Tri-aza Analogue of an Acetylacetonato-complex formed by Nucleophilic Attack of a Co-ordinated Nitrile by Amidines. *X*-Ray Crystal Structure of [Pt{HNC(Ph)NC(Ph)NH}$_2$]·$\frac{2}{3}$PhMe†

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Lithiobenzamidine reacts with [Pt(PhCN)$_2$Cl$_2$], in diethyl ether solution, by attack at the carbon of the co-ordinated nitrile to form [Pt{HNC(Ph)NC(Ph)NH}$_2$]. The crystal structure, obtained on the golden-yellow platelets of the toluene crystallate, showed a planar molecule having six-membered metallo-ring systems containing three nitrogen atoms. [Pt{HNC(Ph)NC(Ph)NH}$_2$].$\frac{2}{3}$PhMe forms monoclinic crystals [a = 15.468(4), b = 12.576(3), c = 25.206(7) Å, β = 117.64°, space group $P2_1/c$ with six molecules of the complex and four toluenes in each unit cell] in which each planar HNC(Ph)NC(Ph)NH ligand adopts symmetrical σ,σ-attachment through two terminal N atoms. The PtN$_4$ unit is planar with a mean Pt–N distance of 1.96 Å. Carbon–nitrogen distances in the ring system are similar, 1.30(7) Å for C–N(C) and 1.36(7) Å for C–N(Pt). This complex is markedly different from the product obtained using lithio-t-butylamidine, LiNHC(Bu)NH, and [Pd(PhCN)$_2$Cl$_2$]. The presence of [Pd$_3$L$_4$]$^+$ ions [L = HNC(Ph)NC(Bu^t)NH] in the mass spectrum and the low solubility of the material suggest a polymeric structure.

Nitrogen nucleophiles are well known to attack co-ordinated ligands to form more complex groups attached to a metal.[1] For example, amines react with metal carbonyls to give carbamoyl derivatives,[2] and with ethene complexes to give 2-aminoethyl derivatives.[3] Interestingly, an early amidine complex was prepared in a similar way though the product was not recognised as such at the time. Treatment of [Pt(MeCN)$_2$Cl$_2$] with ammonia[4] gave an amidine compound resulting from addition of ammonia across the nitrile multiple bond. It was not until 1962 when the crystal structure determination was undertaken[5] that the full nature of the complex was discovered.

Amidines themselves also act as nucleophiles, their reactivity increasing when lithiated.[6] For example, attack at co-ordinated carbon monoxide leads to carbamoyl complexes in which the C(O)N(R′)C(R)NR′ ligand forms a five-membered metallocycle.[7] Such complexes are illustrated by (η-C$_5$H$_5$)(CO)$_2\overline{\text{MoC(O)N(Ph)C(Me)N}}$Ph.[8] We report here studies of the reactions of lithio-amidines with benzonitrile complexes of platinum and palladium(II) in which attack occurs at the co-ordinated nitrile. A six-membered metallocycle, containing three nitrogen atoms, is produced which is isoelectronic and isostructural with the acetylacetonato-group. The crystal structure of [Pt{HNC(Ph)NC(Ph)NH}$_2$] is reported. The ligand is closely related to groups produced in reactions involving CF$_3$CN with [Pt(PPh$_3$)$_4$] or [Ir(CO)(PPh$_3$)$_2$(η-C$_3$H$_5$)] or [Ru(η-C$_5$H$_5$)(PPh$_3$)$_2$Cl], which gave [Pt(PPh$_3$)$_2${N=C(CF$_3$)-N=C(CF$_3$)NH}],[9] [Ir(CO)(PPh$_3$)$_2${HNC(CF$_3$)NC(CF$_3$)-NH}],[10] and [Ru(η-C$_5$H$_5$)(PPh$_3$){HNC(CF$_3$)NC(CF$_3$)-NH}][11] respectively.

Results and Discussion

Lithio-benzamidine reacts with bis(benzonitrile)dichloroplatinum(II)[11] to form air-stable, yellow crystals of [Pt{HNC(Ph)NC(Ph)NH}$_2$].[12] A similar reaction using lithio-t-butylamidine and bis(benzonitrile)dichloropalladium(II)[11] also produced a yellow complex, though this material is air sensitive, and less soluble in polar organic solvents. Both complexes arise from nucleophilic attack of co-ordinated benzonitrile by the lithio-amidine, forming six-membered metallocycles containing three nitrogen atoms. These metallocycles are isoelectronic and isostructural with the acetylacetonato-group.

The nature of the platinum complex was determined by analysis and by spectroscopic techniques. The parent ion is observed in the mass spectrum at m/e 639, and breakdown

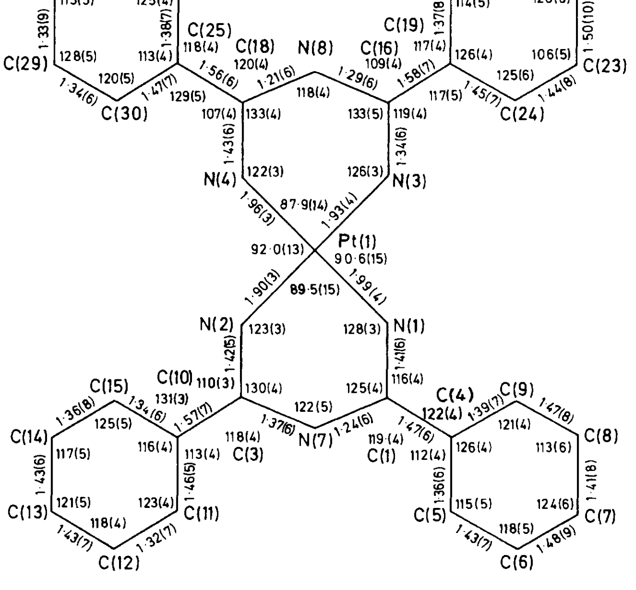

Figure 1. *X*-Ray structural data for molecule 1 of [Pt{HNC(Ph)NC(Ph)NH}$_2$]: distances (Å) and angles (°)

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† Bis(1,3-diphenyl-2,4-diazabutadienylamido-*N*,*N*′)platinum(II)–toluene (1/0.67).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

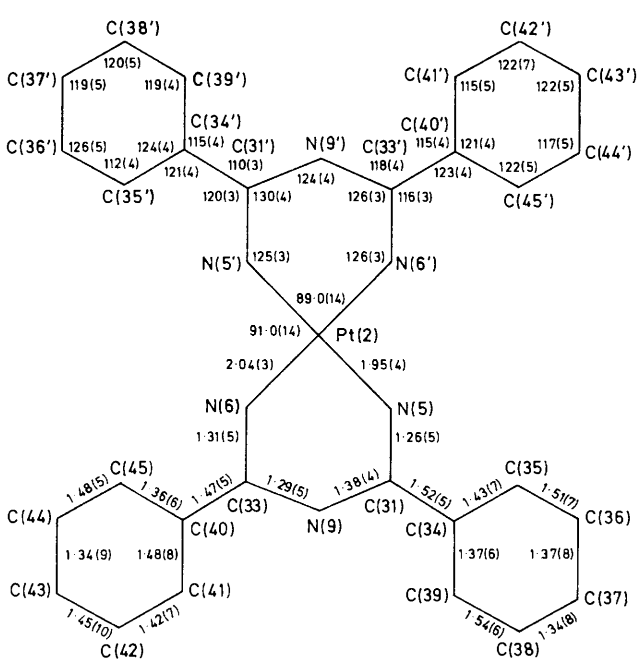

Figure 2. *X*-Ray structural data for molecule 2 of [Pt{HNC(Ph)-NC(Ph)NH}$_2$]: distances (Å) and angles (°)

occurs by fragmentation of the rings, resulting in the loss of benzonitrile. Both rings disrupt in this way and a bis(amidino)-complex ion results. The amidino-group then fragments in the usual way. Two notable features in the i.r. spectrum relate to the ν(N–H) and ν(C=N) stretching region. Absorptions at 3 420 and 3 320 cm^{-1} for the complex are higher than those of the parent amidine at 3 290 and 3 220 cm^{-1}. Also the ν(N–C–N) asymmetric stretching vibration absorbs at 1 640 cm^{-1} in the parent amidine but at a lower wavenumber in the complex (1 630 cm^{-1}) and with a lower intensity.

The ^{1}H n.m.r. spectrum consists of a complex multiplet in the aromatic region, and a weak signal at *ca.* 8.8 p.p.m. which is assigned to the N–H protons. The ^{13}C n.m.r. spectrum (see Experimental section) has been interpreted in accordance with the *X*-ray structure (Figures 1 and 2), the numbering scheme used being shown in Figure 3. The aromatic region of the spectrum is more complex than expected, with three extra signals being observed. The reason for this is not entirely clear, though sample decomposition can not be eliminated: the complex decomposes rapidly in solution in the presence of air. The C^1 carbon signal has been used previously as a criterion for bond type,[13] particularly for differentiating between bridging and bidentate modes of bonding. Here, the C^1 signal has moved only to a small extent but to lower frequency, from 164.6 p.p.m. in benzamidine to 157.6 p.p.m. in the complex. It is, however, at higher frequency than that found for the C^1 carbon in benzonitrile (115.9 p.p.m.).[14] The frequency of the signal contrasts markedly with the signals for bridging and bidentate groups, which occur in the 159—167 and 166—175 p.p.m. regions respectively, *i.e.* both to high frequency of the benzamidine hydrochloride signal. The difference may be attributed to different bond angles at carbon in the groups, as discussed later.

Two independent molecules are found in the crystal (molecules 1 and 2, Figures 1 and 2); their dimensions do not differ significantly. The asymmetric unit of the structure (ignoring solvent molecules) contains one complete molecule and half a molecule, the second molecule sitting at a centre of symmetry.

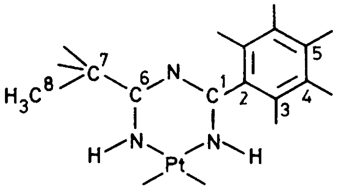

Figure 3. Numbering scheme of the carbon atoms for the ^{13}C n.m.r. spectra

Platinum is co-ordinated in a square-planar complex to two HNC(Ph)NC(Ph)NH ligands forming six-membered metallocycles. The Pt–N distances vary from 1.90(3) to 2.04(3) Å, but do not vary significantly from the mean value of 1.96 Å. This average distance is very similar to distances in related PtN$_4$ systems such as [Pt(NH$_3$)$_2${HNC(Me)NH$_2$}$_2$]Cl$_2$·H$_2$O [1.96(2) Å][5] and bis(dimethylglyoximato)platinum(II) [1.93(4) and 1.95(4) Å],[15] but slightly shorter than in *trans*-[Pt(NH$_3$)$_2$-(mim)$_2$]Cl$_2$·2H$_2$O (mim = *N*-methylimidazole) [2.01(2) Å],[16] and in [Pt(O=CHCH=NOH)$_2$] [2.013(14) and 1.968(14) Å],[17] and [Pt{PhNC(Ph)NPh}$_2$] [2.202 2(6) and 2.203 8(5) Å].[18]

The geometry about the platinum atoms is close to a regular square-planar arrangement, and the 11 atoms involved in the rings all lie approximately in the same plane. The carbon–nitrogen distances in both molecules vary from 1.43(6) to 1.21(6) Å with averages of 1.30(7) Å for the bridge between the CPh groups, but 1.36(7) Å for C–NPt bonds. The bridge bond distances are close to those of *s*-triazine [1.319(4) Å],[19] benzamidine hydrochloride [1.328(7) and 1.293(7) Å],[20] *N*,*N'*-diphenylbenzamidine [1.302(7) and 1.360(7) A],[21] [Pd{*p*-MeC$_6$H$_4$NC(Me)NC$_6$H$_4$Me-*p*}$_2$] [1.322(14) Å],[13] and [Pt{*p*-MeC$_6$H$_4$NC(Ph)NC$_6$H$_4$Me-*p*}$_2$] [1.331(8), 1.340(8) Å],[22] and suggest a similar degree of electron delocalisation.

Ring NCN angles in molecules 1 and 2 vary from 125(4) to 133(5)°, with a mean value of 130(3)°, compensating for the small six-membered ring angle at platinum. These angles are generally larger than those found for bridging (*ca.* 118°) and bidentate (*ca.* 108°) groups, and for PhNHC(Ph)NPh (120.4°),[21] but correspond more closely to the angles in *s*-triazine.[19] Thus the geometry of this group at carbon differs markedly from that of other amidino-groups, and not surprisingly the different electronic properties are reflected in the different n.m.r. frequencies. The ring angles at the nitrogen [av. 121(3)° at the bridge-head, and av. 125(2)° at PtNC] are smaller than those for the six-membered, *ortho*-metallated ring in [Pd(η-C$_5$H$_5$){*p*-MeC$_6$H$_4$NC(Me)NHC$_6$H$_3$Me-*p*] [129.9(7) and 128.2(5)°],[22] though this is expected since the latter complex has a non-planar ring.

Each (phenyl)CCN$_2$ unit is planar, the maximum deviation being 0.02 Å for molecules 1 and 2, except for C(3) which is displaced by 0.07 Å from the mean plane. The dihedral angles between the metallo-ring and the phenyl rings are approximately 40°, but one ring of molecule 1 is clearly different in that this angle is 16.6°. For comparison, the corresponding dihedral angle for [Pd{*p*-MeC$_6$H$_4$NC(Me)NC$_6$H$_4$Me-*p*}$_2$] is 42°.[13] The large dihedral angles in the present structures arise possibly because of steric hindrance between the N–H and the aromatic ring hydrogens.

Close similarity exists between the molecular structure in this complex and those of [Pt(PPh$_3$)$_2${NC(CF$_3$)NC(CF$_3$)-NH}][9] and [Ru(η-C$_5$H$_5$){P(OMe)$_3$}{HNC(CF$_3$)NC(CF$_3$)-NH}][11] (see Table 1). The latter complex was obtained from the ruthenium complex referred to in the introduction, by phosphine–phosphite exchange in decalin solution. Interestingly, this ruthenium compound also exists in the crystal in two

Table 1. Selected structural data for complexes having metal–C_2N_3 ring units (distances in Å and angles in °)

	[Pt{HNC(Ph)NC(Ph)NH}$_2$]			[Ru(η-C_5H_5){P(OMe)$_3$}{HNC(CF_3)NC(CF_3)NH}]^b	
Parameter	Molecule 1	Molecule 2	[Pt(PPh$_3$)$_2${NC(CF_3)NC(CF_3)NH}]^a	Molecule 1	Molecule 2
M–N	1.99(4) 1.90(3) 1.93(4) 1.96(3)	1.95(4) 2.04(3)	2.01, 2.02	2.078(4) 2.089(5)	2.070(5) 2.075(4)
(M)N–C	1.41(6) 1.42(5) 1.34(6) 1.43(6)	1.26(5) 1.31(5)	1.36, 1.24	1.276(7) 1.295(6)	1.294(8) 1.286(8)
C–N(C)	1.24(6) 1.37(6) 1.29(6) 1.21(6)	1.38(4) 1.29(5)	1.34, 1.32	1.345(9) 1.331(7)	1.320(6) 1.362(8)
C–N–C	122(5) 118(4)	124(4)		119.5(5)	119.2(5)
N–M–N	89.5(15) 87.9(14)	89.0(14)		83.6(2)	84.4(2)
N–C–N	125(4) 130(4) 133(5) 133(4)	130(4) 126(3)		130.7(5) 130.6(6)	131.4(6) 130.5(4)

[a] Ref. 9. [b] Ref. 11.

independent molecules, and in addition to very close similarities between bond distances and bond angles for the platinum compound reported here, and the ruthenium compound, small geometrical features are also common. For example, all the atoms of the metallocyclic rings in the two complexes are planar within 0.06 and 0.07 Å respectively. Except for small differences arising from the slightly larger platinum atom, the metallo-ring systems are very similar indeed, and the strongly electron-withdrawing CF_3 groups appear to have little effect on the ring. The rings are all extensively delocalized.

t-Butylamidine hydrochloride was treated with 2 molar equivalents of n-butyl-lithium to form the lithio-amidine reagent, which was subsequently treated with [Pd(PhCN)$_2$Cl$_2$]. The lemon-yellow product was air-sensitive and showed only limited solubility in polar organic solvents. Attempts to purify the complex by fractional crystallization and chromatography proved difficult and final traces of the amidine hydrochloride could not be removed. Mass spectral investigation failed to detect the parent ion, but showed the presence of the trinuclear ion, [Pd$_3${HNC(Bu^t)NC(Ph)NH}$_4$]. In addition di- and mono-nuclear ions were detected, the former having three or two amidino-groups, and the latter two or one group. The general features of the mass spectrum are distinctly different from those of the benzamidine derivative. Also, the general properties of the two complexes differ markedly, which suggests that the two complexes have different structures. Indeed, the nature of the n-butylamidino-derivative points towards a polymeric structure with bridging HNC(Bu^t)NC(Ph)NH groups.

Experimental

Benzamidine hydrochloride and t-butylamidine hydrochloride were purchased from Aldrich Chemicals and Lancaster Chemicals respectively, and n-butyl lithium from Alpha Chemicals. [Pd(PhCN)$_2$Cl$_2$] and [Pt(PhCN)$_2$Cl$_2$] were synthesized by standard methods. Diethyl ether was dried over extruded sodium, and dichloromethane over molecular sieve. Tetrahydrofuran (thf) was freshly distilled under nitrogen from lithium aluminium hydride. All solvents were pumped to remove dissolved air, stored under nitrogen, and transferred by syringe against a counter flow of nitrogen. All reactions were performed with exclusion of oxygen.

Spectra.—Infrared spectra in the range 4 000—250 cm^{-1} were recorded on a Perkin-Elmer 457 spectrometer, and ^{1}H n.m.r. spectra at 60 MHz with a Varian A56/60D spectrometer. A Bruker HX90E spectrometer modified for Fourier-transform operation using a Nicolet B.N.C.12 computer was used for ^{13}C studies. The scheme used to label the carbon atoms is given in Figure 3. Mass spectra were obtained using either an up-graded A.E.I. MS9 or VG 7070E instruments operating at 70 eV (1.12×10^{-17} J) and accelerating potentials of 8 kV and 6 kV respectively. Samples were inserted directly into the ion source at temperatures up to 250 °C.

Analyses.—The carbon, hydrogen, and nitrogen contents of the complexes were determined with a Perkin-Elmer 240 elemental analyser, and the metal contents by atomic absorption spectroscopy using a Perkin-Elmer 403 spectrometer.

Reaction of [Pt(PhCN)$_2$Cl$_2$] *with* LiNHC(Ph)NH.—Benzamidine hydrochloride (1.56 g, 10 mmol), previously dried by heating to 50 °C *in vacuo* for 2 h, was mixed with anhydrous diethyl ether (100 cm^3) to give a white suspension, which was cooled to 0 °C in an ice-bath. n-Butyl-lithium (20 mmol, 2.65 mmol dm^{-3} in hexane) was added and the mixture stirred at room temperature for 1 h before cooling to −196 °C. Solid [Pt(PhCN)$_2$Cl$_2$] (2.36 g, 5 mmol) was added against a counter current of nitrogen, then the mixture was allowed to warm to ambient temperature. Over 48 h, a yellow solution was produced. The solvent was removed *in vacuo*, and the residue recrystallized from dichloromethane (200 cm^3). Yellow platelets of [Pt{HNC(Ph)NC(Ph)NH}$_2$] were obtained. Yield 84%, m.p. 98 °C (decomp.) (Found: C, 52.8; H, 4.90; N, 13.0; Pt, 27.6. $C_{28}H_{24}N_6Pt$ requires C, 52.6; H, 3.75; N, 13.1; Pt, 30.5%). I.r. spectrum (CsI/KBr windows, Nujol/hexachlorobutadiene mulls): 3 420w, 3 320m,br, 3 040w, 2 960w(sh) 2 860w, 2 160vw, 1 630m, 1 582w, 1 560w, 1 530s, 1 450s, 1 420s, 1 300m, 1 260w(sh), 1 040w, 1 030w, 1 000w, 920m,br, 840w,br, 790w(sh),

Table 2. Final fractional atomic co-ordinates

Atom	*x*	*y*	*z*
C(1)	0.749(3)	0.208(3)	0.049(2)
C(3)	0.791(3)	0.033(3)	0.063(2)
C(4)	0.711(3)	0.300(4)	0.009(2)
C(5)	0.632(3)	0.274(4)	−0.043(2)
C(6)	0.602(4)	0.353(4)	−0.089(2)
C(7)	0.638(5)	0.463(6)	−0.071(3)
C(8)	0.715(4)	0.491(5)	−0.015(3)
C(9)	0.750(3)	0.401(4)	0.026(2)
C(10)	0.809(3)	−0.069(4)	0.033(2)
C(11)	0.724(3)	−0.099(3)	−0.022(2)
C(12)	0.721(4)	−0.185(4)	−0.053(2)
C(13)	0.803(3)	−0.254(4)	−0.028(2)
C(14)	0.891(4)	−0.223(5)	0.022(2)
C(15)	0.887(3)	−0.134(3)	0.052(2)
C(16)	0.860(3)	0.224(4)	0.290(2)
C(18)	0.911(3)	0.064(4)	0.307(2)
C(19)	0.850(3)	0.322(3)	0.327(2)
C(20)	0.834(3)	0.297(3)	0.375(2)
C(21)	0.834(5)	0.388(5)	0.410(3)
C(22)	0.851(4)	0.495(4)	0.392(2)
C(23)	0.865(4)	0.525(5)	0.339(3)
C(24)	0.873(3)	0.426(4)	0.312(2)
C(25)	0.949(3)	−0.035(3)	0.348(2)
C(26)	0.952(3)	−0.030(3)	0.403(2)
C(27)	0.988(3)	−0.112(4)	0.448(2)
C(28)	1.019(4)	−0.212(5)	0.432(3)
C(29)	1.014(3)	−0.215(3)	0.378(2)
C(30)	0.987(3)	−0.136(4)	0.337(2)
C(31)	0.501(3)	0.216(3)	0.036(2)
C(33)	0.382(3)	0.191(3)	−0.063(2)
C(34)	0.539(2)	0.307(3)	0.081(1)
C(35)	0.575(4)	0.289(4)	0.143(2)
C(36)	0.620(3)	0.387(4)	0.180(2)
C(37)	0.636(4)	0.481(5)	0.159(3)
C(38)	0.603(4)	0.494(4)	0.100(2)
C(39)	0.547(3)	0.402(3)	0.057(2)
C(40)	0.298(3)	0.236(3)	−0.116(2)
C(41)	0.236(4)	0.309(4)	−0.102(2)
C(42)	0.150(5)	0.344(5)	−0.153(3)
C(43)	0.130(4)	0.317(4)	−0.214(3)
C(44)	0.191(3)	0.257(5)	−0.225(2)
C(45)	0.280(3)	0.218(3)	−0.174(2)
N(1)	0.773(3)	0.227(3)	0.110(2)
N(2)	0.828(2)	0.017(2)	0.125(1)
N(3)	0.824(2)	0.234(3)	0.231(1)
N(4)	0.882(2)	0.028(2)	0.247(1)
N(5)	0.539(3)	0.125(3)	0.051(2)
N(6)	0.402(2)	0.092(3)	−0.068(1)
N(7)	0.763(3)	0.124(3)	0.029(2)
N(8)	0.905(3)	0.149(3)	0.327(2)
N(9)	0.425(2)	0.250(3)	−0.016(1)
Pt(1)	0.828(1)	0.126(1)	0.178(1)
Pt(2)	0.500	0.000	0.000

780m, 720(sh), 689vs, 590w cm^{-1}. Mass spectrum (electron impact): *m/e* 639 (P^+, $^{195}PtC_{28}H_{24}N_6^+$), 536 ($^{195}PtC_{21}H_{19}N_5^+$), 417 ($^{195}PtC_{14}H_{12}N_3^+$), 314 ($^{195}PtC_7H_7N_2^+$), 119 ($C_6H_5CN_2H^+$), 103 ($C_6H_5CN^+$). ^{1}H N.m.r. ($CDCl_3$): δ 7.37—8.25 (complex multiplet), 8.80 p.p.m. (NH, vw). ^{13}C N.m.r. ($CDCl_3$): δ 157.6 (C^1), 139.2 (C^2), 128.0 (C^3), 124.9 (C^4), 126.9 p.p.m. (C^5). Also weak signals at 128.3, 129.2, and 131.8 p.p.m.

Reaction of $[Pd(PhCN)_2Cl_2]$ *with* $LiNHC(Bu^t)NH$.—t-Butylamidine hydrochloride (0.676 g, 0.5 mmol) was suspended in monoglyme (100 cm^3), then cooled to 0 °C, before n-butyl-lithium (10 mmol) was added. After stirring at room temperature for 45 min, the suspension was cooled to −196 °C, and solid $[Pd(PhCN)_2Cl_2]$ (0.096 g, 0.25 mmol) added against a counter-current of nitrogen. The mixture, after reaching ambient temperature, was stirred for 14 h during which time a bright yellow solution formed. Removal of the solvent *in vacuo* gave a yellow-green solid, which was washed with diethyl ether (160 cm) and dichloromethane (100 cm^3) before recrystallization from thf. The product was obtained as a lemon-yellow solid (m.p. 146 °C). A small amount of a red-brown solid remained after the thf extraction. Analytical data for the lemon-yellow solid (Found: C, 43.0; H, 8.50; N, 13.6%) did not lead to its identification. Mass spectrum: *m/e* 1 126 ($^{106}Pd_3C_{49}N_{12}H_{64}^+$), 818 ($Pd_2C_{36}H_{49}N_9^+$), 715 ($Pd_2C_{29}H_{43}N_8^+$), 616 ($Pd_2C_{24}H_{32}N_6^+$), 510 ($PdC_{24}H_{32}N_6^+$), 308 ($PdC_{12}H_{16}N_3^+$), 205 ($PdC_4H_{11}N_2^+$), 103 ($C_6H_5CN^+$). ^{1}H N.m.r. ($CDCl_3$): δ 1.51, 1.58 (9 H), 7.71—8.3 p.p.m. (complex multiplet, 5 H). ^{13}C N.m.r. ($CDCl_3$): δ 132.2 (C^2), 129.2 (C^3), 127.3 (C^4), 128.7 (C^5), 175.9 (C^6), 37.2 (C^7), 28.2 p.p.m. (C^8). Other weaker signals were present at 29.0, 176.0, 132.8, 130.0, and 128.8 p.p.m. No signal could be assigned to C^1.

Structure Determination.—*Crystal data.* $C_{28}H_{24}N_6Pt\cdot\frac{2}{3}C_7H_8$, $M = 701.1$, monoclinic, $a = 15.468(4)$, $b = 12.576(3)$, $c = 25.206(7)$ Å, $\beta = 117.64(2)°$, $U = 4\,343.7$ Å^3, $Z = 6$, $D_c = 1.61$ g cm^{-3}, $F(000) = 2\,072$, Mo-K_α ($\lambda = 0.7107$ Å), $\mu = 51.3$ cm^{-1}, space group $P2_1/c$ from the systematic absences.

After preliminary *X*-ray photography, 3 250 *X*-ray intensities were measured on a Hilger and Watts computer-controlled, four-circle diffractometer. Of these, 1 607 were regarded as significant [$I > 3\sigma(I)$]. The structure was solved by the Patterson, heavy-atom method and was refined by block-diagonal least-squares calculations to a final *R* value of 0.10. Part way through the refinement, a Fourier-difference map revealed disordered toluene molecules, of which only four carbon atoms were included in subsequent calculations.

Refinement was completed with anisotropic thermal parameters for platinum atoms and isotropic thermal parameters for carbon and nitrogen atoms. A weighting scheme of the form $1/w = 1.0 + [(F_o - B)/A]^2$ was applied, with $A = 35.0$, $B = 95.0$, and F_o on the absolute scale. Final atomic co-ordinates so obtained are given in Table 2 and the bond lengths and angles calculated from them are shown in Figures 1 and 2. The structure was solved using the *X*-RAY system of programs.[23] Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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