120°. It appears to be the requirements of palladium that dominate the geometry; the square-planar geometry and typical Pd–N and Pd–C bond lengths are all preserved.

The amidine skeletal C–N bond distances [C(1)–N(1) and C(1)–N(2)] are not equal but 1.285(9) and 1.350(9) Å respectively. Also the ring carbon–nitrogen distance [C(3)–N(2) 1.434(10) Å] is marginally longer than the corresponding bonds in $[\mathrm{Pd}\{p\text{-}\mathrm{CH_3C_6H_4NC(CH_3)NC_6H_4CH_3}\}_2]$ [1.412(4) Å]. Thus there is little delocalisation of electrons in the metallo-ring as a whole, though some limited delocalisation in the NCN amidine skeleton is shown.

The palladium atom does not lie directly over the centroid of the cyclopentadienyl ring, but is shifted about 0.25 Å from this position in the direction of one of the ring carbon atoms [C(21)] and away from two carbon atoms [C(18), C(19)]. The distance between these latter two carbon atoms [1.424(18) Å] is marginally longer than the mean distance 1.386(17) Å and the remaining C–C distances [1.389(16), 1.369(14), 1.387(17), 1.362(19) Å] in the cyclopentadienyl ring, and there is no suggestion that this ring is tending towards η^3 attachment. This is also concluded from the Pd–C_5H_5 carbon distances which vary within the range 2.239(9)–2.440(11) Å, with the palladium 2.031 Å from the C_5H_5 ring which is nearly planar (maximum out of plane deviations 0.036 Å). The CCC ring bond angles vary within the range 104.0(1.3)–111.1(1.1)°. They do not differ significantly therefore from the average angle expected for a regular planar pentagon of 108°.

The dihedral angle between the ring of the *p*-tolyl substituent and the metallocycle (97°) indicates that there is no conjugation between these rings, and this is consistent with the longer N–C(tolyl) bond length [1.445(10) Å] compared with 1.412(4) found for $[\mathrm{Pd}\{p\text{-}\mathrm{CH_3C_6H_4NC(CH_3)NC_6H_4\text{-}CH_3}\text{-}p\}_2]$.[18] Interestingly the amidine skeletal NCN bond angle [122.0(7)°] in the present complex is much larger, as expected, than that for the four-membered ring of the latter complex [108.4(3)°], but similar to that for the six-membered ring of $[\mathrm{Pt}\{\mathrm{HNC(C_6H_5)NC(C_6H_5)NH}\}_2]$ [average 121(3)°].[23] Such a large angle can be accommodated when the nitrogen substituent is hydrogen, and the short contacts other nitrogen substituents would have with C(2), and with substituents at C(8), may explain why we were unable to synthesise orthometallated rings from R′N=C(R)N(CH_3)R′ using the methods described. Since such an amidine does form an orthometallated complex with rhenium,[7] the geometry of the ring and particularly the CNC skeletal angle may be fairly flexible to accommodate the stereochemistry of the additional methyl group.

Experimental

N,N′-Diphenyl-, -di-*p*-tolyl, -di-*p*-fluorophenyl-, -di-*p*-isopropylphenyl-benzamidine and *N,N′*-diphenylacetamidine were prepared by published procedures,[24] whilst *N,N′*-diphenylformamidine was purchased from Aldrich. Other standard chemicals were supplied by BDH. Potassium tetrachloropalladate(II) and -platinate(II) were obtained from Johnson Matthey. Anhydrous nickel chloride was obtained from the monoglyme adduct by heating *in vacuo*, and was handled in a nitrogen-filled glove-box. Precautions were taken to exclude air and moisture and solvents were pre-dried, and degassed, except for reactions involving methanol–water mixtures, Infrared spectra in the range 4000–250 cm^{-1} were recorded using Perkin-Elmer 457 and 577 spectrometers, and ^1H NMR spectra at 60 MHz using a Varian 360L spectrometer. Carbon-13 and ^1H NMR spectra were recorded also at the University of Newcastle-upon-Tyne using a Bruker WH-300 instrument. A Bruker HX 90E instrument modified for Fourier transform operation using a Nicolet B.N.C. 12 computer was used for ^{13}C NMR spectroscopy, together with a Bruker WH 360 at the University of Edinburgh. Tetramethylsilane was used as an internal reference for both ^1H and ^{13}C NMR experiments. Mass spectra were obtained using a FAB source attached to a VG 7070E instrument operating at 70 eV and an accelerating potential of 6 kV, and a VG ZAB-1F instrument at the

P.C.M.U., Harwell. Thiodiglycol and glycerol were used as mulling agents. The ESCA spectra were obtained using an A.E.I. ES200B spectrometer.

The carbon, hydrogen and nitrogen contents of the complexes were determined using a Perkin-Elmer 240 elemental analyser, and nickel, palladium and platinum by atomic absorption spectroscopy using a Perkin-Elmer 403 instrument. Thermogravimetric analyses were undertaken using Stanton Redcroft TG 750 and 760 instruments.

Reactions.—$K_2[PdCl_4]$ *with* p-$FC_6H_4NHC(C_6H_5)NC_6H_4F$-$p$. A mixture of the amidine (0.384 g, 1.25 mmol) and $K_2[PdCl_4]$ (0.408 g, 1.25 mmol) was dissolved in a mixture of methanol (10 cm^3) and water (2 cm^3), and heated to the reflux temperature for 2 h. The resultant black-green solution was filtered whilst hot, then cooled to ambient temperature. A dark green solid separated from a yellow liquor. The precipitate was separated by filtration, washed with methanol (20 cm^3) and hexane (3 × 20 cm^3), and finally dried *in vacuo* to yield a yellow powder identified as $[\{Pd[p\text{-}FC_6H_4NC(C_6H_5)NHC_6H_3F\text{-}p]Cl\}_n]$.

Other palladium complexes were synthesised using a similar procedure.

$K_2[PtCl_4]$ *with* $C_6H_5NHC(C_6H_5)NC_6H_5$. Preliminary investigations showed that the procedure used for palladium complexes could not be applied to the synthesis of platinum complexes because of decomposition to platinum metal during the reflux stage. Consequently the following modified method was adopted.

The amidine (0.135 g, 0.5 mmol) and $K_2[PtCl_4]$ (0.207 g, 0.5 mmol) were dissolved in a mixture of methanol (20 cm^3), water (50 cm^3) and diethyl ether (30 cm^3), and stirred vigorously at room temperature for 4 d. During this period a flow of nitrogen was used to remove very slowly the volatile solvent. After 2 h the solution became orange, and after 4 d a dark green-brown solid formed. After separation by filtration, the solid was washed with methanol (5 cm^3) and hexane (10 cm^3) before drying *in vacuo*. The product $[\{Pt[C_6H_5NC(C_6H_5)NHC_6H_4]Cl\}_n]$ was obtained as a green powder.

Other platinum complexes were prepared using the same procedure.

Anhydrous nickel chloride with p-$CH_3C_6H_4NHC(CH_3)NC_6H_4CH_3$-$p$. Attempts to synthesise nickel complexes using the methods adopted for palladium and platinum were unsuccessful. The following method was used instead.

The amidine (4.76 g, 20 mmol) and anhydrous $NiCl_2$ (2.59 g, 20 mmol) were thoroughly mixed by grinding in a mortar. A Carius tube was then charged with the mixture and sealed *in vacuo* before heating to 200 °C for 24 h. A dark brown insoluble residue resulted which was washed with warm diethyl ether (10 × 100 cm^3) to remove unreacted amidine. Though reaction had occurred, and there were clear indications [*i.e.* ν(N–H) sharp, high-frequency peak] that a nickel complex similar to those for palladium and platinum had formed, separation of the product from unreacted $NiCl_2$ without decomposition of the required material proved difficult, and the analytically pure nickel complex could not be obtained. Similar results were obtained using other amidines.

$K_2[PdCl_4]$ *with* N-p-*tolylacetamide*. The amide (0.74 g, 5 mmol) and $K_2[PdCl_4]$ (1.63 g, 5 mmol) were dissolved in a mixture of methanol (20 cm^3) and water (50 cm^3), and the mixture heated to the reflux temperature for 2 h. During this period a dark grey-green solid separated. This precipitate was separated by filtration, washed with hot water (2 × 20 cm^3), then methanol (2 × 10 cm^3), and dried *in vacuo*. The pale green product was identified by elemental analysis as $[\{Pd[p\text{-}CH_3C_6H_3NHC(CH_3)CO]Cl\}_n]$ (Found: C, 37.1; H, 3.55; Cl, 12.4; N, 5.10; Pd, 36.8. $C_{10}H_{10}ClNOPd$ requires C, 37.3; H, 3.45; Cl, 12.3; N, 4.85; Pd, 36.6%).

Reaction with acetanilide was accomplished using the same method but at a lower temperature (*ca.* 60°) and for a longer period (4 h).

$[\{Pd[p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p]Cl\}_n]$ *with pyridine*. Pyridine (10 cm^3) was added to the orthometallated complex (0.3 g, 0.65 mmol) under nitrogen, to form an initial yellow-green solution, which was stirred rapidly at ambient temperature. A rapid reaction occurred and produced a grey-white precipitate. Pyridine was removed from the reaction mixture *in vacuo*, and the residue extracted with chloroform (10 cm^3). Filtration gave a pale yellow-green solution, and a small quantity of a dark grey residue of palladium metal. Reduction of the volume of the filtrate, *in vacuo*, followed by addition of pentane and cooling to −8 °C, yielded a yellow solid. Recrystallisation from a chloroform–pentane mixture gave $[Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p\}(C_5H_5N)Cl]$ or $[C_5H_6N]^+{}_n[Pd\{p\text{-}CH_3C_6H_3NC(CH_3)NC_6H_4CH_3\text{-}p\}Cl]_n{}^{n-}$ [10] as a yellow powder (yield 57%) (Found: C, 54.6; H, 5.40; Cl, 8.05; N, 8.85; Pd, 23.1. $C_{21}H_{21}ClN_3Pd$ requires C, 55.2; H, 4.60; Cl, 7.75; N, 9.20; Pd, 23.3%).

This reaction is typical of the reactions of all the orthometallated complexes with pyridine.

With dimethyl sulphoxide. When dimethyl sulphoxide (5 cm^3) was added to the complex (0.42 g, 1.2 mmol) a deep yellow solution formed which when slowly evaporated at ambient temperature deposited yellow crystals of $[Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p\}\{(CH_3)_2SO\}Cl]$. (Found: C, 52.3; H, 5.85; N, 6.40; Pd, 24.9. $C_{18}H_{23}ClN_2OPdS$ requires C, 52.5; H, 5.60; N, 6.80; Pd, 25.8%). ^1H NMR [$(CD_3)_2SO$, 90 MHz]: δ 1.91(3), 2.16(3), 2.31(3), 6.73(2), 7.02(4), 7.65(1) and 10.1(1).

A similar reaction occurred for the other orthometallated complexes. In all cases the green powders of the starting complexes were converted into light yellow crystalline materials.

$[\{Pd(C_6H_5NCHNHC_6H_4)Cl\}_n]$ *with acetone*. In an attempt to obtain crystals of the above complex, it was dissolved in acetone, and the volume of solution reduced *in vacuo*. On storing under nitrogen for 3 months at room temperature, yellow crystals of *trans*-$[Pd\{(CH_3)_2C{=}NC_6H_5\}_2Cl_2]$ were obtained in small yield and characterised by mass spectral and X-ray analysis.[12] Palladium metal also separated from solution. Further concentration of the solution gave a white solid identified as $(CH_3)_2C{=}NC_6H_5$ by mass spectrometry. Evaporation of the solution produced a residue containing *N*-phenylformamide, identified in the same way.

$[\{Pd[C_6H_5NC(CH_3)NHC_6H_4]Cl\}_n]$ *with carbon monoxide*. The complex (0.30 g, 0.85 mmol) was placed in a glass liner of a high-pressure vessel together with toluene (20 cm^3) and pyridine (0.2 cm^3). A brown suspension resulted, which was pressurised to 100 atm carbon monoxide and heated at 150 °C for 6 h. After cooling and venting the carbon monoxide, a black residue was present with a clear colourless solution. The residue after extraction with chloroform gave a residue of palladium metal and a yellow solution from which pale yellow crystals of quinazolin-4-one were obtained (m.p., 147–148.5; lit., 147–148 °C) (Found: C, 76.2; H, 5.10; N, 11.9. $C_{15}H_{12}N_2O$ requires C, 76.3; H, 5.10; N, 11.9%).

Related compounds were obtained using other amidine complexes of the same type, *e.g.* **IV** (R = CH_3, R′ = p-tolyl, R″ = CH_3). Mass spectrum: m/z (P^+) 264; 249, 157, 133, 132 and 131 corresponding to $[P - CH_3]^+$, $[P - CH_3 - CH_3C_6H_4]^+$, $[CH_3C_6H_4NCO]^+$, $[CH_3C_6H_4NCCH_3]^+$ and/or $[CH_3C_6H_3NCO]^+$, and $[CH_3C_6H_3NCCH_3]^+$ respectively.

$[\{Pt[p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p]Cl\}_n]$ *with carbon monoxide*. The complex (0.148 g, 0.32 mmol), pyridine (0.2 cm^3) and toluene were placed in a glass liner of a high-pressure vessel, which was pressurised to 130 atm carbon monoxide and heated to 150 °C for 5 h. After depressurising at ambient temperature, a clear, almost colourless solution was obtained together with a small amount of a black residue, presumably palladium metal. The solution was filtered, then reduced to a yellow oily residue *in vacuo*, which was extracted with chloro-

Table 6 Final fractional atomic coordinates of non-hydrogen atoms in $[\overline{Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC}_6H_3CH_3\text{-}p\}(\eta^5\text{-}C_5H_5)]$

Atom	X/a	Y/b	Z/c
Pd	−0.026 97(8)	−0.066 38(8)	0.773 50(7)
N(1)	0.119 9(8)	0.073 9(7)	0.727 9(6)
N(2)	0.356 3(9)	−0.035 1(7)	0.794 3(7)
C(1)	0.267(1)	0.067 0(8)	0.737 8(7)
C(2)	0.351(1)	0.168(1)	0.685(1)
C(3)	0.323 8(9)	−0.141 5(8)	0.863 5(7)
C(4)	0.170(1)	−0.168 3(9)	0.865 4(7)
C(5)	0.160(1)	−0.274 1(9)	0.938 8(8)
C(6)	0.292(1)	−0.350 4(9)	1.004 8(8)
C(7)	0.438(1)	−0.323(1)	0.997 1(9)
C(8)	0.457(1)	−0.217(1)	0.928 2(9)
C(9)	0.271(2)	−0.463(2)	1.083(2)
C(10)	0.030(1)	0.186 0(9)	0.668 1(8)
C(11)	−0.070(1)	0.184(1)	0.538(1)
C(12)	−0.164(1)	0.290(1)	0.481(1)
C(13)	−0.151(1)	0.398(1)	0.555(1)
C(14)	−0.042(2)	0.401(1)	0.688(1)
C(15)	0.044(1)	0.295(1)	0.743(1)
C(16)	−0.249(3)	0.515(2)	0.495(3)
C(17)	−0.340(1)	−0.152(1)	0.643(1)
C(18)	−0.319(1)	−0.012(1)	0.675(1)
C(19)	−0.241(1)	0.014(2)	0.811(1)
C(20)	−0.202(1)	−0.109(2)	0.857(1)
C(21)	−0.258(1)	−0.210(1)	0.757(1)

form. After refiltering, the extract was reduced to small bulk and hexane slowly added to precipitate a white solid. Recrystallisation from a chloroform–hexane mixture gave white crystals of $[Pt\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p\}(CO)Cl]$ (Found: C, 40.8; H, 3.35; N, 6.00; Pt, 39.4. $C_{17}H_{17}ClN_2OPt$ requires C, 41.3; H, 3.25; N, 5.65; Pt, 39.4%). IR spectrum (KBr disc): ν(CO) 2097s, and ν(N–H) 3290m cm^{-1}.

$C_6H_5NHC(CH_3)NC_6H_5$ *with* $[Pd(C_6H_5CN)_2Cl_2]$. The amidine (1.05 g, 5.0 mol) and the palladium complex (1.92 g, 5.0 mmol) in chloroform (30 cm^3) were stirred at room temperature for 2 h, at the end of which time the bulk of the solvent was removed *in vacuo*. A yellow-orange powder precipitated in high yield (≈80%), and after recrystallisation from chloroform–hexane mixtures was identified as $[Pd\{C_6H_5NC(CH_3)NH\text{-}C_6H_5\}_2Cl_2]$ (Found: C, 55.6; H, 4.80; Cl, 11.0; N, 9.25. $C_{28}H_{28}Cl_2N_4Pd$ requires C, 56.3; H, 4.70; Cl, 11.9; N, 9.35%). Extraction of the initial yellow-orange powder with toluene gave a pale yellow residue of the *trans* isomer [m.p. 195 °C, ν(Pd–Cl) 349 cm^{-1}] and an orange-red solution from which red crystals of the *cis* isomer were produced by slow removal of the solvent *in vacuo* [m.p. 183 °C (decomp.), ν(Pd–Cl) 348 and 307 cm^{-1}].

$p\text{-}CH_3C_6H_4NHC(CH_3)NC_6H_4CH_3\text{-}p$ *with* $[Pd(C_6H_5CN)_2Cl_2]$. The amidine (1.2 g, 5.0 mmol) and the palladium complex (1.92 g, 5.0 mmol) were placed in a flask and chloroform (30 cm^3) added. The compounds readily dissolved on stirring at room temperature, and after 2 h the solvent was slowly removed *in vacuo* to yield a yellow-orange powder. Recrystallisation from chloroform–hexane mixtures gave $[Pd\{p\text{-}CH_3C_6H_4NC(CH_3)\text{-}NHC_6H_4CH_3\text{-}p\}_2Cl_2]$ in almost quantitative yield (Found: C, 58.6; H, 5.90; Cl, 10.3; N, 8.40. $C_{32}H_{36}Cl_2N_4Pd$ requires C, 58.8; H, 5.50; Cl, 10.9; N, 8.55%). ^1H NMR (CH_2Cl_2): δ 7.22(m), 2.33 ($p\text{-}CH_3$) and 1.75 (CH_3CN_2); *cf.* free ligand (CH_2Cl_2) 7.12(m), 2.30 and 1.90.

Similar adducts for palladium and platinum were obtained for other amidines, and in addition to $[M(C_6H_5CN)_2Cl_2]$, MCl_2 and $K_2[MCl_4]$ (M = Pd or Pt) may also be used as starting materials. Toluene and monoglyme, amongst others, were found to be very suitable media for the reactions.

Action of heat on $[Pd\{p\text{-}CH_3C_6H_4NC(C_6H_5)NHC_6H_4\text{-}CH_3\text{-}p\}_2Cl_2]$. (*i*) The complex (0.306 g, 0.39 mmol) was mixed with toluene (50 cm^3) and the solution heated in a dry atmosphere ($CaCl_2$ guard tube). The pale yellow suspension dissolved forming a yellow-brown solution, which was kept at the reflux temperature for 2 h. On cooling, the complex was recovered unchanged from solution. Similar results were found for $[Pd\{CH_3NC(C_6H_5)NHCH_3\}_2Cl_2]$.

(*ii*) The *N*-*p*-tolyl complex (0.40 g, 0.51 mmol) was mixed with methanol (25 cm^3) and water (10 cm^3) and the suspension heated to the reflux temperature for 2 h. Solid remained in suspension throughout the heating period, and after cooling the mixture the solid was separated by filtration, heated with hot toluene before separation again by filtration from the hot mixture. After drying *in vacuo* the solid product was identified using the sharp, medium-intensity IR absorption at 3340 cm^{-1} as the orthometallated complex **IV**.

$[\{\overline{Pd[p\text{-}CH_3C_6H_4NC(CH_3)NHC}_6H_3CH_3\text{-}p]Cl\}_n]$ *with sodium cyclopentadienide*. Sodium cyclopentadienide was prepared freshly in thf solution (50 cm^3) using freshly cracked cyclopentadiene (0.30 g, 4.5 mmol) and freshly extruded sodium (0.13 g, 5.6 mmol). The solution was added to the solid palladium complex (1.52 g, 4.0 mmol) cooled in liquid nitrogen, and the mixture allowed to reach ambient temperature. The complex reacted over several hours (4 h) and dissolved in solution. Reaction was judged complete when the solution clarified. The solvent was removed *in vacuo*, and the residue extracted with toluene. Slow removal of solvent *in vacuo* and addition of hexane produced a purple air-stable precipitate, which on recrystallisation from toluene–hexane mixtures gave purple crystals of $[\overline{Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC}_6H_3CH_3\text{-}p\}(\eta^5\text{-}C_5H_5)]$ (decomp. > 160 °C) (Found: C, 61.8; H, 5.15; N, 6.85; Pd, 25.7. $C_{21}H_{22}N_2Pd$ requires C, 62.2; H, 5.15; N, 6.95; Pd, 26.0%). Mass spectrum: m/z 408(P^+) + ions derived from the amidine ligand. ^1H NMR ($CDCl_3$, 60 MHz); δ 1.80(3), 2.25(3), 2.40(3), 5.33(5), 6.90(2), 7.10(4) and 7.31(1).

With $p\text{-}CH_3C_6H_4N(Li)C(CH_3)NC_6H_4CH_3\text{-}p$. The lithio reagent (2.0 mmol), freshly prepared in monoglyme solution (40 cm^3) from the amidine and butyllithium, was added to the solid orthometallated complex (0.76 g, 2.0 mmol) at room temperature and the mixture stirred for 2 h. During this period most of the solid reagent slowly dissolved to produce a yellow-brown solution. The solvent was removed *in vacuo* and the residue was extracted with toluene. Reduction of the extracts to small bulk *in vacuo*, followed by addition of pentane, gave a yellow powder of $[Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p\}\text{-}\{p\text{-}CH_3C_6H_4NC(CH_3)NC_6H_4CH_3\text{-}p\}]$ which was recrystallised from hot monoglyme (Found: C, 65.2; H, 6.05; N, 9.40. $C_{32}H_{34}N_4Pd$ requires C, 66.2; H, 5.85; N, 9.65%). Mass spectrum: m/z (P^+) 580. ν(NH) 3485 cm^{-1}, ν(Pd–Cl) absent.

The complex $[\overline{Pd\{p\text{-}FC_6H_4NC(C_6H_5)NHC}_6H_3F\text{-}p\}\{p\text{-}FC_6H_4NC(C_6H_5)NC_6H_4F\text{-}p\}]$, prepared in a similar way, gave the following ions by FAB mass spectrometry (thiodiglycerol was used as the mulling agent): m/z 720 (P^+), 413 ($[Pd\{FC_6H_3NHC(C_6H_5)NC_6H_4F\}]^+$), 198 ($[FC_6H_4NCC_6H_5]^+$) and 122 ($[FC_6H_4NHC]^+$).

With $Mg(C_3H_5)Cl$. The Grignard reagent was prepared in monoglyme (50 cm^3) from allyl chloride (0.16 g, 2.1 mmol) by a standard procedure, and the solution was added to the solid complex (0.76 g, 2.0 mmol) at room temperature. Stirring for 2 h caused most of the complex to dissolve and a cloudy yellow-brown solution resulted. Evaporation to dryness *in vacuo*, followed by extraction of the residue with toluene, gave a yellow solution. Reduction *in vacuo* to small bulk and addition of pentane gave $[Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p\}\text{-}(C_3H_5)]$ as a yellow powder (Found: C, 58.6; H, 6.10; N, 6.85. $C_{19}H_{22}N_2Pd$ requires C, 59.3; H, 5.70; N, 7.30%). Mass spectrum: m/z 384 (P^+).

$[Pd\{p\text{-}CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3\text{-}p\}Cl]$ *with acetylacetonatothallium*(I). The orthometallated complex (0.83 g, 2.2 mmol), acetylacetonatothallium (0.67 g, 2.2 mmol) and toluene (40 cm^3) were stirred at room temperature for 2 h. A yellow-

Table 7

Bond distances (Å) and angles (°)

Pd–N(1)	2.040(6)	C(3)–C(8)	1.387(10)	C(17)–C(18)	1.389(16)	C(9)–H(10)	0.83(15)
Pd–C(4)	1.984(7)	C(4)–C(5)	1.397(11)	C(17)–C(21)	1.369(14)	C(11)–H(11)	0.77(7)
Pd–C(17)	2.410(9)	C(5)–C(6)	1.388(11)	C(18)–C(19)	1.424(18)	C(12)–H(12)	0.84(12)
Pd–C(18)	2.419(8)	C(6)–C(7)	1.360(12)	C(19)–C(20)	1.362(19)	C(14)–H(14)	0.84(10)
Pd–C(19)	2.440(11)	C(6)–C(9)	1.516(12)	C(20)–C(21)	1.387(17)	C(15)–H(15)	0.73(9)
Pd–C(20)	2.274(9)	C(7)–C(8)	1.377(12)	C(2)–H(1)	1.17(13)	C(16)–H(13)	0.90(17)
Pd–C(21)	2.239(9)	C(10)–C(11)	1.350(13)	C(2)–H(2)	0.83(9)	C(16)–H(16)	0.95(18)
N(1)–C(1)	1.285(9)	C(11)–C(12)	1.400(13)	C(2)–H(3)	0.73(13)	C(16)–H(22)	0.85(14)
N(1)–C(10)	1.445(10)	C(12)–C(13)	1.349(15)	C(5)–H(5)	0.94(8)	C(17)–H(17)	0.82(6)
N(2)–C(1)	1.350(9)	C(13)–C(14)	1.392(16)	C(7)–H(7)	0.92(9)	C(18)–H(18)	0.68(9)
N(2)–C(3)	1.434(10)	C(13)–C(16)	1.518(15)	C(8)–H(8)	0.92(11)	C(19)–H(19)	0.79(15)
N(2)–H(4)	0.63(7)	C(14)–C(15)	1.362(14)	C(9)–H(6)	0.80(13)	C(20)–H(20)	0.93(12)
C(1)–C(2)	1.492(11)	C(10)–C(15)	1.361(14)	C(9)–H(9)	0.99(15)	C(21)–H(21)	0.98(13)
C(3)–C(4)	1.382(10)						

N(1)–Pd–C(4)	91.3(3)	C(7)–C(6)–C(9)	121.2(8)	H(1)–C(2)–H(2)	94(8)	C(15)–C(14)–H(14)	126(7)
Pd–N(1)–C(1)	128.2(5)	C(3)–C(8)–C(7)	120.4(8)	H(1)–C(2)–H(3)	111(12)	C(14)–C(15)–H(15)	120(8)
Pd–N(1)–C(10)	111.4(5)	N(1)–C(10)–C(11)	121.2(8)	H(2)–C(2)–H(3)	127(12)	C(10)–C(15)–H(15)	118(8)
C(1)–N(1)–C(10)	120.2(6)	N(1)–C(10)–C(15)	120.3(8)	C(4)–C(5)–H(5)	121(5)	C(13)–C(16)–H(13)	102(12)
N(1)–C(1)–N(2)	122.0(7)	C(11)–C(10)–C(15)	118.6(9)	C(6)–C(5)–H(5)	116(5)	C(13)–C(16)–H(16)	119(13)
N(1)–C(1)–C(2)	123.1(7)	C(10)–C(11)–C(12)	120.8(10)	C(6)–C(7)–H(7)	125(6)	C(13)–C(16)–H(22)	116(10)
N(2)–C(1)–C(2)	114.8(7)	C(11)–C(12)–C(13)	120.7(10)	C(8)–C(7)–H(7)	116(6)	H(13)–C(16)–H(16)	109(15)
C(1)–N(2)–C(3)	129.9(7)	C(12)–C(13)–C(14)	117.9(9)	C(7)–C(8)–H(8)	124(6)	H(13)–C(16)–H(22)	133(15)
C(1)–N(2)–H(4)	119(5)	C(12)–C(13)–C(16)	121.5(14)	C(3)–C(8)–H(8)	115(6)	H(16)–C(16)–H(22)	78(14)
C(3)–N(2)–H(4)	111(5)	C(14)–C(13)–C(16)	120.6(14)	C(6)–C(9)–H(6)	114(10)	C(18)–C(17)–H(17)	136(4)
N(2)–C(3)–C(4)	122.7(7)	C(13)–C(14)–C(15)	120.7(11)	C(6)–C(9)–H(9)	118(8)	C(21)–C(17)–H(17)	117(4)
N(2)–C(3)–C(8)	115.6(7)	C(10)–C(15)–C(14)	121.3(11)	C(6)–C(9)–H(10)	108(10)	C(17)–C(18)–H(18)	117(8)
C(4)–C(3)–C(8)	121.8(7)	C(17)–C(18)–C(19)	109.9(12)	H(6)–C(9)–H(9)	112(13)	C(19)–C(18)–H(18)	133(9)
Pd–C(4)–C(3)	124.2(6)	C(18)–C(19)–C(20)	104.0(13)	H(6)–C(9)–H(10)	95(13)	C(18)–C(19)–H(19)	139(11)
Pd–C(4)–C(5)	120.2(6)	C(19)–C(20)–C(21)	111.1(11)	H(9)–C(9)–H(10)	108(12)	C(20)–C(19)–H(19)	117(11)
C(3)–C(4)–C(5)	115.7(7)	C(17)–C(21)–C(20)	108.1(11)	C(10)–C(11)–H(11)	122(6)	C(19)–C(20)–H(20)	125(7)
C(4)–C(5)–C(6)	123.3(7)	C(18)–C(17)–C(21)	106.4(11)	C(12)–C(11)–H(11)	117(6)	C(21)–C(20)–H(20)	123(7)
C(5)–C(6)–C(7)	118.8(8)	C(1)–C(2)–H(1)	109(6)	C(11)–C(12)–H(12)	109(9)	C(20)–C(21)–H(21)	129(7)
C(5)–C(6)–C(9)	120.0(8)	C(1)–C(2)–H(2)	114(6)	C(13)–C(12)–H(12)	131(9)	C(17)–C(21)–H(21)	123(7)
C(6)–C(7)–C(8)	120.0(8)	C(1)–C(2)–H(3)	101(11)	C(13)–C(14)–H(14)	113(7)		

Dihedral angles between mean planes of rings

Tolyl/metallocycle	97	Tolyl/C_5H_5	162	Metallocycle/C_5H_5	86
Tolyl/orthometallated	100	Metallocycle/orthometallated	5	Orthometallated/C_5H_5	85

brown solution resulted and was reduced to dryness *in vacuo*. The residue was extracted with toluene, the solution reduced in volume *in vacuo* and pentane added. A yellow powder separated and on recrystallisation from toluene yellow crystals of $[\mathrm{Pd}\{p\text{-}\mathrm{CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3}\text{-}p\}(\mathrm{C_5H_7O_2})]$ were produced. (Found: C, 56.1; H, 6.05; N, 6.05. $C_{21}H_{24}N_2O_2Pd$ requires C, 57.0; H, 5.40; N, 6.35%). ν(NH) 3375 cm^{-1}. Mass spectrum: m/z 422 (P^+).

$[\{\mathrm{Pd}[p\text{-}i\text{-}\mathrm{C_3H_7C_6H_4NC(C_6H_5)NHC_6H_3C_3H_7}\text{-}i\text{-}p]\mathrm{Cl}\}_n]$ *with lithiodiphenyltriazine.* Diphenyltriazine (98.6 mg, 0.5 mmol) in diethyl ether (25 cm^3) was cooled in an ice-bath (– 10 °C) and butyllithium (0.5 mmol) in hexane added. After stirring for a few minutes the solution became deep red. Following further stirring for 30 min at ambient temperature the solution was frozen at – 196 °C and the palladium complex (0.25 g, 0.5 mmol) added against a counter current of nitrogen. The mixture was allowed to warm to ambient temperature, then stirred for 16 h. The resulting brown solution was evaporated to dryness *in vacuo* and the residue extracted with toluene (25 cm^3), producing a brown solution. After filtration and reduction in volume using a flow of nitrogen gas, the product $[\mathrm{Pd}\{p\text{-}i\text{-}\mathrm{C_3H_7C_6H_4NC(C_6H_5)NHC_6H_3C_3H_7}\text{-}i\text{-}p\}(\mathrm{C_6H_5NNNC_6H_5})]$ separated as a yellow-brown solid (Found C, 67.7; H, 5.85; N, 8.65. $C_{37}H_{37}N_5Pd$ requires C, 67.5; H, 5.65; N, 10.65%). Mass spectrum: m/z 356 (amidine ligand) and 196 (triazine ligand).

$[\{\mathrm{Pd}[p\text{-}\mathrm{FC_6H_4NC(C_6H_5)NHC_6H_3F}\text{-}p]\mathrm{Cl}\}_n]$ *with silver ethanoate.* Silver ethanoate (83 mg, 0.5 mmol) was added to a solution of the complex (0.224 g, 0.5 mmol) in thf (25 cm^3), and the mixture stirred at ambient temperature for 3 d. The colour became very dark and a precipitate separated. The mixture was evaporated to dryness *in vacuo*, and the residue extracted with toluene (25 cm^3) to form a yellow-brown solution. After reducing the volume *in vacuo* and cooling to – 10 °C, the yellow-brown product, $[\mathrm{Pd}\{p\text{-}\mathrm{FC_6H_4NC(C_6H_5)NHC_6H_3F}\text{-}p\}(\mathrm{O_2CCH_3})]$ separated. Though consistent analytical data could not be obtained, the spectroscopic data were consistent with the above formulation.

Structure Determination of $[\mathrm{Pd}\{p\text{-}\mathrm{CH_3C_6H_4NC(CH_3)NHC_6H_3CH_3}\text{-}p\}(\eta^5\text{-}\mathrm{C_5H_5})]$.—*Crystal data.* $C_{21}H_{22}N_2Pd$, M = 408.8, triclinic, space group $P\bar{1}$ (assumed), a = 9.0267(2), b = 9.8949(8), c = 12.1519(3) Å, α = 89.855(3), β = 121.278(2), γ = 99.199(3)°, U = 911.5 $Å^3$, D_m = 1.52(2), Z = 2, D_c = 1.488 g cm^{-3}, $F(000)$ = 416, Mo-$K\alpha$ (λ = 0.710 69 Å), μ = 10.45 cm^{-1}.

After preliminary X-ray photography, 2390 significant [$I > 3\sigma(I)$], unique X-ray intensities were measured on a Hilger and Watts computer-controlled four-circle diffractometer within the range $0 < \theta \leqslant 25°$. 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 0.054. Part way through the refinement all the hydrogen atoms were located in a Fourier difference map. They were then refined with isotropic thermal parameters whilst the non-hydrogen atoms were assumed to vibrate anisotropically. In the later stages a weighting scheme of the form $w = 1/\{1 + [|F_o| - P(2)]^2/P(1)^2\}$ was applied, with $P(1)$ = 15.0, $P(2)$ = 15.0, and $|F_o|$ on the absolute scale. Final atomic coordinates so obtained are given in Table 6 and the bond lengths and angles calculated from them in Table 7. The Oxford CRYSTALS system of programs was employed.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Thermogravimetric Studies.—The thermograms are given in Fig. 1. % Weight loss for $[\{\overline{\text{Pd}[\text{R}'\text{C}_6\text{H}_4\text{NC(R)NH}\text{C}}_6\text{H}_3\text{R}]\text{Cl}\}_n]$ complexes (theoretical weight loss for loss of amidine is shown in parentheses): R = C_6H_5, R′ = *i*-C_3H_7, 70(72), 20–439 °C; R = C_6H_5, R′ = CH_3, 68(68), 20–400 °C; R = C_6H_5, R′ = H, 66(65), 20–410 °C; R = C_6H_5, R′ = F, 39(72), 20–321 °C; R = R′ = H, 58(44), 20–331 °C; R = CH_3, R′ = H, 60(61), 20–321 °C.

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References

1 M. G. B. Drew and J. D. Wilkins, *Acta Crystallogr., Sect B*, 1977, **31**, 177; J. Barker, N. Cameron, M. Kilner, M. M. Mahmoud and S. C. Wallwork, *J. Chem. Soc., Dalton Trans.*, 1986, 1359; F. A. Cotton, T. Inglis, M. Kilner and T. R. Webb, *Inorg. Chem.*, 1975, **14**, 2023.

2 L. D. Brown and J. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 1597; E. Pfeiffer and K. Olie, *Cryst. Struct. Commun.*, 1975, **4**, 605; M. Corbett and B. F. Hoskins, *J. Am. Chem. Soc.*, 1967, **89**, 1530; *Chem. Commun.*, 1968, 1602; D. S. Moore and S. D. Robinson, *Adv. Organomet. Chem.*, 1986.

3 T. Inglis, *Inorg. Chim. Acta Rev.*, 1973, **3**, 35.

4 W. Bradley and I. Wright, *J. Chem. Soc.*, 1956, 640.

5 G. W. Parshall, *Acc. Chem. Res.*, 1975, **8**, 113; J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, 1976, **18**, 327; M. Orchin and D. Bollinger, *Struct. Bonding* (*Berlin*), 1975, **23**, 182.

6 A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909.

7 J. A. Clark and M. Kilner, *J. Chem. Soc., Dalton Trans.*, 1983, 2613.

8 N. D. Cameron and M. Kilner, *J. Chem. Soc., Chem. Commun.*, 1975, 687.

9 F. R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science, London, 1973 and refs. therein.

10 J. Dupont, M. Pfeffer, J.-C. Daran and J. Gouteron, *J. Chem. Soc., Dalton Trans.*, 1988, 2421.

11 S. A. Johnson, personal communication.

12 D. Briggs, *Handbook of X-Ray Photoelectric Spectroscopy and Ultraviolet Photoelectron Spectroscopy*, Heyden, London, 1976.

13 W. Clegg, J. Barker and M. Kilner, *Acta Crystallogr., Sect. C*, 1987, **43**, 1211.

14 R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Allyn and Bacon, Boston, 1966.

15 D. H. Busch, *Helv. Chim. Acta*, 1967, 174.

16 V. A. Dorokhov, K. L. Cherkasova and A. T. Lutsenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, **10**, 2351.

17 A. Rosenthal and I. Wender, *Organic Synthesis via Metal Carbonyls*, eds. I. Wender and P. Pino, Interscience, New York, 1968, vol. 1.

18 J. Barker, N. Cameron, M. Kilner, M. M. Mahmoud and S. C. Wallwork, *J. Chem. Soc., Dalton Trans.*, 1986, 1359.

19 L. Tschugaev and W. Lebendinski, *C.R. Acad. Sci., Paris*, 1915, **161**, 563.

20 N. C. Stephenson, *J. Inorg. Nucl. Chem.*, 1962, **24**, 801.

21 F. P. Boer, V. B. Carter and J. W. Turley, *Inorg. Chem.*, 1971, **10**, 651.

22 J. R. Wiesner and E. C. Lingafelter, *Inorg. Chem.*, 1966, **5**, 1770.

23 J. Barker, M. Kilner, M. M. Mahmoud and S. C. Wallwork, *J. Chem. Soc., Dalton Trans.*, 1989, 837.

24 F. Krohnke and H. H. Steuernagel, *Chem. Ber.*, 1963, **96**, 486; S. P. Joshi, A. P. Khanolkar and T. S. Wheeler, *J. Chem. Soc.*, 1936, 793; E. C. Taylor and W. A. Ehrhart, *J. Org. Chem.*, 1963, **28**, 1108.

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