Reactivity of Primary Amines Co-ordinated to Palladium and Platinum. Part II.† Cyclometallation and Rearrangement of the Co-ordinated Ligands

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Reaction of *trans*-$[PdCl_2(NH_2X)_2]$ (X = NPhR or $PhCH_2$; R = Ph, Me, or H) with acetophenone gives the cyclopalladated dimer $[\{PdCl(C_6H_4CMe{=}NX)\}_2]$, the acetophenone phenyl ring being orthometallated. Reaction of $[PtCl_4]^{2-}$ and $[Pd_2Cl_6]^{2-}$ with 2-aminothiazoline and 2-aminothiazole (L) affords in acid media the cyclic N-co-ordinated monosubstituted $[NBu_4][PdCl_3L]$ and disubstituted *cis*-$[PtCl_2L_2]$ and *trans*-$[PdCl_2L_2]$ complexes. In basic solution, the monomeric $[PdCl_2L'_2]$ and dimeric $[\{MCl_2L'\}_2]$ species are obtained [$M = Pt^{II}$ or Pd^{II}; L′ = $HS{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C\vdots N$ and $HS{\cdot}CH{:}CH{\cdot}NH\vdots N$. The combined presence of the metal and hydroxide ions appears to induce the ring opening and rearrangement of the amine ligands.

As part of our investigation into the reactions of co-ordinated ligands, we became interested in the unusual reactivity of amine substituents when bound to a heavy transition metal. Some works have recently shown [1-4] that the C=N bond of benzylideneaniline can be cleaved in the presence of salts of Pd^{II}, Pt^{II}, Rh^{I}, and Rh^{III}, with subsequent formation of aniline–metal complexes and of free benzaldehyde. However, the reaction mechanism has not been clearly identified. We have shown [5-7] that the imine bond may be formed by reaction of palladium co-ordinated amines with several ketones. Moreover, we have observed that amine ligands may themselves undergo intramolecular rearrangement, when the amine is already bound to Pd^{II} and Pt^{II},[8] to give a stable carbodi-imide (or cyanamide) group.

EXPERIMENTAL

Preparation.—The synthesis of the complexes obtained in reactions (1) and (2) have been reported elsewhere.[6,7]

$[NBu_4][PdCl_3L]$ [L = 2-*Aminothiazoline* (ath) *or* 2-*aminothiazole* (atz)]. An ethanol solution of L (1 mmol), adjusted to pH 4 with 1N HCl, was added to a hot solution of $[NBu_4]_2[Pd_2Cl_6]$ (0.5 mmol) in dichloromethane. Reddish brown crystals were deposited on evaporating and cooling the solution; they were recrystallised from dichloromethane–diethyl ether.

trans-$[PdCl_2L_2]$ (L = ath *or* atz). These complexes were obtained by addition of $[NBu_4][PdCl_3L]$ (1 mmol) to an ethanol solution of L (1 mmol) at pH 4 and stirred under reflux until a yellow solid was formed. The precipitate was recrystallised from dichloromethane–diethyl ether.

cis-$[PtCl_2L_2]$. These complexes were precipitated progressively by addition of 2 mmol of L (acidified ethanol solution) to an aqueous solution of $K_2[PtCl_4]$ (1 mmol). The red-brown products were recrystallised from *NN*-dimethylformamide–water.

cis-$[\{MCl_2L'\}_2]$ [M = Pt *or* Pd; L′ = 2-*iminothiazoline* (ith) *or* 2-*iminothiazole* (itz)]. A hot ethanol solution of L (1 mmol), adjusted to pH 9 by addition of K[OH], was added to $K_2[PtCl_4]$ (1 mmol) in water or to $[NBu_4]_2[Pd_2Cl_6]$ (1 mmol) in ethanol. The insoluble greenish brown products were washed with water, then ethanol, and dried with diethyl ether. The complexes *trans*-$[PdCl_2L'_2]$ were prepared in the same way, with a Pd : L ratio of 1 : 2.

The compounds ath and atz were acetylated to give 2-acetamidothiazoline (acth) and 2-acetamidothiazole (actz) as described by McOmie.[9]

Physical Measurements.—I.r. spectra were recorded on a Polytec FIR 30 interferometer (50—400 cm^{-1}) and on a Beckman IR 12 spectrophotometer (400—4 000 cm^{-1}). The complexes were sampled as polyethylene and KBr pellets respectively. ^1H N.m.r. spectra were recorded at room temperature on a Bruker WH 90 spectrometer, in CD_2Cl_2 or $[^2H_6]$dmso solutions, with $SiMe_4$ as external standard.

RESULTS AND DISCUSSION

We observed different types of reactions, according to the nature of the substituent bound to the co-ordinated amine. When this substituent was an amino- (NPhR; R = H, Me, or Ph), benzyl, or phenyl group, and in the presence of a ketone, an imine group was formed, bound to the metal through the nitrogen. In the case of an aromatic ketone, subsequent cyclometallation also occurred. When this substituent was a thiazole or thiazoline, in the presence of hydroxide ions, a complete rearrangement of the ligands occurred, and a cyanamide group was formed, bound to the metal through one or both nitrogen atoms.

Condensation Reactions with Ketones.—The condensation reactions of palladium-co-ordinated amines with carbonyl groups depend on the nature of both the amine and the ketone. We thus obtained either a series of complexes [see reaction (1)] where the imine is only bound to the metal through the tertiary nitrogen atom,[5,6] or cyclopalladated dimers [see reaction (2)] where the newly condensed ligand is chelated. Reaction (1a) also occurred with methanal, but the final complex

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† Part I is ref 6.

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[3] B. N. Cockburn, D. V. Hove, T. Keating, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 404.

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[6] J. Dehand and M. Pfeffer, *Bull. Soc. chim. France*, 1974, 2782.

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[8] J. Dehand and J. Jordanov, *J.C.S. Chem. Comm.*, 1975, 743.

[9] J. F. W. McOmie, ' Protective Groups in Organic Chemistry,' Plenum Press, New York, 1973, p. 46.

decomposes immediately. In the case of reaction (2) with benzaldehyde, decomposition occurs even at

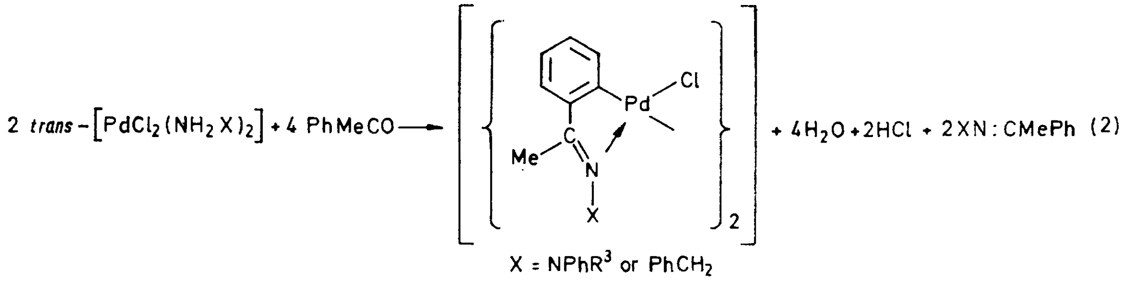
$$trans\text{-}[PdCl_2(NH_2X)_2] + 2R^1R^2CO \longrightarrow trans\text{-}[PdCl_2(XN{=}CR^1R^2)_2] + 2H_2O \quad (1)$$

(I)

(a) $X = NPhR^3$; $R^1 = R^2 =$ Me or Et; $R^3 =$ H, Me, or Ph

(b) $X = Ph$; $R^1 = Me$; $R^2 = Ph$

−40 °C. The platinum(II) complex of phenylhydrazine, $[PtCl_2(NH_2NHPh)_2]$, also reacted with acetophenone, but with decomposition and we were unable to characterise the final product obtained.



(II)

TABLE 1

Analytical (%) [a] and i.r. data (cm^{-1})

		Analysis				I.r. data						
Complex (type)	Colour	C	H	N	Pt	ν(N–H)	ν(NCN)	ν(C=N), (C=C)	γ(C–H)[b]	Φ(C–C)[b]	ν(M–Cl)	ν(M–N)
$[PdCl_2(PhN{=}CMePh)_2]$ (I)	Red	60.55 (59.2)	4.7 (4.6)	4.75 (4.95)				1 616, 1 593	767, 756	700	340	
$[\{PdCl(C_6H_4CMe{=}NNPhH)\}_2]$ (II)	Pale yellow	47.7 (47.9)	3.8 (3.7)	7.95 (8.0)				1 600, 1 576	755, 738	718, 693	340, 253 197, 162 (Br) 189, 141 (I)	
$[\{PdCl(C_6H_4CMe{=}NNMePh\}_2]$ (II)	Yellow	48.95 (49.35)	4.5 (4.1)	7.7 (7.65)				1 599, 1 576	756	717, 692	330, 261 204, 163 (Br)	
$[\{PdCl(C_6H_4CMe{=}NNPh_2\}_2]$ (II)	Orange	56.65 (56.2)	4.65 (4.0)	6.4 (6.55)				1 589, 1 577	756	719, 701, 692	347, 260	
$[\{PdCl(C_6H_4CMe{=}NCH_2Ph)\}]$ (II)	White	50.7 (51.45)	4.05 (4.0)	4.6 (4.0)				1 599, 1 580, 1 560	756, 742, 734	717, 703, 698	335, 252 188, 153 (Br)	
$[NBu_4][PdCl_3(ath)]$ (III) [c]	Brick-red	40.7 (40.9)	7.5 (7.55)	7.6 (7.55)		3 290 3 230		1 575, 1 462			325, 304	271
$[PdCl_2(ath)_2]$ (IV)	Yellow	18.5 (18.85)	3.3 (3.15)	14.8 (14.7)		3 280 3 200		1 557w, 1 450 (sh)			351	272
$[PtCl_2(ath)_2]$ (IV)	Yellow	15.7 (15.3)	2.4 (2.55)	11.4 (11.9)	41.1 (41.5)	3 290 3 210		1 565, 1 460w			330, 320	264
$[NBu_4][PdCl_3(atz)]$ (III) [c]	Brick-red	40.5 (40.1)	7.3 (7.20)	7.6 (7.60)		3 380 3 220		1 475			335, 315	261
$[PdCl_2(atz)_2]$ (IV)	Yellow	19.4 (19.1)	2.5 (2.1)	14.9 (14.85)		3 385 3 270		1 500			352	277
$[PtCl_2(atz)_2]$ (IV)	Red-brown	15.6 (15.45)	1.6 (1.7)	11.9 (12.0)	41.5 (41.7)	3 400 3 300		1 500			325, 312	283
$[\{PdCl_2(ith)\}_2]$ (V) [c]	Olive-green	12.3 (12.5)	2.2 (2.05)	7.8 (9.7)		3 195	2 165 2 125				322, 306	426, 272
$[PdCl_2(ith)_2]$ (VI)	Orange	18.5 (18.85)	3.3 (3.15)	14.2 (14.7)		3 295	2 170 2 130				362	260
$[\{PtCl_2(ith)\}_2]$ (V)	Yellow	9.9 (9.8)	1.8 (1.65)	7.5 (7.6)	52.7 (53.0)	3 180	2 200 2 136				327, 318	422, 275
$[\{PdCl_2(itz)\}_2]$ (V) [c]	Brown	12.8 (13.0)	1.5 (1.45)	10.3 (10.1)		3 140 3 090w	2 156				326, 318	414, 270
$[PdCl_2(itz)_2]$ (VI)	Brown	19.2 (19.1)	2.5 (2.1)	14.4 (14.85)		3 280w	2 160				368	260
$[\{PtCl_2(itz)\}_2]$ (V)	Brown	9.6 (9.85)	1.1 (1.1)	7.2 (7.65)	53.0 (53.3)	3 160w 3 125w	2 145				330, 320	416, 270

[a] Calculated values are given in parentheses. The isolated rearranged ligands have the following values (%): ith C, 35.1 (35.9); H, 3.6 (3.85); N, 27.3 (27.45) and itz C, 35.85 (36.0); H, 3.95 (4.0); N, 27.9 (28.0). [b] These vibrations are C–H out-of-plane deformations and a trigonal deformation of the phenyl ring.[6] [c] I.r. data of the free ligands: ath 3 300m, 3 230m [ν(NH)], 1 585m, 1 475m, 1 430m [ν(C=N)]; atz 3 410m, 3 290m [ν(NH)], 1 520s, 1 480s [ν(C=N)]; ith 3 260m [ν(N–H), 2 295s [ν(NCN)]; itz 3 270m [ν(N–H)], 2 280s [ν(NCN)].

The complexes *trans*-$[PdCl_2(NH_2X)_2]$ ($X = Ph$ or $PhCH_2$) reacted only with acetophenone. In the case of the aniline complex, we did not observe any cyclopalladation reaction, in agreement with the results of Onoue and Moritani[2] and of Cockburn *et al.*[3] The latter workers obtained the complex of type (I) by reaction of benzylideneaniline with $[PdCl_2(NCPh)_2]$ or $Na_2[PdCl_4]$. Molnar and Orchin[10] claim that by this reaction they obtained the cyclopalladated dimeric complex.

The stereochemistry of complexes (II) is supported by our i.r. data: the absorption band at *ca.* 720 cm^{-1} is characteristic of an *ortho*-disubstituted phenyl ring.[11,12] Moreover, according to Crociani *et al.*,[13] there were two bands due to ν(Pd–X), at frequencies characteristic of bridged halogens between two palladium atoms in similar complexes. The ^{1}H n.m.r. spectra showed a

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[11] M. A. Bennet and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

[12] L. Maresca, G. Natile, L. Cattalini, and F. Gasparrini, *J.C.S. Dalton*, 1975, 1601.

[13] B. Crociani, T. Boschi, R. Pietropaolo, and U. Belluco, *J. Chem. Soc.* (*A*), 1970, 531.

deshielding of the aromatic proton resonances for complexes (II), which indicates an *ortho*-disubstituted phenyl ring.[12-14] These complexes appear to be monomers when dissolved in dimethyl sulphoxide (dmso), although we were unable to isolate complexes in which the dmso is co-ordinated to the metal. The NH proton deshielding (see Table 2), as well as the i.r. frequency of the ν(N–H) vibration at *ca.* 3 200 cm^{-1}, which were observed for the dmso solution of complex (II; X = NPhH), suggest the existence of a non-bridged chloride.[15]

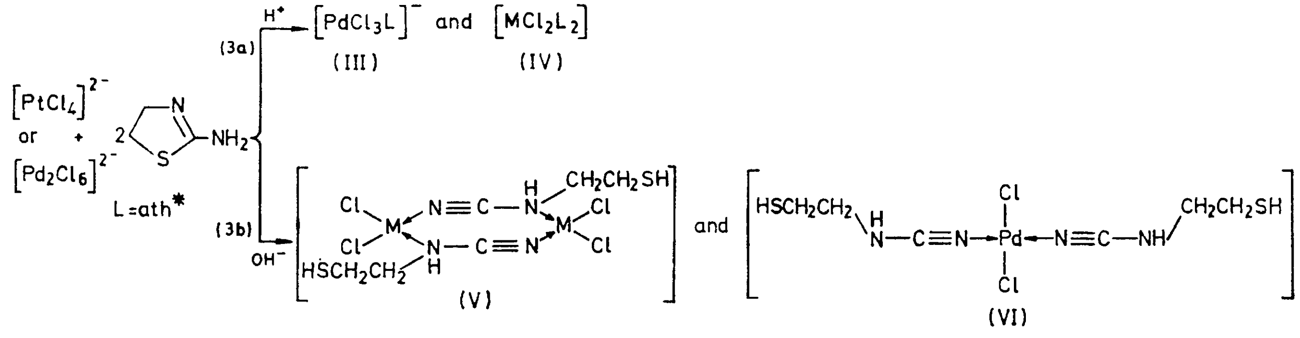
TABLE 2

Proton chemical shifts (δ downfield from SiMe$_4$)

Complex Type	X	R^1	R^2	Solvent	NH (s)	$C_6H_{5(4)}$ (m)	N–CH$_3$ (s)	$=\mathrm{C}<^{\mathrm{CH_3}}$ (s)	⩾C–H	Others
(I)	PhNH	Me	Me	CDCl$_3$	6.65	6.8—7.5		2.5, 2.1		3.0 (q) 2.5 (q) CH$_2$ 1.2 (tr) 1.0 (tr) CH$_3$
	PhNH	Et	Et	CDCl$_3$	6.6	6.8—7.5				
	NMePh	Me	Me	CDCl$_3$		6.9—7.7	3.6, 3.3	3.1, 2.8, 2.1		
	NPh$_2$	Me	Me	CDCl$_3$		7.0—7.5		2.15, 1.8		
	Ph	Me	Ph	CD$_2$Cl$_2$		8.2,[a] 6.8—7.5		2.1		
(II)	NPhH	Me	C$_6$H$_4$	(D$_3$C)$_2$SO	8.55	6.6—7.85		2.35		
	NMePh	Me	C$_6$H$_4$	CD$_2$Cl$_2$		6.45—7.35	3.2, 2.8	2.3		
				(D$_3$C)$_2$SO		6.8—8.3	3.35	2.4		
	NPh$_2$	Me	C$_6$H$_4$	(D$_3$C)$_2$SO		6.9—7.45		2.45		
	PhCH$_2$	Me	C$_6$H$_4$	(D$_3$C)$_2$SO		7.25—8.1		2.4		5.1 (m) CH$_2$
(III)	[NBu$_4$][PdCl$_3$(ath)] [b]			CD$_3$OD	5.3				4.3	1.65—1.9 (m) [NBu$_4$]$^+$
(IV)	[PdCl$_2$(ath)$_2$]			(D$_3$C)$_2$SO	5.6				3.85—4.15	
(IV)	[PtCl$_2$(ath)$_2$]			(D$_3$C)$_2$SO	5.6				3.8—4.1	
(III)	[NBu$_4$][PdCl$_3$(atz)] [b]			CD$_3$OD	5.1				7.35	1.2—1.6 (m) [NBu$_4$]$^+$
(IV)	[PdCl$_2$(atz)$_2$]			(D$_3$C)$_2$SO	5.15				6.85—7.35	
(IV)	[PtCl$_2$(atz)$_2$]			(D$_3$C)$_2$SO	5.1				6.8—7.3	
(VI)	[PdCl$_2$(ith)$_2$] [b]			(D$_3$C)$_2$SO	4.55				3.1	1.0 (tr) SH
(VI)	[PdCl$_2$(itz)$_2$] [b]			(D$_3$C)$_2$SO	4.05				6.3	

s = Singlet, tr = triplet, q = quadruplet, and m = multiplet.

[a] Due to the *ortho*-protons of the R^2 phenyl ring (see text). [b] Free-ligand resonances: ath 5.15 (NH), 3.65—4.0 (CH); atz 5.0 (NH), 6.55—7.0 (CH); ith 4.4 (NH), 3.0 (CH); itz 3.9 (NH), 6.15 (CH).



M = Pd^{II} or Pt^{II}. * The same reactions occur when L = atz and the rearranged ligand is N≡C–NH–CHCHSH.

In the [PdCl$_2$(PhN=CMePh)$_2$] complex, the acetophenone phenyl rings probably have a preferential long-range interaction with the palladium atom, giving rise to a metastable conformation which may explain the observed metal σ bonding to the phenyl group. Thus, in the ^{1}H n.m.r. spectrum of this complex, some of the aromatic protons were considerably deshielded (see Table 2). This may be due to the proximity of the acetophenone phenyl *ortho*-protons to the chlorine atoms, which has recently been confirmed in the case of bis(azobenzene)dichloropalladium(II) by the *X*-ray crystal structure.[16] This latter complex is known to be quite unstable, and in fact it readily undergoes a cyclopalladation reaction.[17]

Intramolecular Ligand Rearrangements.—When the metal-bound amine has a thiazole or a thiazoline as a substituent, it does not undergo any condensation in the presence of a ketone group but an internal rearrangement occurs when in a basic medium [see reaction (3b)]. The reaction of 2-aminothiazoline (ath) and 2-aminothiazole (atz) with [PtCl$_4$]$^{2-}$ or [Pd$_2$Cl$_6$]$^{2-}$, in an acid medium at pH 4 [see reaction (3a)], produced the monosubstituted [NBu$_4$][PdCl$_3$L], (III), and the disubstituted [MCl$_2$L$_2$], (IV), complexes (L = ath or atz; M = Pt or Pd). The monosubstituted species could be isolated only with Pd, because of the presence of the stabilising bulky [NBu$_4$]$^+$.[18,19] I.r. and n.m.r. studies (see Table 1) show that, as expected, co-ordination has

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[19] P. Braunstein, J. Dehand, and M. Pfeffer, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 581.

occurred [20-24] only through the heterocyclic nitrogen, the amine being still protonated (pK_a 4.7).[25] Thus, the NH vibrations in the complexes were unaffected and remained at the same frequency as in the free ligands, while ν(C=N) was shifted to lower frequencies and was often split, because of the decrease in symmetry in the complexes. The general features of the i.r. and n.m.r. spectra, both in the free ligands and in their complexes, remained essentially the same, indicating no major structural changes.

When the reaction between the same initial compounds occurred in a basic medium [see (3b)], it afforded a monomeric $[PdCl_2L'_2]$, (VI), and a dimeric $[\{MCl_2L'\}_2]$ species, (V) (M = Pt or Pd; and L′ = rearranged ith or itz). I.r. and n.m.r. spectra now indicated a considerable change in the ligands on co-ordination. The appearance of a new, very intense, i.r. absorption in the range 2 200—2 100 cm^{-1}, for all the complexes of this form, strongly suggests the presence of a nitrile group. Moreover, we observed a medium band at *ca.* 2 950 cm^{-1} and a strong band at 1 255—1 260 cm^{-1}, which we attribute to an aliphatic ν(C–H) and to ν(C–N) vibrations respectively. The far-i.r. region showed one band, due to ν(M–Cl), in the case of the complexes (VI), two bands in the case of (V). These results are consistent with the *trans*-$[PdCl_2(L')_2]$ and *cis*-$[\{MCl_2L'\}_2]$ stereochemistries. The ^1H n.m.r. spectra also showed new resonance signals, *e.g.* at δ 1.00 p.p.m. which may be due to a thiol group. The CH_2 resonances were also considerably shielded in comparison with those in the free ligands, from δ 3.80 to 3.10 p.p.m. in the case of ath. This shielding may result from the disappearance of a cylic conformation.

We reported [8] that the α-primary amine first co-ordinates to the metal, thus lowering the electron density on C^2 and allowing the subsequent nucleophilic addition of the hydroxide anion and the C–S bond cleavage. The NH_2 protons are labilised on co-ordination of the nitrogen to the metal, and a water molecule may ultimately be eliminated. The heterocyclic ring of the ligands has thus undergone internal rearrangement to give L′ = ith = $HS{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C{\vdots}N$ from ath and L′ = itz = $HS{\cdot}CH{\vdots}CH{\cdot}NH{\cdot}C{\vdots}N$ from atz. The rearranged ligands could be removed only from the monomeric complexes (VI) [in the dimers (V), they appeared to be too strongly bound] by substitution with a stoicheiometric amount of triethylphosphine. We isolated ith and itz as liquids and, after distillation, the microanalytical, i.r., and n.m.r. results confirm the new conformations we propose above.

The role of the co-ordinated α-amine appears to be important since we observed no such rearrangement when the reaction was carried out in acid media (where the amine would not be bound to the metal), or when the ligands alone were dissolved in basic aqueous solution. In order to confirm the particular reactivity of such a metal-bound primary amine, we carried out the same reaction using the acetylated amine, in order to alter its accessibility to the metal. The acetylated ligands reacted very slowly in basic media with salts of Pt^{II} and Pd^{II} and gave complexes of the type $[MCl_2L_2]$, co-ordinated only through the cyclic nitrogen. Moreover, with analogous α-mercapto- or α-methyl-substituted ligands no cleavage reaction occurred.[26,27] The ring cleavage and the ligand rearrangement were thus confirmed to be induced by the previous co-ordination of the primary amine to Pd^{II} or Pt^{II}.

Conclusions.—We would like to emphasise two points from this study. (*i*) It was generally believed that strongly co-ordinated primary amines are rather unreactive.[28] Our results, on the contrary, confirm some recently reported studies concerning the further reactions which such amines may undergo.[29,30] We were, however, unable to verify that the condensation reactions are specific to the ligands bound to the palladium. We nevertheless proposed elsewhere [6] a reaction mechanism which takes such specificity into account, according to a hypothesis of other workers.[29] (*ii*) The newly isolated groups, whether imines, carbodi-imides, or cyanamides, were always obtained by water elimination, and were sufficiently stabilised by complexation to the metal that no further hydrolysis was observed.[29,30] It is to be noted that these groups are known to be readily hydrolysed in basic or hydroxy-solvents in the absence of a metal.

[6/089 *Received*, 14*th January*, 1976]

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