

Fluxionality and Bonding in Formamidine and Formamidinate Complexes of Pt^{II} and Pd^{II} containing the 2,6-Bis[(dimethylamino)methyl]phenyl Ligand: A Proton Nuclear Magnetic Resonance Study with X-Ray Crystal Structures of [Pt{C₆H₃(CH₂NMe₂)₂-2,6}{*p*-MeC₆H₄N=CHN(H)C₆H₄Me-*p*}] [CF₃SO₃]⁻ and [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(*p*-MeC₆H₄N=CHNC₆H₄Me-*p*)]⁺†

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The *N*¹,*N*²-di-*p*-tolylformamidine ligand [*p*-MeC₆H₄N=CHN(H)C₆H₄Me-*p*, Hdptf] reacts smoothly with the ionic species [M{C₆H₃(CH₂NMe₂)₂-2,6}(H₂O)]X (M = Pd or Pt, X = BF₄⁻ or CF₃SO₃⁻) to generate [M{C₆H₃(CH₂NMe₂)₂-2,6}(Hdptf)]X [M = Pd (**1**) or Pt (**2**)]. The ¹H n.m.r. data (250-MHz, CD₂Cl₂) for (**2**) (room temperature) and (**1**) (203 K) are consistent with a rigid monodentate bonding mode of neutral Hdptf; for the palladium species (**1**) Hdptf dissociation becomes an important process at higher temperatures. The structure of (**2b**) (M = Pt; X = CF₃SO₃⁻) was revealed by a single-crystal X-ray diffraction study. Crystals of this complex are triclinic, space group *P*1, with unit-cell dimensions *a* = 11.912(3), *b* = 14.372(6), *c* = 9.449(5) Å, α = 92.04(4), β = 95.28(3), γ = 72.40(3)°, and *Z* = 2. Structure solution and refinement by standard methods gave *R* = 0.046 for 5 421 independent reflections. Complex (**2b**) is the first structurally characterized organometallic species containing a neutral formamidine and it possesses a monodentate imine-*N*² bonding mode of neutral Hdptf to an approximately square planar Pt^{II} centre [Pt-N(3) = 2.16(1) Å]. The cationic species (**1**) and (**2**) react with NaOH to afford, in high yield, neutral [M{C₆H₃(CH₂NMe₂)₂-2,6}(dptf)] [M = Pd (**3**) or Pt (**4**); dptf = *p*-MeC₆H₄N=CHNC₆H₄Me-*p*] for which low-temperature ¹H n.m.r. studies indicate the uncommon σ-*N*¹ monodentate bonding mode of the formamidinate anion. However, at room temperature in CD₂Cl₂ both (**3**) and (**4**) are subject to an intramolecular fluxional process that would be consistent with the existence of a chelate bonded formamidinate intermediate. A single-crystal X-ray study of (**4**) has been carried out. Crystals of this complex are monoclinic, space group *P*2₁/*n*, with unit-cell dimensions *a* = 17.28(2), *b* = 15.148(6), *c* = 9.62(2) Å, β = 101.1(2)° and *Z* = 4. In a manner analogous to that used for (**2b**) the structure of (**4**) was solved to *R* = 0.024 for 4 211 independent reflections. The virtually flat *N*¹,*N*²-di-*p*-tolylformamidinate ion is σ-*N*¹ monodentate bonded [Pt-N(3) = 2.132(6) Å] and is orientated almost perpendicular to the co-ordination plane of this approximately square-planar Pt^{II} species.

Formal substitution of the carbon atoms in an allyl system by heteroatoms (*e.g.* N, O, or S) leads to a variety of important anionic ligands of which carboxylates, dithiocarbamates, formamidinates, and triazenides are probably the best known. For the RNYNR' (Y = CH or N) heteroallylic systems the pseudo-allyl η³ bonding mode (I) (Figure 1) is not known although both formamidinates (Y = CH) and triazenides (Y = N) do display a variety of other metal co-ordination modes. The situations most commonly met with formamidinate

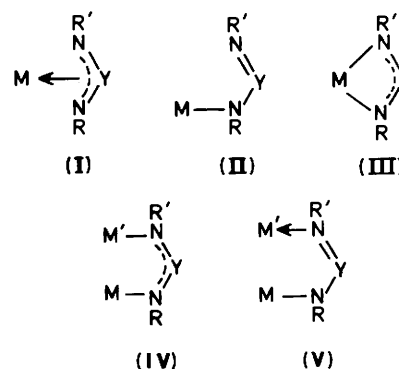


Figure 1. Possible co-ordination modes of the RNYNR' (Y = CH or N) anion

† {2,6-Bis[(dimethylamino)methyl]phenyl-*C,N,N'*}(*N*¹,*N*²-di-*p*-tolylformamidine-*N*²)platinum trifluoromethanesulphonate and {2,6-bis[(dimethylamino)methyl]phenyl-*C,N,N'*}(*N*¹,*N*²-di-*p*-tolylformamidinato-*N*¹)platinum.

Supplementary data available (No. SUP 56439, 11 pp.): thermal parameters, H-atom co-ordinates, least-squares planes data, stereoscopic view of (**2b**). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Throughout this paper formamidine and formamidinate are used as generic names for variously substituted formamidines and formamidinate anions.

are monodentate σ-*N*¹ (II),¹ bidentate (chelate) σ-*N,N'* (III),² and homobridging σ,σ-*N,N'* (IV)³ shown schematically in Figure 1; in osmium cluster chemistry other bridging forms have recently been identified.⁴

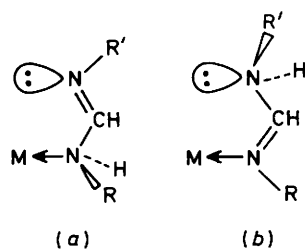


Figure 2. Possible monodentate co-ordination modes of N^1,N^2 -disubstituted formamidines; (a) via amine- N^1 , (b) via imine- N^2

As a consequence of the RNYNR' geometry the M-N bonds formed in dinuclear complexes are often positioned mutually parallel and accordingly the metal atoms are then close enough for the eventual production of metal-metal interaction. The anions of N,N' -diarylacetylformamidines [$R'NHC(Me)NR'$] and N,N' -diarylbenzamidines [$R'NHC(Ph)NR'$], for example, appear to function particularly well as bridging units for homonuclear metal-metal multiple bonds.⁵ Recent examples of heterodinuclear bridged systems of type (V) (Figure 1), using both formamide and triazene anions have come principally from our own laboratory, e.g. Ir-M (M = Ag,^{6a,c,d} Cu,^{6b,d,h} or Hg^{6f}), Rh-M (M = Ag,^{6a} Cu,^{6b,g} or Hg^{6e,f}), Pt-Ag,⁷ and Pt-Hg.⁸ Although mononuclear formamidinate^{1,9a} and formamide^{9b,c} complexes (which may be seen as precursors to bimetallic species) may show fluxional behaviour there is little known concerning either (i) the co-ordination behaviour of the neutral formamidines [$RN=CHN(H)R'$],^{9b-e} which have two possible monodentate bonding modes (Figure 2), or (ii) the inter-relationship between species containing anionic formamidinate and neutral formamide.

We now report the syntheses and characterization of the new N^1,N^2 -di-*p*-tolylformamidinate complexes [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(Hdptf)X$] [$Hdptf = p-MeC_6H_4N=CHN(H)C_6H_4-Me-p$, M = Pd (1) or Pt (2), X = BF_4^- or $CF_3SO_3^-$] and their conversion to the formamidinate derivatives [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(dptf)X$] [$dptf = p-MeC_6H_4N=CHNC_6H_4-Me-p$, M = Pd (3) or Pt (4)]. Members of both series show fluxional behaviour in solution and the bonding mode(s) present are discussed in the light of variable-temperature ¹H n.m.r. data and the results of X-ray structure determination studies of the representative Pt^{II} species (2b) (X = $CF_3SO_3^-$) and (4).

Experimental

All reactions were carried out using previously distilled solvents. ¹H n.m.r. data were obtained on Bruker WM250 and Varian T-60 spectrometers. The complexes [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(H_2O)[BF_4]$] (M = Pd or Pt) were prepared as previously described.¹⁰ The neutral species [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(CF_3SO_3)$] (M = Pd or Pt) are formed in a similar manner from [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}Br$]¹⁰ and AgO_3SCF_3 in dry benzene.¹¹ N^1,N^2 -Di-*p*-tolylformamidine (Hdptf) was obtained according to published methods.¹² Microanalyses were performed by the Institute for Applied Chemistry TNO, Zeist, The Netherlands.

Preparation of the N^1,N^2 -Di-*p*-tolylformamidinate Complexes.—(a) [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(Hdptf)[BF_4]$] [M = Pd (1a) or Pt (2a)]. To a solution of [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(H_2O)[BF_4]$] (0.5 mmol) in acetone (5 cm³) was added solid Hdptf (123 mg, 0.55 mmol) and after 5 min the solvent removed *in vacuo*. The solid residue was washed with pentane (5 cm³) leaving a white (Pt) or cream (Pd) solid which was recrystallized from acetone-diethyl ether to produce the pure

product in typically 85–95% yield [Found (1a): C, 53.2; H, 5.8; F, 12.1; N, 9.05. $C_{27}H_{35}BF_4N_4Pd$ requires C, 53.3; H, 5.8; F, 12.5; N, 9.2%. Found (2a): C, 46.4; H, 5.1; F, 10.4; N, 7.9. $C_{27}H_{35}BF_4N_4Pt$ requires C, 46.5; H, 5.1; F, 10.9; N, 8.0%].

(b) [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(Hdptf)[CF_3SO_3]$] [M = Pd (1b) or Pt (2b)]. These complexes were prepared in a manner analogous to that described above for (1a) and (2a) by reacting [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(CF_3SO_3)$] with Hdptf in acetone [Found (1b): C, 50.0; H, 5.2; N, 8.5. $C_{28}H_{35}F_3O_3PdS$ requires C, 50.1; H, 5.3; N, 8.35%. Found (2b): C, 44.2; H, 4.65; N, 7.5. $C_{28}H_{35}F_3N_4O_3PtS$ requires C, 44.3; H, 4.6; N, 7.4%].

Preparation of the N^1,N^2 -Di-*p*-tolylformamidinate Complexes [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(dptf)X$] [M = Pd (3) or Pt (4)].—A solution of [$M\{C_6H_3(CH_2NMe_2)_2-2,6\}(Hdptf)[BF_4]$] (0.2 mmol) in 5 cm³ of an acetone-water (95:5) mixture was stirred for 15 min with an excess of NaOH (15 mg, 0.4 mmol). After this time the solvent was removed *in vacuo* from the resulting mixture containing a pale yellow precipitate. The product was obtained by extraction with benzene (10 cm³), concentration of the filtrate, addition of pentane, and cooling to -20 °C. Yields of the yellow microcrystalline solids are 80–90% [Found (3): C, 62.0; H, 6.6; N, 10.5. $C_{27}H_{34}N_4Pd$ requires C, 62.4; H, 6.6; N, 10.75%. Found (4): C, 53.1; H, 5.6; N, 9.2. $C_{27}H_{34}N_4Pt$ requires C, 53.2; H, 5.6; N, 9.2%].

X-Ray Analysis.—**Crystal data for (2b).** $C_{28}H_{35}F_3N_4O_3PtS$, $M = 759.8$, triclinic, space group $P1$ (no. 2), $a = 11.912(3)$, $b = 14.372(6)$, $c = 9.449(5)$ Å, $\alpha = 92.04(4)$, $\beta = 95.28(3)$, $\gamma = 72.40(3)^\circ$, $U = 1535.4$ Å³, D_m not measured, $Z = 2$, $D_c = 1.649$ g cm⁻³, $F(000) = 720$, Mo- K_α X-radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu(Mo-K_\alpha) = 47.3$ cm⁻¹.

Crystal data for (4). $C_{27}H_{34}N_4Pt$, $M = 609.7$, monoclinic, space group $P2_1/n$ (no. 14), $a = 17.28(2)$, $b = 15.148(6)$, $c = 9.62(2)$ Å, $\beta = 101.1(2)^\circ$, $U = 2471.0$ Å³, D_m not measured, $Z = 4$, $D_c = 1.649$ g cm⁻³, $F(000) = 1208$, Mo- K_α X-radiation (graphite monochromator) $\lambda = 0.71069$ Å, $\mu(Mo-K_\alpha) = 57.6$ cm⁻¹.

Intensity data collection. Crystals of [$Pt\{C_6H_3(CH_2NMe_2)_2-2,6\}(Hdptf)[CF_3SO_3]$] (2b) grow as colourless needles from methylene chloride-diethyl ether and [$Pt\{C_6H_3(CH_2NMe_2)_2-2,6\}(dptf)$] (4) crystallizes less easily as yellow blocks on slow evaporation of a benzene-toluene solution. Suitable crystals of (2b) (0.33 × 0.21 × 0.11 mm) and of (4) (ca. 0.2 × 0.15 × 0.15 mm; accurate dimensions not available) were mounted on an Enraf-Nonius CAD-4 automated diffractometer. 8865 independent intensities in the range $1.1 < \theta < 30^\circ$ were collected for compound (2b) and 5578 in the range $2 < \theta < 27^\circ$ for (4). During the data collection there was no observed decay in intensity of a standard reflection checked every 10 000 (2b) and 5000 s (4) of measurement time. For (2b) and (4) respectively 5421 and 4211 significant independent reflections with $I \geq 3\sigma(I)$ were derived from the data sets and used for subsequent solution and refinement of the structures.

Structure solutions and refinements. The structures of both (2b) and (4) were solved by standard Patterson and Fourier techniques and the heavy atoms refined by means of block-diagonal least-squares calculations. An empirical absorption correction was applied.¹³ The H atoms were found from a ΔF synthesis and introduced in the refinement with isotropic thermal parameters. The anomalous scattering of Pt was taken into account and the weighting schemes $w = 1/(3.1 + F_o + 0.038F_o^2)$ and $w = 1/(1.2 + F_o + 0.02F_o^2)$ were applied for (2b) and (4), respectively. The final R value for (2b) was 0.046 and for (4) was 0.024. Fractional atomic co-ordinates for the non-hydrogen atoms of (2b) are given in Table 1, and selected bond distances and angles in Table 2. The corresponding data for (4) are to be found in Tables 3 and 4, respectively.

Table 1. Non-hydrogen atomic co-ordinates for (2b) with estimated standard deviations in parentheses

Atom	x	y	z
Pt	0.204 07(8)	0.128 28(3)	0.189 65(4)
C(1)	0.244 1(9)	0.032 0(9)	0.043 4(13)
C(2)	0.236 9(11)	-0.062 3(9)	0.066 8(16)
C(3)	0.261 3(13)	-0.132 5(10)	-0.038 4(19)
C(4)	0.291 7(13)	-0.108 9(10)	-0.163 6(19)
C(5)	0.300 5(12)	-0.014 4(13)	-0.190 8(14)
C(6)	0.278 5(10)	0.057 2(9)	-0.084 2(13)
C(7)	0.206 1(13)	-0.075 6(10)	0.215 3(19)
C(8)	0.268 2(11)	0.165 1(11)	-0.090 3(12)
C(9)	0.010 7(11)	0.045 4(12)	0.225 4(18)
C(10)	0.150 8(16)	0.015 3(13)	0.433 9(17)
C(11)	0.411 9(9)	0.173 3(10)	0.108 5(15)
C(12)	0.236 2(12)	0.308 3(9)	0.065 4(14)
C(13)	0.040 7(9)	0.290 9(9)	0.361 1(10)
C(14)	0.238 0(9)	0.256 9(9)	0.459 5(11)
C(15)	0.344 1(10)	0.182 9(9)	0.490 5(13)
C(16)	0.428 1(10)	0.199 0(10)	0.592 3(13)
C(17)	0.414 7(10)	0.288 1(10)	0.659 5(11)
C(18)	0.308 1(11)	0.361 0(9)	0.626 8(12)
C(19)	0.220 8(9)	0.347 3(9)	0.526 7(13)
C(20)	0.508 7(12)	0.305 6(12)	0.767 8(16)
C(21)	-0.165 8(8)	0.331 0(7)	0.270 0(9)
C(22)	-0.212 1(11)	0.318 3(10)	0.396 4(11)
C(23)	-0.332 0(10)	0.353 3(10)	0.408 7(12)
C(24)	-0.410 8(9)	0.396 2(9)	0.295 2(14)
C(25)	-0.362 2(10)	0.403 0(10)	0.167 4(13)
C(26)	-0.242 5(9)	0.371 9(9)	0.155 6(13)
C(27)	-0.544 1(11)	0.430 5(12)	0.305 7(19)
C(28)	-0.064 6(14)	0.417 3(10)	0.782 2(13)
N(1)	0.139 1(9)	0.023 7(8)	0.274 0(11)
N(2)	0.284 3(7)	0.199 9(7)	0.060 7(9)
N(3)	0.151 7(7)	0.239 9(7)	0.350 7(8)
N(4)	-0.042 4(7)	0.292 7(7)	0.252 9(9)
F(1)	0.043 8(11)	0.421 0(9)	0.797 2(13)
F(2)	-0.124 4(13)	0.476 7(7)	0.876 5(15)
F(3)	-0.106 4(13)	0.454 7(9)	0.655 2(13)
S	-0.076 1(2)	0.295 8(2)	0.797 5(3)
O(1)	-0.006 6(10)	0.243 7(7)	0.687 5(9)
O(2)	-0.027 7(7)	0.288 3(7)	0.938 4(8)
O(3)	-0.200 1(8)	0.309 4(8)	0.773 1(11)

Results

Syntheses.—The neutral diaryl-substituted formamidine Hdptf substitutes the rather weakly held water molecule from the cation of the previously described $[M\{C_6H_3(CH_2NMe_2)_2-2,6\}(H_2O)][BF_4]$ ($M = Pd$ or Pt)¹⁰ species to afford the new ionic formamidine complexes $[M\{C_6H_3(CH_2NMe_2)_2-2,6\}(Hdptf)][BF_4]$ [$M = Pd$ (**1a**) or Pt (**2a**)]. Similarly $[M\{C_6H_3(CH_2NMe_2)_2-2,6\}(Hdptf)][CF_3SO_3]$ [$M = Pd$ (**1b**) or Pt (**2b**)] have been prepared from $[M\{C_6H_3(CH_2NMe_2)_2-2,6\}(CF_3SO_3)]$, which is known to generate the same $[M\{C_6H_3(CH_2NMe_2)_2-2,6\}(H_2O)]^+$ cations in aqueous media.¹¹ The Pd^{II} and Pt^{II} Hdptf complexes are air-stable solids which, consistent with an ionic formulation, have a limited solubility in diethyl ether and hexane but are readily soluble in polar solvents such as acetone and $CHCl_3$. Both of the Pd and Pt complexes are susceptible to attack by a strong base ($NaOH$) which removes a (acidic) proton from the co-ordinated Hdptf to produce the neutral metal-formamidinate species $[M\{C_6H_3(CH_2NMe_2)_2-2,6\}(dptf)]$ [$M = Pd$ (**3**) or Pt (**4**)]. The latter complexes have a distinct yellow colour, are air-stable, and have significant solubility in most organic solvents. These synthetic results are summarised in the Scheme.

The stoichiometry and characterization of the new complexes (1)—(4) have been accomplished using elemental analysis

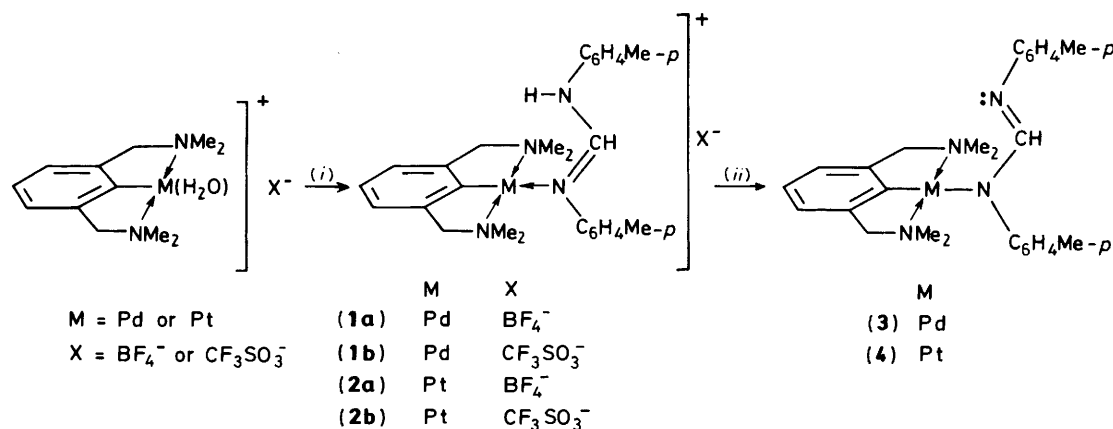
Table 2. Selected interatomic distances (Å) and angles (°) for $[Pt\{C_6H_3(CH_2NMe_2)_2-2,6\}(Hdptf)][CF_3SO_3]$ (**2b**)

Pt-N(1)	2.10(1)	N(2)-C(12)	1.49(2)
Pt-N(2)	2.09(1)	N(3)-C(13)	1.31(1)
Pt-N(3)	2.16(1)	N(3)-C(14)	1.45(1)
Pt-C(1)	1.91(1)	N(4)-C(13)	1.35(1)
N(1)-C(7)	1.52(2)	N(4)-C(21)	1.43(1)
N(1)-C(9)	1.50(2)	C(1)-C(2)	1.41(2)
N(1)-C(10)	1.51(2)	C(1)-C(6)	1.40(2)
N(2)-C(8)	1.51(1)	C(2)-C(7)	1.52(2)
N(2)-C(11)	1.48(1)	C(6)-C(8)	1.52(2)
N(1)-Pt-N(2)	163.0(4)	Pt-N(1)-C(9)	108.9(9)
N(1)-Pt-N(3)	97.8(4)	Pt-N(1)-C(10)	116.7(10)
N(1)-Pt-C(1)	82.1(5)	Pt-N(2)-C(8)	107.9(8)
N(2)-Pt-N(3)	99.2(4)	Pt-N(2)-C(11)	108.3(7)
N(2)-Pt-C(1)	80.9(5)	Pt-N(2)-C(12)	114.1(7)
N(2)-C(8)-C(6)	107.2(10)	Pt-N(3)-C(13)	122.2(7)
N(3)-Pt-C(1)	177.7(4)	Pt-N(3)-C(14)	120.8(6)
N(3)-C(13)-N(4)	120.8(9)	Pt-C(1)-C(2)	118.7(10)
Pt-N(1)-C(7)	107.7(9)	Pt-C(1)-C(6)	119.2(10)
C(1)-C(2)-C(7)	113.3(12)	C(7)-N(1)-C(9)	108.9(11)
C(1)-C(6)-C(8)	112.5(10)	C(7)-N(1)-C(10)	107.0(11)
C(2)-C(1)-C(6)	122.0(12)	C(9)-N(1)-C(10)	107.4(12)
C(2)-C(7)-N(1)	108.7(11)	C(8)-N(2)-C(11)	109.8(9)
C(3)-C(2)-C(7)	126.5(13)	C(8)-N(2)-C(12)	109.0(9)
C(5)-C(6)-C(8)	130.0(12)	C(11)-N(2)-C(12)	107.7(10)
		C(13)-N(3)-C(14)	116.8(8)
		C(13)-N(4)-C(21)	122.1(8)

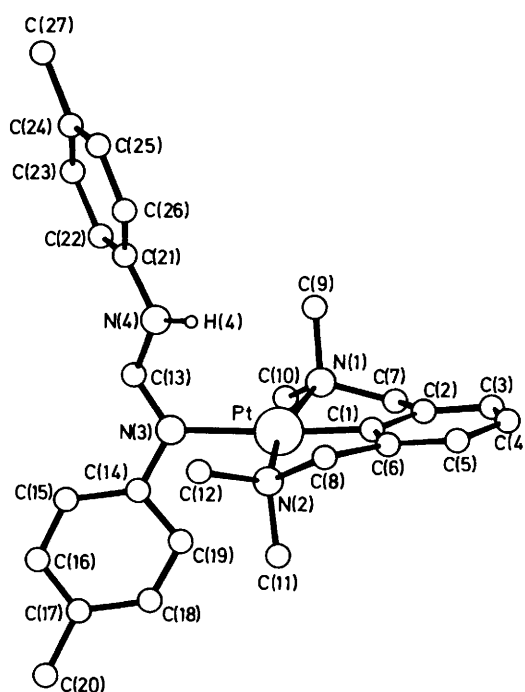
Table 3. Non-hydrogen atomic co-ordinates for (4) with estimated standard deviations in parentheses

Atom	x	y	z
Pt	0.146 50(1)	0.006 85(1)	0.291 90(2)
N(1)	0.125 8(2)	0.131 0(3)	0.374 0(5)
N(2)	0.131 2(2)	-0.116 7(3)	0.195 1(4)
N(3)	0.272 2(3)	0.008 6(3)	0.331 3(5)
N(4)	0.269 6(3)	0.081 4(3)	0.119 5(4)
C(1)	0.033 7(3)	0.002 2(3)	0.257 5(5)
C(2)	-0.007 3(3)	0.064 8(4)	0.320 4(5)
C(3)	-0.089 7(3)	0.060 8(4)	0.297 2(5)
C(4)	-0.129 4(4)	-0.005 3(4)	0.210 4(6)
C(5)	-0.087 6(3)	-0.067 7(4)	0.144 3(5)
C(6)	-0.006 2(3)	-0.063 5(3)	0.170 0(5)
C(7)	0.046 7(3)	0.127 3(4)	0.417 7(5)
C(8)	0.048 7(3)	-0.118 3(3)	0.102 8(5)
C(9)	0.122 7(4)	0.195 3(4)	0.256 3(6)
C(10)	0.186 9(3)	0.159 8(4)	0.495 6(6)
C(11)	0.136 5(4)	-0.185 1(4)	0.307 4(7)
C(12)	0.190 5(4)	-0.135 3(4)	0.105 6(6)
C(13)	0.309 0(3)	0.044 0(4)	0.233 4(5)
C(14)	0.318 3(3)	-0.036 7(4)	0.446 6(5)
C(15)	0.395 2(3)	-0.065 5(5)	0.455 5(6)
C(16)	0.435 3(4)	-0.112 1(5)	0.573 2(7)
C(17)	0.399 5(3)	-0.131 5(4)	0.685 5(6)
C(18)	0.322 5(3)	-0.103 8(4)	0.676 9(5)
C(19)	0.283 1(3)	-0.057 9(4)	0.560 5(5)
C(20)	0.443 2(4)	-0.183 1(5)	0.811 1(6)
C(21)	0.310 9(3)	0.103 2(3)	0.013 6(5)
C(22)	0.285 3(3)	0.175 4(3)	-0.073 4(5)
C(23)	0.322 0(3)	0.198 8(4)	-0.183 2(5)
C(24)	0.385 0(3)	0.151 0(4)	-0.212 6(5)
C(25)	0.410 4(4)	0.076 9(4)	-0.128 7(6)
C(26)	0.373 4(3)	0.053 8(4)	-0.018 3(6)
C(27)	0.423 1(4)	0.174 3(5)	-0.337 7(7)

(see Experimental section) and variable-temperature ¹H n.m.r. (Table 5) together with single-crystal structure determinations on representative members of both the formamidine and formamidinate types [(2b) and (4)], respectively, (see later).

Scheme. (i) Hdptf, acetone; (ii) NaOH, acetone-H₂O**Table 4.** Selected distances (Å) and angles (°) for [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(dptf)]

Pt-N(1)	2.097(5)	N(3)-C(13)	1.345(8)
Pt-N(2)	2.084(5)	N(3)-C(14)	1.412(7)
Pt-N(3)	2.132(6)	N(4)-C(13)	1.303(7)
Pt-C(1)	1.914(6)	N(4)-C(21)	1.392(8)
N(1)-C(7)	1.507(7)	C(1)-C(2)	1.390(8)
N(1)-C(9)	1.487(8)	C(1)-C(6)	1.397(7)
N(1)-C(10)	1.482(7)		
N(2)-C(8)	1.527(6)	C(2)-C(7)	1.519(8)
N(2)-C(11)	1.487(8)	C(6)-C(8)	1.498(8)
N(2)-C(12)	1.487(8)		
N(1)-Pt-N(2)	163.2(1)	C(8)-N(2)-C(11)	109.3(4)
N(1)-Pt-N(3)	99.4(2)	C(8)-N(2)-C(12)	109.3(4)
N(1)-Pt-C(1)	81.7(2)	C(9)-N(1)-C(10)	108.9(4)
N(1)-C(7)-C(2)	109.5(4)	C(11)-N(2)-C(12)	109.6(4)
N(2)-Pt-N(3)	97.3(2)	C(13)-N(3)-C(14)	118.2(5)
N(2)-Pt-C(1)	81.5(2)	C(13)-N(4)-C(21)	117.4(5)
N(2)-C(8)-C(6)	109.8(4)	Pt-N(1)-C(7)	107.6(3)
N(3)-Pt-C(1)	178.6(2)	Pt-N(1)-C(9)	106.5(4)
N(3)-C(13)-N(4)	121.4(5)	Pt-N(1)-C(10)	114.5(3)
C(1)-C(6)-C(8)	112.0(4)	Pt-N(2)-C(8)	107.3(3)
C(1)-C(2)-C(7)	112.9(4)	Pt-N(2)-C(11)	108.4(3)
C(2)-C(1)-C(6)	121.0(5)	Pt-N(2)-C(12)	112.7(3)
C(3)-C(2)-C(7)	127.6(5)	Pt-N(3)-C(13)	118.9(3)
C(5)-C(6)-C(8)	127.2(4)	Pt-N(3)-C(14)	122.3(4)
C(7)-N(1)-C(9)	109.6(4)	Pt-C(1)-C(2)	119.1(4)
C(7)-N(1)-C(10)	109.7(4)	Pt-C(1)-C(6)	119.9(4)

**Figure 3.** PLUTO drawing of the cation of [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(Hdptf)][CF₃SO₃] (2b) with all hydrogen atoms except H(4) omitted for clarity

Description of the Structures.—The crystal structure of [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(Hdptf)][CF₃SO₃] (2b) comprises two cation-anion pairs per unit cell. Figure 3 shows the molecular structure of the [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(Hdptf)]⁺ cation along with the adopted numbering scheme. The CF₃SO₃⁻ anion shows no unusual features and is well separated from the cation (see Figure, supplementary publication No. SUP 56439), the closest approach being O(1)-H(22) = 2.51(12) Å. The four-co-ordinate Pt^{II} centre exhibits a slightly distorted square-planar co-ordination geometry. It is bonded to the terdentate C₆H₃(CH₂NMe₂)₂-2,6 ligand by C(1) of the aryl nucleus and by N(1) and N(2), the two mutually *trans*-positioned donor atoms. The fourth co-ordination site *trans* to C(1) is occupied by a single N atom of the Hdptf ligand [Pt-N(3) = 2.16(1) Å]. The largest distortion from square-planar geometry is the N(1)-Pt-N(2) angle of 163.0(4)° which is a consequence of the two N-Pt-C(1) angles of *ca.* 81.5° resulting

from the restraints of the five-membered PtNCCC(1) chelate rings. The particular configuration of these rings and the two-fold axis puckering that they exhibit is a common feature of metal complexes containing C₆H₃(CH₂NMe₂)₂-2,6.¹⁴ The Pt-C(1), Pt-N(1), and Pt-N(2) distances [1.91(1), 2.10(1), and 2.09(1) Å respectively] are as to be expected for Pt^{II} with this chelating ligand. The most important structural feature of this complex is the adopted geometry of the Hdptf ligand and its bonding *via* the imino N(3) atom to the metal centre [Pt-N(3) = 2.16(1) Å]. Examination of the N(3)-C(13) and N(4)-C(13) distances of the formamidine skeleton [1.31(1) and 1.35(1) Å respectively] indicates that the former has somewhat greater multiple bond character. Both distances lie between the values expected for isolated C=N bonds (1.24 Å) and C-N bonds (1.48 Å) with C_{sp²}-N_{sp²} and C_{sp²}-N_{sp³} hybridization, respectively (see Discussion section). On this basis N(3) is an imino-nitrogen and N(4) the amino site. The sums of the

Table 5. ^1H n.m.r. data for Hdptf and complexes (1)–(4); a L = $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2$ -2,6, n.o. = not observed, n.r. = not resolved

Complex	T/K	S.f. ^b	L				Hdptf/dptf			
			C_6H_3 [³ J(HH)]	CH_2 [³ J(PtH)]	NMe_2 [³ J(PtH)]	CH, NH [³ J(PtH)]	C_6H_4 [³ J(HH)]	$\text{C}_6\text{H}_4'$ [³ J(HH)]	CH_3	CH_3'
(1) [PdL(Hdptf)] ⁺	303	250	6.85(d), 7.05(t) [7.4]	4.1(br)	2.72(br)	8.31, 10.06(br)	7.2(m)	7.4(br)	2.36	
	233	250	6.84(d), 7.02(t) [7.5]	3.93, 4.23 <i>c</i>	2.48, 2.73	8.28, 10.16(d) <i>d</i>	7.55, 7.24 [8.0]	7.24, 7.16 [8.3]	2.33	2.29
(2) [PtL(Hdptf)] ⁺	298	250	6.94(d), 7.08(t) [7.4]	4.12, 4.35 [48, 52]	2.76, 2.99 [33, 37]	8.80, 9.89 [42] ^d	7.69, 7.29 [8.0]	7.28, 7.23 [8.5]	2.35	2.39
	(3) [PdL(dptf)] ^e	310	60	6.85(m)	4.0	2.8	8.6, —	7.0–7.2(m)	2.3	
298		250	6.83(d), 6.98(t) [7.3]	4.03	2.78	8.85, —	7.17, 7.01(d) [8.1]	2.27		
(4) [PtL(dptf)] ^e	193	250	ca. 6.8(d), 7.0(t) [ca. 7]	3.95, 4.04 <i>c</i>	2.57, 2.74	8.3, — [45]	7.49, 7.0 [7]	7.0, 7.68 [7]	2.22	
	(4) [PtL(dptf)] ^e	310	60	6.85(m)	4.05	2.95	8.9, — [45]	7.0–7.2 [n.o.]	2.3	
(4) [PtL(dptf)] ^e		298	250	6.89(d), 7.03(t) [7]	4.08 [48]	2.93(br) [n.r.]	8.87, — [45]	7.0–7.5(m)	2.29	
	(4) [PtL(dptf)] ^e	193	250	6.8(d), 7.0(t) [ca. 7]	3.99, 4.08 <i>c</i>	2.69, 2.89 [n.o.]	8.64, — [n.o.]	7.54, 7.0	7.0, 6.8	2.21
Hdptf		183	250				8.28; 11.78 ^f	7.0(m)	6.89(m)	2.29

^a In CD_2Cl_2 unless otherwise stated. ^b Spectrometer frequency (^1H) in MHz. ^c $^2J(\text{HH})$ 14 Hz. ^d $^3J(\text{CHNH})$ 12 Hz. ^e In CDCl_3 . ^f Observed at 180 K.

interbond angles around N(3) [$359.8(7)^\circ$] and N(4) [$360(7)^\circ$] are consistent with the former having sp^2 hybridization and the latter being an aryl-substituted amine.¹⁵ This conclusion is confirmed by the location of H(4) on the N(4) atom. This imino bonding of the formamidate moiety, using a lone pair of N(3) to interact with the positively charged metal centre, is that shown in the Scheme and Figure 2(b). The atoms of the PtN(3)C(13)N(4) fragment, which has a 'cisoid' arrangement, lie in a plane that makes an angle of 80.4° to the platinum co-ordination plane. The *p*-tolyl substituents of N(3) and of N(4) are twisted out of the N(3)C(13)N(4) plane (35.3 and 41.0° respectively) in such a way that their interplane angle is 74.3° . One final point concerning the Hdptf co-ordination is that not only is the amine proton found situated above the metal [Pt...H(4) 2.85(3) Å] but one of the *ortho* protons of the N(3) *p*-tolyl group also makes a close approach to the metal from below the co-ordination plane [Pt...H(19) 2.92(3) Å].

The crystal structure of [Pt{ $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2$ -2,6}(dptf)] (4) comprises four molecules per unit cell separated by normal van der Waals distances. The molecular structure along with the adopted numbering scheme is shown in a PLUTO drawing (Figure 4). Each molecule comprises an approximately square-planar Pt^{II} centre with three of the co-ordination sites being occupied by the terdentate $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2$ -2,6 ligand. The geometry of this portion of the molecule as well as of the puckering of the chelate C(1)CCNPt rings is similar to that found for (2b). The fourth co-ordination site is filled by the anionic dptf ligand which is co-ordinated in a monodentate manner *via* N(3) to the metal centre [Pt–N(3) = 2.132(6) Å]. This σ -N¹ bonding of formamidate is that shown in the Scheme and (II) (Figure 1). The observed N(3)–C(13) and N(4)–C(13) bond lengths [1.345(8) and 1.303(7) Å respectively] as well as the hybridization of N(3), C(13), and N(4) are all consistent with this bonding description. These three atoms define a plane that is almost perpendicular (86.3°) to the metal co-ordination plane. Furthermore, although the two *p*-tolyl groupings are twisted to a noticeable extent out of this plane [N(3)-*p*-tolyl 16.7° and N(4)-*p*-tolyl 38.2° , with an interplanar angle of 25.1° between them] the whole dptf ligand may be conveniently described as being close to planar. As was the case in (2b), a single *ortho* proton on the N(3) *p*-tolyl group lies close to the Pt^{II} centre [Pt...H(19) 2.87(5) Å].

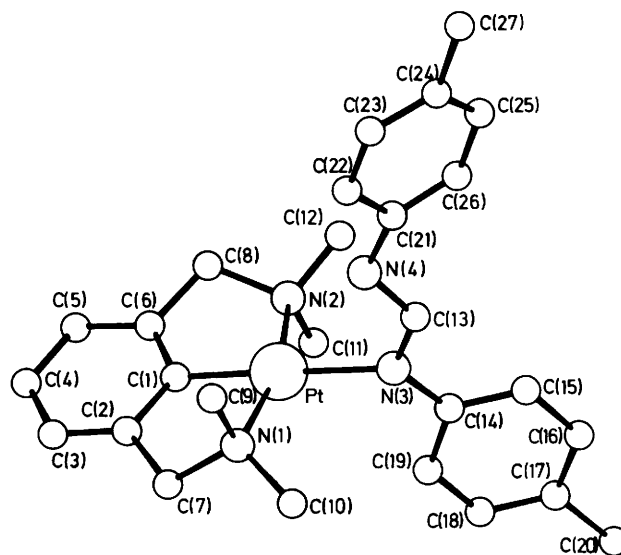


Figure 4. PLUTO drawing of [Pt{ $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2$ -2,6}(dptf)] (4) with hydrogen atoms omitted for clarity

Geometrical Comparison of Hdptf and dptf in (2b) and (4).— Apart from the unco-ordinated CF_3SO_3^- anion in (2b) which is a basic distinguishing feature, it is perhaps surprising to find that (2b) and (4) representing Pt^{II} bonding to two different ligand types should present co-ordination spheres which are virtually identical. The bonding of the terdentate ligand as reflected in the C(1)–Pt and N–Pt separations is not sensitive to the change from neutral Hdptf to anionic dptf and even the Pt–N σ bond of (4) is only slightly shorter [2.132(6) Å] than the donative Pt–N in (2b) [2.16(1) Å]. Within the N(3)–C(13)–N(4) skeleton, where the different positioning of the single and double bonds would be one of the better indications of the bonding type present, the situation is similar. Although in both complexes the C(13)=N and C(13)–N bonds are consistently identifiable [1.31(1) vs. 1.35(1) Å in (2b) and 1.303(7) vs. 1.345(8) Å in (4)] it is apparent not only that the differentiation of these bonds as

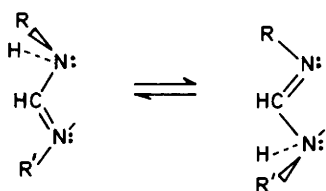


Figure 5. Formamidine tautomerism

expressed by the bond lengths is not great but also that the type of Pt–N interaction present is having little overall effect on the N=C(H)–N unit. As was noted above, isolated double and single bonds of this type should be *ca.* 1.24 and 1.48 Å respectively^{15,16} and it is clear that the discrepancy between expectation and fact in both (2b) and (4) can best be explained by the existence of substantial electron delocalization.*

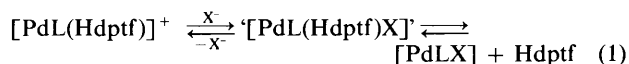
¹H N.M.R. Data.—The most relevant ¹H n.m.r. data for the complexes (1)–(4), and the Hdptf ligand are summarized in Table 5 and their interpretation together with a more detailed description of those systems exhibiting temperature dependence is set out below.

(a) Free N¹,N²-di-*p*-tolylformamidine, Hdptf. At room temperature Hdptf (in CD₂Cl₂ or CDCl₃) shows a single resonance for the unique imine CH proton (δ 8.3) and only one type of *p*-tolyl grouping. The NH signal is not apparent but on cooling to 240 K (CD₂Cl₂) a very broad peak becomes visible and at 180 K it is well defined at δ 11.78 (linewidth *ca.* 15 Hz). At this latter temperature (which is close to the limiting structure for Hdptf) viscosity effects produced significant line broadening and it was not possible to observe either the coupling ³J(HH) between the imine CH and the amine NH or separate signals from the two anticipated inequivalent *p*-tolyl units. These observations are fully consistent with Hdptf in solution being subject to inter- or intra-molecular exchange of the amine hydrogen atom; a process that is fast on the n.m.r. time-scale at ambient temperature and which, as shown schematically in Figure 5, results in the amine and imine N atoms (and hence the two *p*-tolyl groups) losing their separate identities. This tautomerism is a characteristic property of amidines¹⁷ and the various results¹⁸ including recent ¹H n.m.r. studies^{18b} suggest that an intramolecular mechanism involving bimolecular intermediates is operative.

(b) Hdptf complexes (1) and (2). The ¹H n.m.r. spectra of (2) (X = BF₄[−] or CF₃SO₃[−]) at room temperature (r.t.) in [²H₆]acetone or CD₂Cl₂ show signal multiplicities that reflect a molecular geometry corresponding closely to the solid-state structure (Figure 3).† Since the Hdptf is N²-bonded and orientated virtually perpendicular to the co-ordination plane containing the terdentate C₆H₃(CH₂NMe₂)₂-2,6 system then within this latter ligand the Me groups of each NMe₂ unit and the two protons of the CH₂ units become diastereotopic. The corresponding signals exhibit platinum satellites, ³J(PtH), evidencing the inert Pt–N interaction of this ligand on the n.m.r. time-scale. A monodentate bonding mode of Hdptf may also be

independently inferred from the observation of two inequivalent *p*-tolyl systems with two Me signals and two AB patterns in the aromatic region. The signals from the amino NH and imino CH protons are well separated (δ 9.89 and 8.80 respectively), with the latter showing distinct strong coupling to platinum [³J(PtH) = 42 Hz] consistent with bonding of the imino N to the metal centre. Unlike the free ligand, co-ordinated Hdptf does not undergo fast NH proton exchange as evidenced by the well resolved ³J(NHCH) of 12 Hz. This value taken together with the strongly deshielded NH resonance suggests that in solution the conformation of this ligand is similar to that found in the solid state with H(4) in the vicinity of the metal centre. The ¹H n.m.r. data also show one of the four aromatic resonances of the *p*-tolyl groups to be significantly to low field of the others. Bearing in mind that rotation of such aromatic groups about the N(3)–C(14) and N(4)–C(21) axes is fairly easy it may be concluded that this resonance (δ 7.69) is attributable to the two *ortho* protons of the N(3) bound *p*-tolyl group [*i.e.* H(15) and H(19)]. These protons, in their turn, are brought into the sphere of metal influence and like the amino proton experience the magnetic anisotropy of the metal co-ordination plane.⁷ It should be noted that for steric reasons rotation of the co-ordinated diarylformamidine about the Pt–N(3) axis is not likely and no evidence for this process has been obtained. N.m.r. evidence also indicates blocked rotation of the *o*-tolyl group around the Pt–C(*ipso*) axis in the complex [Pt{C₆H₃(CH₂NMe₂)₂-2,6}{C₆H₄Me-2}].¹¹

In the 250-MHz ¹H n.m.r. spectra of the palladium complex (1) below 220 K ([²H₆]acetone or CD₂Cl₂) the chemical shift data compare so closely with those from the platinum analogue (2), described above, that there is little doubt that under the stated conditions the bonding situation in these two species is essentially the same. However, unlike the Pt species the Pd analogues produce temperature-dependent spectra attributable to dynamic behaviour of the Hdptf system. On raising the temperature from the slow exchange limit of 240 K (CD₂Cl₂) ‡ to 305 K broadening and eventual coalescence occurs of not only the diastereotopic NMe₂ and NCH₂ signals but also of the two *p*-tolyl methyl signals and several of the corresponding aryl multiplets. Over this range the AB₂ multiplet from the C₆H₃ unit of the terdentate ligand system and the imine proton still resonate at essentially the same frequencies. However, at 350 K neither the amine NH signal (*ca.* δ 10.1), which is extremely broad, nor the imine CH show any sign of splitting due to ³J(CHNH). The operative mechanism behind this temperature dependence is proposed, on the basis of the following ¹H n.m.r. experimental results, to be the result of anion-assisted Hdptf dissociation [equation (1), L = –C₆H₃(CH₂NMe₂)₂-2,6].



First, addition of free Hdptf to a solution of (1) (CD₂Cl₂, 273 K) produces *no* new signals, *i.e.* free and co-ordinated ligand are evidently in fast exchange. In separate experiments the process was studied at both constant ligand concentration and constant complex concentration and up to complex:Hdptf concentrations of 10:1 the coalescence temperatures of the various ¹H signals are not noticeably affected. Secondly, coalescence temperatures of the pure complex in the range 0.005–0.2 mol dm^{−3} were also found to be concentration independent. These observations point to a fluxional process that, although dissociative in nature, is not initiated by traces of free ligand and has a mechanism for which the rate-determining step does not

* Even in the free formamidine Me₂NC(H)=NC₆H₄Cl-4 (which has incidentally an almost planar skeleton) there is also a trend towards equalization of the C–N and C=N distances (1.36 and 1.29 Å respectively, M. R. Gifkins and R. A. Jacobson, *Cryst. Struct. Commun.*, 1980, 9, 959).

† ¹H n.m.r. signals of the CH₂ and NMe₂ units in C₆H₃(CH₂NMe₂)₂-2,6 are a powerful probe for the determination of the symmetry of the metal and associated groupings. See, for example, A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, and A. L. Spek, *Inorg. Chem.*, 1982, 21, 2014.

‡ Similar behaviour occurs in [²H₆]acetone but the use of this solvent was, in the first instance, avoided in order to minimise any effects attributable to solvent co-ordination.

involve a bimolecular complex-complex interaction. Finally, a *ca.* 0.1 mol dm⁻³ [²H₆]acetone solution of (**1b**) was treated with anhydrous LiBF₄ and with the presence of this poorly co-ordinating anion at equimolar concentration a slight lowering of the coalescence temperature was apparent, whereas in great excess (*ca.* 5 mol dm⁻³) the system was still in fast exchange even at 193 K (250-MHz ¹H n.m.r.). This direct evidence for the intervention of an anion in the fluxional process is supported by another observation: namely, the weighted average of the chemical shifts of the NMe₂ protons of pure (**1b**) in the slow exchange (δ 2.60) and at coalescence (δ 2.72) differ significantly, with the latter value being shifted upfield towards the value obtained for pure [Pd{C₆H₃(CH₂NMe₂)₂-2,6}(CF₃SO₃)] (δ 2.87), *i.e.* in the direction anticipated on the basis of equation (1). These combined data are fully consistent with a dissociative process for which one anticipates a marked temperature dependence of the chemical shifts in the fast (intermediate) exchange limit, with the observed average chemical shift depending on the degree of dissociation and the true chemical shift of the individual species.¹⁹

Since ligand dissociation can in unfavourable cases be catalysed by the presence of small amounts of impurities one must exercise due caution in the detailed interpretation of such systems. For this reason control measurements have also been made on solutions of (**1b**) with base (NEt₃), acid (HCOOH), H₂O and the neutral Pd-dptf complex (**3**). In no case was there any indication that these species were capable of inducing the observed dynamic behaviour of (**1b**) in solution.

(c) Pt and Pd complexes of dptf. The 60-MHz ¹H n.m.r. spectra of (**3**) and its platinum analogue (**4**) at r.t. are similar and show an equivalence of the two *p*-tolyl groupings of dptf with no evidence for diastereotopic NMe₂ or CH₂ units within the C₆H₃(CH₂NMe₂)₂-2,6 moiety. The two co-ordination modes of dptf consistent with this data are (i) chelated bonding (**III**) (Figure 1), with a five-co-ordinate Pt^{II} centre, and (ii) a fluxional σ -heteroallyl system in which the M atom changes its point of attachment between the N atoms (see Discussion section). At 250 MHz the spectra of (**3**) and (**4**) in CD₂Cl₂ (193 K) are also similar but completely different from spectra obtained at r.t. As with the cationic complexes (**1**) and (**2**) a limiting situation has been reached in which the *p*-tolyl units have become inequivalent and the NMe₂ and CH₂ groups diastereotopic. These data are compatible with monodentate σ -N¹ bonding of the formamidate ion as was found in the X-ray crystal structure of (**4**) (Figure 4). The observation of platinum satellites on the imine CH proton of (**4**), over the whole temperature range studied (180–300 K), shows that the dynamic process is intramolecular and this conclusion was independently confirmed for both (**3**) and (**4**) through the measured concentration independence of the NMe₂ and CH₂ signal coalescence temperatures.

Discussion

Co-ordination of Hdptf.—Our results show unambiguously that [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(Hdptf)]X (**2**) and the analogous Pd species (**1**) possess the monodentate imine-N² bonding mode of Hdptf both in solution and the solid state. In species of the type [M{C₆H₃(CH₂NMe₂)₂-2,6}L]⁺ it is to be anticipated that, although the M^{II} centre formally accommodates a positive charge, the presence of the hard *trans* N-donor atoms will to some extent reduce the acceptor capability of this metal centre. Co-ordination of neutral ligands with π -back-bonding capability will thus be favoured and isolation of the Pt species with L' = CO or PPh₃¹⁰ supports this argument. With a formamidine such as Hdptf imine-N² co-ordination is to be expected since, regardless of the nucleophilicity of the two different N-donor sites, this mode with two *sp*² N centres is

energetically more favourable than amine-N¹ co-ordination where enforced *sp*³ hybridization of this N atom would result in loss of electron delocalization capability.

Despite the presence of two different N-donor sites in formamidines it is somewhat surprising that other reports of the co-ordination properties of these and related (isoelectronic) systems are limited. Evidence for unstable [Cu^{II}(O₂CMe)₂(Hdptf)]₂ was given in 1956¹ but only in 1975^{9a} was there spectroscopic identification of a number of Co, Rh, Zn, Cd, Hg, and Ag complexes by Toniolo *et al.* In 1979 this latter group also reported some fluxional formamidine π -allyl palladium species^{9c} and it was suggested that here at least co-ordination was *via* the 'more basic' amine N atom. Our ¹H n.m.r. data for (**1**) bear close comparison with those reported for [PdCl(1—3- η -C₃H₅)(Hdptf)] at low temperature [δ (NH) 8.2, δ (CH) 10.2, ³J(NHCH) 12 Hz] and contrary to the earlier suggestion it is likely that these allyl palladium species also possess imino-N² bonded formamidine. The fluxional process in these allyl complexes was found to be concentration dependent and a bimolecular mechanism involving bridging Hdptf was proposed. For the fluxional process observed for (**1**) this type of mechanism is unlikely on purely steric and electronic grounds and so it is not surprising that an anion-assisted dissociation as expressed by equation (1) plays an important role.

Without detailed kinetic measurements it would not be possible to determine whether the process in the palladium system, (**1**), is concerted or does indeed possess a true five-co-ordinate [Pd{C₆H₃(CH₂NMe₂)₂-2,6}(Hdptf)X] intermediate. However, our observations are consistent with the extensive literature on substitution reactions of square-planar complexes where associative mechanisms seem to dominate.²⁰ In general it is found that although Pt^{II} and Pd^{II} complexes react by similar mechanisms the reactions of Pd^{II} are *ca.* 10⁵–10⁶ times faster than those of Pt^{II}. This difference in reaction rate clearly explains why [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(Hdptf)X] (**2**), unlike (**1**) do not show this type of fluxional behaviour on the n.m.r. time-scale.

There are no structural data available for valid comparison with those of (**2b**). A spectroscopically-characterized series of Re^I benzamidine complexes²¹ has been reported as well as an example of an acetamidine complex²² for which the authors mention preliminary X-ray data of the triazenide analogue [Rh(CO)(PPh₃)₂(RNNNHR)] (R = C₆H₄F-*p*). This latter result has been used to support the claim that monodentate imine-N² bonded formamidines are intermediates in the reaction of some rhodium formamidate complexes with HCl.^{3d} The inference is that anionic metal-bonded formamidate can be protonated to afford formamidine species. The present study emphasizes the reverse aspect: namely, complexes of neutral formamidine, *i.e.* (**1**) and (**2**), possess an acidic (amine) proton that may be removed by strong base to afford species containing the anionic formamidate group, *i.e.* (**3**) and (**4**).

Anionic Formamidate.—The present study has unambiguously characterized a monodentate σ -N¹ bonding mode for the N¹,N²-di-*p*-tolylformamidate ion in [M{C₆H₃(CH₂NMe₂)₂-2,6}(dptf)] (M = Pt or Pd). This type of bonding had been identified previously using spectroscopic techniques for several formamidate complexes but confirmation by X-ray methods was lacking. In contrast, there are several crystallographic studies reported on species in which isoelectronic triazenide exhibits this type of co-ordination.^{1,16,23} These latter species like (**4**) all show the 'cisoid' M-N-Y-N (Y = CH or N) skeleton as a common feature. This conformation is apparently favoured over the 'transoid' one on purely electronic (*e.g.* delocalization) grounds since there are only minor steric differences between the two situations. Using (**4**) as an example the only noteworthy change on going from the 'cisoid' to the 'transoid' form would be

that the N(4) lone pair points towards an *ortho* proton of a *p*-tolyl group in the latter hypothetical case whereas in the actually observed situation it points towards a filled d_{z^2} metal orbital.

The observed 'cisoid' arrangement of the M–N–C–N skeleton in (4) [and by analogy in the Pd complex (3) also] can be seen to be consistent with the fluxionality of these species which produces equivalence of the two N–*p*-tolyl groupings. The most likely process involves the intermediacy of a chelate *N,N'*-bonded formamidinate that can be formed from the ground-state (*X*-ray) structure by only a relatively small movement of the dptf skeletal atoms. This type of intermediate is also suggested by the many reports in which formamidinate (and triazenide) complexes have been shown either spectroscopically or crystallographically to possess the chelate bonding mode. If the imine N lone pair were to function as a donor not to the same but to another metal centre then a dinuclear species with bridging formamidinate ligands would result. Looking more closely at the M^{2+} centre in (3) and (4) it is clear that the d_{z^2} orbital, perpendicular to the co-ordination plane, is also a potential donor unit and by using this orbital and the imine lone pair these molecules can be visualized as a potentially chelating MN system.

For (4), at least, the validity of this formulation is to be found in the solid-state structure of heterodinuclear $[\{2,6-(Me_2NCH_2)_2C_6H_3\}Pt\{\mu-p-MeC_6H_4NC(H)NPr^i\}HgBrCl]^7$ and in the spectroscopic data for related Pt–Hg–Ag containing species,^{7,8} all of which may be regarded as resulting from a platinum–formamidinate unit co-ordinating in a bidentate manner to a post-transition metal salt.* As indirectly suggested above analogous species should also be obtainable through the reaction of a post-transition metal salt and a formamidinate species and this is indeed the case, e.g. (4) with HgX_2 generates $[Pt\{C_6H_3(CH_2NMe_2)_2-2,6\}(\mu-dptf)HgX_2]$ [$X = Cl$ or Br ; $^1J(PtHg) = 7\ 100\ Hz$].¹¹ Reactions of this latter type, in which organometallic species can function as chelating ligands to metal salts or co-ordinatively unsaturated species, would appear to be a most interesting and fruitful field in the search for the tailored construction of heteronuclear clusters.

References

- W. Bradley and I. Wright, *J. Chem. Soc.*, 1956, 640.
- E. W. Abel and J. Skittral, *J. Organomet. Chem.*, 1980, **185**, 391; V. H. de Roode, M. L. Beekes, A. Oskam, and K. Vrieze, *ibid.*, 1977, **142**, 337; 1978, **154**, 273; A. D. Robinson, S. D. Robinson, A. Sahajpal, and M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, 1981, 1327; E. Forsellini, U. Casellato, R. Graziani, L. Toniolo, R. Rossi, and L. Magon, *Inorg. Chim. Acta*, 1982, **61**, 255.
- (a) W. H. de Roode, K. Vrieze, E. A. Koerner von Gustorf, and A. Ritter, *J. Organomet. Chem.*, 1977, **135**, 183; (b) W. H. de Roode and K. Vrieze, *ibid.*, 1978, **145**, 207; (c) E. W. Abel and J. Skittral, *ibid.*, 1980, **193**, 389; (d) P. Piraino, G. Tresoldi, and F. Faraone, *ibid.*, 1982, **224**, 305.

- A. J. Deeming and R. Peters, *J. Organomet. Chem.*, 1982, **235**, 221; R. D. Adams, D. A. Katahira, and J. P. Selegue, *ibid.*, 1981, **213**, 259.
- F. A. Cotton, T. Inglis, M. Kilner, and J. Webb, *Inorg. Chem.*, 1975, **14**, 2023; F. A. Cotton and L. W. Shire, *ibid.*, 1975, **14**, 2027; F. A. Cotton, W. H. Isley, and W. Kaim, *ibid.*, 1980, **19**, 2360.
- (a) J. Kuyper, P. I. van Vliet, and K. Vrieze, *J. Organomet. Chem.*, 1976, **105**, 379; (b) 1975, **96**, 289; (c) J. Kuyper, K. Vrieze, and K. Olie, *Cryst. Struct. Commun.*, 1976, **5**, 179; (d) P. I. van Vliet, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, 1979, **182**, 105; (e) 1980, **188**, 301; (f) P. I. van Vliet, J. Kuyper, and K. Vrieze, *J. Organomet. Chem.*, 1976, **122**, 99; 1980, **187**, 413; (g) R. T. Kops, A. R. Overbeek, and H. Schenk, *Cryst. Struct. Commun.*, 1976, **5**, 125; (h) 1976, **5**, 193.
- A. F. M. J. van der Ploeg, G. van Koten, and C. Brevard, *Inorg. Chem.*, 1982, **21**, 2026, 2878.
- A. F. M. J. van der Ploeg, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, 1982, **226**, 93; A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, A. L. Spek, and A. J. M. Duisenberg, *Organometallics*, 1982, **1**, 1066.
- (a) L. Toniolo, G. Deganello, P. L. Sandrini, and G. Bombieri, *Inorg. Chim. Acta*, 1975, **15**, 11, L. Toniolo, A. Immirzi, U. Croatto, and G. Bombieri, *ibid.*, 1976, **19**, 209; (b) L. G. Kuz'mina, N. G. Bokii, Yu. T. Struchkov, V. I. Minkin, L. P. Olekhovich, and I. E. Mikhailov, *Zh. Strukt. Khim.*, 1977, **18**, 122; (c) T. Boschi, U. Belluco, L. Toniolo, R. Favez, and R. Roulet, *Inorg. Chim. Acta*, 1979, **34**, 37; (d) G. Minghetti, G. Banditelli, and F. Bonati, *ibid.*, 1975, **12**, 85; (e) R. D. Adams, D. A. Katahira, and J. P. Selegue, *J. Organomet. Chem.*, 1981, **213**, 259.
- D. M. Grove, G. van Koten, J. N. Louwen, J. G. Noltes, A. L. Spek, and H. J. C. Ubbels, *J. Am. Chem. Soc.*, 1982, **104**, 6609.
- J. Terheijden, unpublished work.
- R. M. Roberts, *J. Am. Chem. Soc.*, 1949, **71**, 3848.
- N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- D. M. Grove, G. van Koten, H. J. C. Ubbels, and A. L. Spek, *J. Am. Chem. Soc.*, 1982, **104**, 4285; D. M. Grove, G. van Koten, H. J. C. Ubbels, R. Zoet, and A. L. Spek, *J. Organomet. Chem.*, 1984, **263**, C10; J. Terheijden, G. van Koten, J. L. de Booy, H. J. C. Ubbels, and C. H. Stam, *Organometallics*, 1984, **2**, 1882.
- P. Vaughan and J. Donohue, *Acta Crystallogr.*, 1952, **5**, 530 and refs. therein.
- L. D. Brown and J. A. Ibers, *Inorg. Chem.*, 1976, **15**, 2744.
- P. A. S. Smith, 'The Chemistry of Open Chain Organic Nitrogen Compounds', W. A. Benjamin Inc., New York, 1965, vol. 1.
- (a) R. M. Roberts, *J. Am. Chem. Soc.*, 1950, **72**, 3608 and refs. therein; (b) H. H. Limbach, personal communication.
- J. P. Jesson and E. L. Muetterties, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, San Francisco, and London, 1975.
- See, for example, F. Basolo, in 'Mechanisms of Inorganic Reactions,' Adv. Chem. Ser. 49, ed. R. F. Gould, American Chemical Society, Washington D.C., 1965; J. Coe, in 'Mechanisms of Inorganic and Organometallic Reactions,' ed. M. V. Twigg, Plenum Press, New York and London, 1983, vol. 1.
- J. A. Clark and M. Kilner, *J. Chem. Soc., Dalton Trans.*, 1984, 389 and refs. therein.
- N. G. Connelly and Z. Demidowicz, *J. Chem. Soc., Dalton Trans.*, 1978, 50.
- L. D. Brown and J. A. Ibers, *Inorg. Chem.*, 1976, **15**, 2788; G. Bombieri, A. Immirzi, and L. Toniolo, *ibid.*, p. 2428; A. Immirzi, W. Porzio, G. Bombieri, and L. Toniolo, *J. Chem. Soc., Dalton Trans.*, 1980, 1098 and refs. therein.

* Although somewhat extreme, the cationic formamidine species (2b) can be envisaged as (4) acting as a chelate system to H^+ .