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Nucleophilic Attack of Amine and Hydroxide to Platinum Dibenzonitrile Dichloride. Crystal Structure of [Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl(NHCOPh)] (2) and *cis*-[Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl$_2$(NCPh) (3)

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Abstract: The trans and cis isomers of [PtCl$_2$(NCPh)$_2$] react with *N,N'*-di-*tert*-butylethylenediamine (*t*-Bu$_2$en) under normal conditions to give [Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl(NCPh)]Cl (**1**) and *cis*-[Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl$_2$(NCPh)] (**3**), respectively. In both cases one end of *t*-Bu$_2$en adds to benzonitrile forming an amino-amidine ligand which is chelated in **1** (forming a seven-membered metallacycle) and monocoordinated in **3**. The residual benzonitrile in the cationic complex **1** readily reacts with base to give a benzamidate species, [Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl(NHCOPh)] (**2**). Compound **3** exhibits, in solution, isomerization about the azomethine double bond (ΔG^{*}_{223} = 10.8 ± 0.3 kcal mol^{-1}) and more slowly undergoes an internal rearrangement with substitution of the residual benzonitrile by the uncoordinate end of the diamine and formation of [Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl$_2$] (**4**). The structures of **2** and **3** have been solved by single-crystal diffraction. Compound **2** crystallizes as methanol solvate (1:1) in the monoclinic space group $P2_1/n$ with a = 25.374 (13) Å, b = 11.351 (8) Å, c = 9.338 (5) Å, β = 92.03 (4)°, and Z = 4. Compound **3** crystallizes as toluene solvate (2:1) in the monoclinic space group $P2_1/a$ with a = 18.090 (10) Å, b = 9.376 (4) Å, c = 17.297 (7) Å, β = 91.76 (4)°, and Z = 4. Both compounds contain a strong intramolecular hydrogen bond which involves the oxygen atom of the benzamidate anion and the cis amine group of the chelate amino-amidine ligand in **2**, the free and coordinate ends of the monocoordinate amino-amidine ligand, so forming a pseudo-seven-membered ring, in **3**.

Reaction of coordinated ligands is a topic of wide interest in view of its synthetic possibilities and perspectives.

The synthetic and structural chemistry of coordinated nitriles which are susceptible to undergo nucleophilic attack by water, alcohols, and amines to yield the corresponding amides, imidic esters, and amidines has already been broadly established.[1]

Braunstein et al. demonstrated that the cyanide carbons in the benzonitrile complex [PtCl$_2$(NCPh)$_2$] undergo the nucleophilic attack of carbanions C$^-$H(PPh$_2$)X (X = CO$_2$Et and CN) to afford *trans*-[Pt(NHCPh=CXPPh$_2$)$_2$].[2] Similar reactions of the metal complex with β-diketonate ions, C$^-$H(COMe)(COR) (R = Me, Ph), were performed by Uchiyama et al. and shown to give *trans*-[Pt{N(COMe)=CPhCH=COR}$_2$] and *cis*-[Pt{NH=CPhC(COR)=COMe}$_2$].[3]

We now find that [PtCl$_2$(NCPh)$_2$], which is widely used as a starting material for the preparation of organoplatinum(II) complexes,[4] reacts readily with a much weaker nucleophile such as *N,N'*-di-*tert*-butylethylenediamine and with hydroxide ion to give amidine and amidate platinum(II) species. The structures of two of them, [Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl(NHCOPh)] (**2**) and [Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl$_2$(NCPh)] (**3**), have been determined by X-ray methods. In addition, the NMR spectrum of **3** has revealed the unprecedented free rotation of the amidine ligand about the azomethine double bond.

Materials and Methods

Starting Materials. Commercial reagent grade chemicals were used without further purification.

cis- and *trans*-[PtCl$_2$(NCPh)$_2$] were first separated and characterized by Uchiyama et al.[5] We have prepared them by a slightly different procedure. According to Hofmann's method,[6] stoichiometric amounts of potassium tetrachloroplatinate(II) (dissolved in the minimum quantity of water) and benzonitrile were stirred at room temperature for 1 week. The yellow precipitate which developed was collected, dried in air, and then dissolved in a small volume of dichloromethane, and the solution was passed through a column of Celite. Evaporation of the solvent under reduced pressure afforded a yellow solid of *cis*- and *trans*-[PtCl$_2$(NCPh)$_2$] in 80% yield. The mixture was extracted several times with small portions of hot benzene, and the solid which was left was determined to be the cis isomer practically pure (60% yield). The first extract with benzene, cooled to room temperature, afforded yellow crystals of the trans isomer (20% yield). The purity of the two compounds was checked by TLC on silica gel by using dichloromethane as eluent.

Preparation of Complexes. [Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl(NCPh)]Cl (1). This compound was prepared from the trans isomer of [PtCl$_2$(NCPh)$_2$] and *N,N'*-di-*tert*-butylethylenediamine, *t*-Bu$_2$en. In a typical experiment 1 mmol of the starting complex was allowed to react with an equimolar amount of the amine in 50 cm^3 of dichloromethane at 10 °C under stirring for 1 day. The filtered solution was reduced to small volume (2-3 cm^3) under reduced pressure, and benzene was added to precipitate a white solid which was collected and dried in air (80% yield). The crude product, recrystallized from chloroform, gives

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Table I. Experimental Data for the X-ray Diffraction Study on the Complexes **2** and **3**

	2	**3**
	$C_{24}H_{35}ClN_4OPt\cdot CH_3OH$	$C_{24}H_{34}Cl_2N_4Pt\cdot {}^1/_2C_6H_5CH_3$
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/a$
a, Å	25.374 (13)	18.090 (10)
b, Å	11.351 (8)	9.376 (4)
c, Å	9.338 (5)	17.297 (7)
β, deg	92.03 (4)	91.76 (4)
V, Å^3	2688 (3)	2932 (2)
Z	4	4
D_{calcd}, g cm^{-3}	1.626	1.564
mol wt	658.15	1381.25
cryst dimens, mm	0.10 × 0.19 × 0.47	0.11 × 0.23 × 0.33
linear absorptn, cm^{-1}	54.01	50.39
diffractometer	Siemens AED	Siemens AED
scan type	$\theta/2\theta$	$\theta/2\theta$
scan speed	3–12°θ/min	3–12°θ/min
scan width	$(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]$ $\{\Delta\theta = [(\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda] \tan\theta\}$	
radiatn, Nb-filtrd Mo Kα, Å	$\lambda = 0.7107$	$\lambda = 0.7107$
2θ range, deg	6–50	6–46
reflctns measd	$\pm h,k,l$	$\pm h,k,l$
std reflcn	1 measd after every 50 reflcns	
unique tot. data	5070	4364
unique osbd data [$I > 2\sigma(I)$]	2890	1684
no. of variables	393	200

colorless crystals of a 1:1 solvate: IR (cm^{-1}) 3370, 3250 (ν_{NH}), 2285 ($\nu_{C\equiv N}$), 1560 ($\nu_{C=N}$), 325 (ν_{PtCl}). Anal. Calcd for $C_{24}H_{34}Cl_2N_4Pt\cdot CHCl_3$: C, 39.3; H, 4.6; Cl, 23.2; N, 7.3. Found: C, 39.5; H, 5.1; Cl, 23.7; N, 7.5.

$[\overline{\mathrm{Pt(NH{=}CPhN\text{-}}t\mathrm{\text{-}BuCH_2CH_2NH}}\mathrm{\text{-}}t\mathrm{\text{-}Bu)Cl(NHCOPh)}]$ (2). This compound was obtained from **1** by the action of base. In a typical experiment 1 mmol of **1** was dissolved in methanol (50 cm^3), and the stoichiometric amount of LiOH, in the same solvent, was added dropwise. The solution was taken to dryness under reduced pressure, and the solid residue was extracted with dichloromethane. Evaporation of the solvent afforded a white solid which was determined to be compound **2** practically pure (90% yield). The crude product can be recrystallized from methanol incorporating one molecule of solvent: IR (cm^{-1}) 3400, 3255 (ν_{NH}), 1570–1550 ($\nu_{C=N}+\nu_{C=O}$), 315 (ν_{PtCl}). Anal. Calcd for $C_{24}H_{35}ClN_4OPt$: C, 46.0; H, 5.6; Cl, 5.7; N, 8.9. Found: C, 45.6; H, 5.7; Cl, 6.3; N, 8.3.

***cis*-$[\mathrm{Pt(NH{=}CPhN\text{-}}t\mathrm{\text{-}BuCH_2CH_2NH\text{-}}t\mathrm{\text{-}Bu)Cl_2(NCPh)}]$ (3).** This compound was obtained from the cis isomer of $[PtCl_2(NCPh)_2]$ and t-Bu$_2$en. Typically 1 mmol of the platinum complex and the equimolar amount of diamine, dissolved in dichloromethane (50 cm^3), were kept under stirring at 10 °C for 1 day. The solution was then filtered to separate a slight amount of side products and concentrated to small volume under reduced pressure, and benzene was added to precipitate a yellow solid (60% yield). This compound is rather unstable and crystals, suitable for X-ray diffraction, were obtained by a fast crystallization performed by adding an upper layer of toluene or benzene to a solution of the compound in chlorinated solvents at a temperature below 15 °C. The yellow crystals incorporate one molecule of aromatic solvent per two molecules of complex: IR (cm^{-1}) a rather peculiar behavior of this compound is the practical absence of bands in the region of ν_{NH} and the presence of only a very weak absorption at 2280 assignable to $\nu_{C\equiv H}$; other significant bands are at 1565 ($\nu_{C\equiv N}$), 345, 325 (ν_{PtCl}). Anal. Calcd for $C_{24}H_{34}Cl_2N_4Pt$: C, 44.7; H, 5.3; Cl, 11.0; N, 8.7. Found: C, 44.6; H, 5.8; Cl, 10.7; N, 8.4.

$[\overline{\mathrm{Pt(NH{=}CPhN\text{-}}t\mathrm{\text{-}BuCH_2Ch_2NH}}\mathrm{\text{-}}t\mathrm{\text{-}Bu)Cl_2}]$ (4). This compound is obtained from **3** by release of a benzonitrile molecule. From a solution of **3**, on standing at room temperature, compound **4** is formed and precipitates out owing to its low solubility in common organic solvents. The rate of transformation is very much dependent upon the nature of the solvent; the reaction is almost instantaneous in acetone or isopropyl ketone and rather fast if a few drops of water are added to a solution in dry chloroform. The transformation of **3** into **4** takes place also in the solid state and can be followed by running from time-to-time the IR spectrum of the compound in KBr pellet: IR (cm^{-1}) 3210, 3170 (ν_{NH}), 1570 ($\nu_{C=N}$), 330, 320 (ν_{PtCl}). Anal. Calcd for $C_{17}H_{29}Cl_2N_3Pt\cdot {}^1/_2(CH_3)_2CO$: C, 38.9; H, 5.6; Cl, 12.4; N, 7.4. Found: C, 38.8; H, 5.8; Cl, 12.2; N, 7.2.

X-ray Crystallography. A prismatic colorless crystal of **2** and a prismatic pale yellow crystal of **3** were selected for the X-ray analyses. The crystallographic data for both complexes are given in Table I. Unit-cell parameters were obtained by least-squares refinement of the θ values (in the range 10–15°) of 27 (**2**) and 24 (**3**) carefully centered reflections chosen from different regions of the reciprocal space. Data were collected at room temperature, the individual reflection profiles having been analyzed following Lehmann and Larsen.[7] The structure amplitudes were obtained after usual Lorentz and polarization reduction.[8] A correction for absorption effects was applied (maximum and minimum transmission factor values 1.2527 and 0.8567 for **2** and 1.1589 and 0.7355 for **3**).[9] Only the observed reflections were used in the structure solution and refinement.

Both structures were solved by using conventional Patterson and Fourier techniques and refined by full matrix least squares. The difference electron-density map showed an additional molecule of solvation in **2** (CH_3OH) and **3** ($C_6H_5CH_3$) (this last is disordered and distributed in two centrosymmetrically related positions of equal occupancy factors). In the last cycles of refinement anisotropic thermal parameters were used for all the non-hydrogen atoms (except those of the *tert*-butyl groups and of the solvent molecule) of **2** and for Pt, Cl, N, and C(1)–C(4) atoms of **3**. All hydrogen atoms except those of the methanol of **2** were located in the final difference Fourier maps and refined isotropically. It was not possible to locate clearly the positions of all the hydrogen atoms of **3**, so they were placed at their geometrically calculated positions and included in the final structure calculations with fixed isotropic thermal parameters (B = 7.0 Å^2). The function minimized during the refinements was $\sum w|\Delta F|^2$. The weighing scheme used in the last cycles was $w = K/[\sigma^2(F_o) + gF_o^2]$; at convergence the values for K and g were 0.7039 and 0.005 for **2** and 0.7181 and 0.004 for **3**. The final R and R_w values were 0.039 and 0.048 for **2** and 0.053 and 0.064 for **3** ($R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$). The scattering factors were taken from ref 10 with the exceptions of those of the hydrogen atoms which were taken from ref 11. Corrections for the real and imaginary components of the anomalous dispersion were made for Pt and Cl atoms.[10] Final atomic coordinates for **2** are listed in Tables II and SI and for **3** in Tables III and SII; thermal parameters for **2** and **3** are given in Tables SIII and SIV, respectively.

Physical Measurements. IR spectra in the range 4000–400 cm^{-1} were recorded as KBr pellets; spectra in the range 400–200 cm^{-1} were recorded as polythene pellets on a Perkin Elmer 683 spectrophotometer. ^{1}H NMR spectra were obtained with a Varian XL 200 spectrometer. Conductivity measurements were performed in nitromethane by using a Halosis SAT bridge.

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Table II. Fractional Atomic Coordinates (×10^4)[a]

atom	X/A	Y/B	Z/C
Pt	3975 (1)	4276 (1)	5314 (1)
Cl	4340 (1)	4620 (2)	3108 (3)
O(1)	2950 (3)	2469 (7)	5893 (8)
N(1)	3674 (3)	3964 (7)	7286 (9)
N(2)	4318 (3)	5737 (7)	6100 (9)
N(3)	3612 (3)	6946 (7)	6684 (9)
N(4)	3610 (3)	2875 (8)	4398 (9)
C(1)	3488 (5)	5054 (10)	7994 (12)
C(2)	3264 (4)	5936 (9)	6930 (15)
C(3)	4132 (4)	6746 (9)	6460 (11)
C(4)	3178 (4)	2309 (9)	4728 (11)
C(5)	2947 (4)	1457 (9)	3636 (11)
C(6)	3206 (5)	1033 (11)	2528 (13)
C(7)	2981 (7)	220 (13)	1570 (17)
C(8)	2476 (6)	−120 (12)	1718 (16)
C(9)	2191 (7)	313 (13)	2814 (18)
C(10)	2426 (5)	1099 (11)	3817 (15)
C(11)	4527 (4)	7657 (9)	6868 (12)
C(12)	4572 (5)	8028 (11)	8277 (14)
C(13)	4954 (6)	8821 (14)	8746 (20)
C(14)	5288 (6)	9282 (13)	7755 (21)
C(15)	5270 (6)	8886 (12)	6344 (22)
C(16)	4893 (4)	8079 (10)	5911 (14)
C(17)	4019 (4)	3196 (10)	8320 (11)
C(18)	4134 (6)	2036 (13)	7595 (16)
C(19)	3721 (6)	2914 (15)	9666 (16)
C(20)	4542 (6)	3808 (16)	8735 (19)
C(21)	3338 (5)	8125 (10)	6401 (15)
C(22)	3157 (7)	8645 (15)	7797 (17)
C(23)	3674 (6)	9018 (13)	5650 (16)
C(24)	2862 (8)	7920 (19)	5389 (21)
O(2)	1005 (7)	1659 (17)	4021 (21)
C(25)	1014 (8)	2553 (21)	2992 (24)

[a] esd's are in parentheses for the non-hydrogen atoms of compound **2**.

Results and Discussion

General Description of the Reactions and Products. The reactions of *trans*- and *cis*-[PtCl$_2$(NCPh)$_2$] with *N*,*N'*-di-*tert*-butylethylenediamine, *t*-Bu$_2$en, were performed in dichloromethane at 10 °C and were complete in 1 day, and the products were isolated by concentration to small volume and addition of benzene. The trans isomer afforded a white solid which was recrystallized from chloroform to give colorless crystals of **1** in 80% yield. Neutralization (LiOH) of a methanol solution of this compound develops a new species, **2**. The formula and molecular structures of **1**, $[\overline{\text{Pt(NH=CPhN-}t\text{-BuCH}_2\text{CH}_2\text{N}}\text{H-}t\text{-Bu)Cl(NCPh)]Cl}$, and **2**, $[\overline{\text{Pt(NH=CPhN-}t\text{-BuCH}_2\text{CH}_2\text{N}}\text{H-}t\text{-Bu)Cl(NHCOPh)]}$, were deduced from analytical data, IR and NMR spectra, and conductivity measurements; that of **2** was also confirmed by single-crystal X-ray analysis on its methanol solvate.

Both compounds contain a seven-membered metallacycle made of a *N*-*tert*-butyl, *N*-(2-(*tert*-butylamino)ethyl)benzamidine ligand cis-chelated to platinum. The reaction course can be described as (i) nucleophilic attack of one end of *t*-Bu$_2$en to the cyanide carbon atom of a coordinate benzonitrile and (ii) substitution of a cis chloride ion by the second end of *t*-Bu$_2$en to form a metallacycle.

It is noticeable that while one end of *t*-Bu$_2$en (a secondary and sterically hindered amine) adds smoothly to a coordinate benzonitrile, the second end does not react with the other nitrile to form a trans-bonding nine-membered chelate spanning over the platinum (any effort to isolate such a species has been unsuccessful) but, instead, coordinates to the metal to give a rather unusual and sterically unfavored seven-membered chelate.[12]

The remaining benzonitrile in **1** is very susceptible to nucleophilic attack and reacts readily with base to give an amidate species (compound **2**).[13] Such an enhanced reactivity of benzonitrile is unprecedented in platinum complexes of this sort and probably stems from an electrostatic attraction between the positively charged substrate and the incoming nucleophile. This result also supports the hypothesis that the key step of catalysis in the hydration of nitriles is the attack of the hydroxide ion on a cationic metal–nitrile intermediate.[14]

Table III. Fractional Atomic Coordinates (×10^4)[a]

atom	X/A	Y/B	Z/C
Pt	632 (1)	2470 (2)	2563 (1)
Cl(1)	924 (4)	4606 (8)	3146 (4)
Cl(2)	−367 (3)	3444 (8)	1952 (4)
N(1)	−899 (11)	−930 (25)	2687 (12)
N(2)	323 (10)	543 (23)	2131 (11)
N(3)	451 (11)	−1670 (23)	1550 (12)
N(4)	1495 (9)	1610 (24)	3062 (11)
C(1)	−764 (15)	−2190 (31)	2211 (19)
C(2)	104 (13)	−2378 (45)	2167 (13)
C(3)	674 (13)	−211 (29)	1644 (14)
C(4)	1988 (14)	1204 (29)	3389 (14)
C(5)	2638 (14)	549 (32)	3775 (15)
C(6)	3297 (13)	552 (28)	3496 (14)
C(7)	3906 (16)	45 (35)	3859 (18)
C(8)	3851 (19)	−488 (39)	4593 (19)
C(9)	3156 (18)	−500 (38)	4990 (18)
C(10)	2504 (15)	89 (32)	4555 (17)
C(11)	1380 (12)	319 (28)	1359 (13)
C(12)	1402 (14)	1599 (33)	991 (15)
C(13)	2084 (16)	2112 (31)	707 (16)
C(14)	2698 (20)	1407 (47)	920 (21)
C(15)	2731 (16)	120 (35)	1305 (17)
C(16)	2016 (15)	−528 (32)	1517 (15)
C(17)	−1726 (14)	−489 (32)	2707 (15)
C(18)	−1694 (19)	770 (41)	3223 (21)
C(19)	−1940 (21)	2 (44)	1907 (23)
C(20)	−2168 (18)	−1760 (40)	3027 (18)
C(21)	590 (12)	−2450 (45)	819 (12)
C(22)	1185 (15)	−3631 (34)	924 (15)
C(23)	−192 (14)	−3155 (29)	592 (14)
C(24)	784 (13)	−1517 (29)	106 (13)
C(25)[b]	4913 (40)	4016 (66)	4496 (45)
C(26)	5400 (20)	5147 (42)	4344 (20)
C(27)	5411 (20)	6395 (42)	4784 (21)
C(28)[b]	5796 (37)	7590 (54)	4554 (36)
C(251)[b]	4993 (36)	6415 (64)	5466 (30)

[a] esd's are in parentheses for the non-hydrogen atoms of the compound **3**. [b] These atoms have an occupancy factor of 0.5.

Under strictly analogous reaction conditions the cis isomer of [PtCl$_2$(NCPh)$_2$] gives a pale yellow compound, **3**, in 60% yield. This compound is rather unstable and either in the solid (KBr pellet) or in solution decomposes releasing one molecule of benzonitrile and forming a new compound, **4**. The formula and molecular structures of **3**, *cis*-[Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl$_2$(NCPh)], and **4**, *cis*-[Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl$_2$], were also deduced from elemental analysis, IR and NMR spectra, and X-ray diffraction data on the toluene solvate of **3**. The former complex contains a monodentate, the latter a chelate amino–amidine ligand. It is noticeable that starting with the cis isomer it has been possible to separate the addition of one end of *t*-Bu$_2$en to one benzonitrile (**3**) from the coordination of the second end to platinum (**4**) in spite of the fact that in this case the ligand to be displaced is a benzonitrile generally considered to be labile.

The isolation of compound **3** also indicates that coordination of the nucleophile to the metal is not a prerequisite for its addition to a nitrile group.[15]

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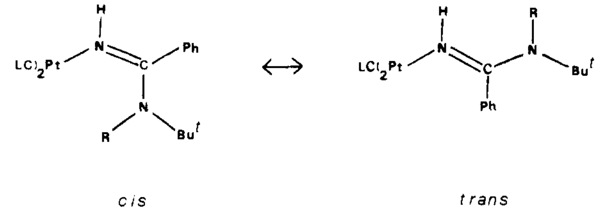
Table IV. Proton Chemical Shifts (δ, ppm Downfield from $SiMe_4$) of Complexes **1**, **2**, and **3**[a]

complex	solvent	temp/°C	HN(1)[b]	*t*-BuN (1)	H_2C (1)	H_2C (2)	*t*-BuN (3)	HN (2)	HN (4)
1	CD_2Cl_2	+20	9.32 (80)	1.18	3.70, 2.62	5.68, 4.12	1.40	6.08	
2	CD_2Cl_2	+20	11.32 (97)	1.17	3.45, 2.72	5.93, 3.85	1.36	6.40	5.73
3	CD_2Cl_2	+20		1.05	2.68	3.31	1.30	8.32	
		−60		1.14	2.77	3.33	0.95	10.75	
				1.05	2.44	3.11	1.35	5.94	
	$CDCl_3$	+35		1.05	2.67	3.34	1.40	8.25	
		−50		1.16	2.83	3.40	1.00	10.77	
				0.95	2.47	3.14	1.52	6.13	

[a] Numbering of ligand atoms as in Figures 1 and 2.
[b] Values of *J*(Pt–H) in Hz are given in parentheses.

Scheme I



NMR Spectra. The NMR spectra of **1** and **2** are characteristic of compounds with a cis-chelate amino–amidine ligand, Table IV. The most peculiar feature is a large separation of the ethylene-proton resonances of the diamine which are spread over a range of 3 ppm. The reason for this is to be found in a rather static conformation of the seven-membered metallacycle which keeps these protons in fixed positions with respect to the metal center so that they feel very different magnetic environments. No significant spectral changes are observed by lowering the temperature from 20 to −60 °C.

On the contrary, compound **3**, which contains a monocoordinate amino–amidine ligand, exhibits a very different resonance pattern for the ethylene protons with signals grouped in two triplets 0.63 ppm apart one from the other. An unusual feature of the room-temperature spectrum of this compound is a very broad resonance attributable to the iminic proton which is ca. 2 ppm downfield with respect to the corresponding resonance in compounds **1** and **2**. Lowering the temperature the spectrum splits into two sets of signals, of unequal intensity (ca. 10:1 in CD_2Cl_2, 2:1 in $CDCl_3$), one (the less intense) having a proton resonance in the region of the iminic proton of **1** and **2** and the other (the more intense) having a proton resonance ca. 4.5 ppm downfield. These data are in accord with the presence, in solution, of two isomers: one having the iminic proton cis to the phenyl group with respect to the C═N double bond (as found in **1** and **2**) and the other having the iminic proton and the phenyl radical trans to each other (Scheme I). The two isomers can interconvert one into the other, and the activation energy ($\Delta G^{\ddagger}_{223}$) for this process was calculated to be 10.8 ± 0.3 kcal mol^{-1} in chloroform. A spontaneous isomerization of amidines about the C═N double bond has not been reported previously and is reminiscent of the isomerization about the C═N double bond observed in platinum-coordinate hydrazones.[16] In both cases the organic moiety contains an aminic nitrogen adjacent to a C═N π-system. Further discussion about the amidine group is detailed in a later section of this paper concerned with structural data.

It is finally to be noted that a broadened singlet at ca. 9.1 ppm attributable to an iminic proton was observed in *trans*-[Pt{NH═C(OMe)(C_6F_5)}(PH_3)(PMe_2Ph)$_2$] and other strictly related complexes which also could be indicative of a similar cis–trans interconversion process taking place.[17]

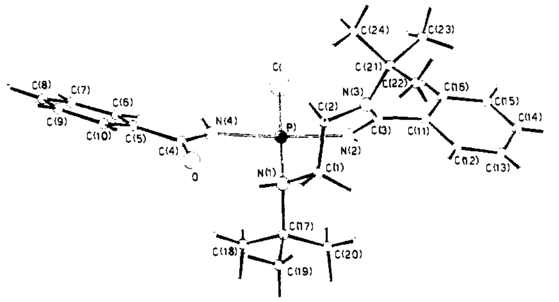


Figure 1. Molecular structure of the complex [Pt(NH═CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl(NHCOPh)] (**2**).

Table V. Selected Bond Distances (Å) and Angles (deg) in Complex **2**

	Distances		
Pt–Cl	2.321 (3)	C(17)–C(20)	1.54 (2)
Pt–N(1)	2.049 (8)	C(21)–C(22)	1.52 (2)
Pt–N(2)	2.000 (8)	C(21)–C(23)	1.51 (2)
Pt–N(4)	2.015 (9)	C(21)–C(24)	1.52 (2)
N(1)–C(1)	1.487 (14)	C(11)–C(12)	1.38 (2)
C(1)–C(2)	1.507 (16)	C(12)–C(13)	1.38 (2)
C(2)–N(3)	1.470 (13)	C(13)–C(14)	1.38 (2)
N(3)–C(3)	1.362 (13)	C(14)–C(15)	1.39 (3)
N(2)–C(3)	1.288 (13)	C(15)–C(16)	1.37 (2)
N(1)–C(17)	1.549 (13)	C(11)–C(16)	1.40 (2)
C(3)–C(11)	1.480 (14)	C(5)–C(6)	1.33 (2)
N(3)–C(21)	1.527 (14)	C(6)–C(7)	1.39 (2)
N(4)–C(4)	1.316 (13)	C(7)–C(8)	1.35 (2)
C(4)–O	1.263 (13)	C(8)–C(9)	1.37 (2)
C(4)–C(5)	1.509 (14)	C(9)–C(10)	1.41 (2)
C(17)–C(18)	1.51 (2)	C(5)–C(10)	1.40 (2)
C(17)–C(19)	1.52 (2)		
	Angles		
Cl–Pt–N(2)	90.2 (3)	C(2)–N(3)–C(21)	116.0 (8)
N(1)–Pt–N(2)	89.1 (3)	C(3)–N(3)–C(21)	123.8 (8)
N(1)–Pt–N(4)	93.7 (3)	N(3)–C(3)–N(2)	123.6 (9)
Cl–Pt–N(4)	87.0 (3)	N(3)–C(3)–C(11)	119.6 (9)
Pt–N(1)–C(1)	112.9 (6)	N(2)–C(3)–C(11)	115.9 (9)
Pt–N(1)–C(17)	115.9 (6)	Pt–N(2)–C(3)	132.4 (7)
C(1)–N(1)–C(17)	111.9 (8)	Pt–N(4)–C(4)	131.3 (7)
N(1)–C(1)–C(2)	112.2 (9)	N(4)–C(4)–O	122.8 (9)
C(1)–C(2)–N(3)	114.0 (9)	N(4)–C(4)–C(5)	117.5 (9)
C(2)–N(3)–C(3)	119.0 (8)	C(5)–C(4)–O	119.7 (9)

The very poor solubility of **4** in suitable solvents prevented solution studies of this compound which, however, can be expected to give a NMR spectrum similar to those of **1** and **2**.[18]

Description of the Structure of Compound 2. In the crystals of **2** two enantiomeric species with opposite absolute configuration at the aminic nitrogen, N(1), are present. They are related by the glides or by the centers of symmetry. The structure of one of them [with *R* configuration at N(1)] is shown in Figure 1 together with the atomic labeling scheme. Selected bond distances

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(18) The structure of compound 4 has also been confirmed by X-ray crystallography showing a conformation of the amino–amidine ligand completely similar to that of compound 2.

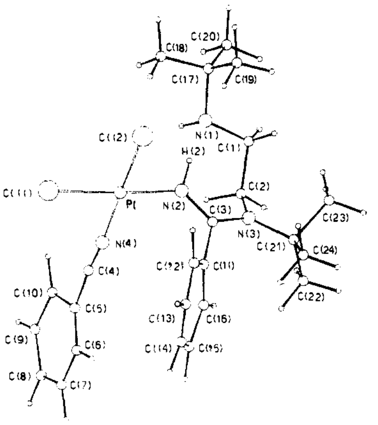


Figure 2. Molecular structure of the complex *cis*-[Pt(NH=CPhN-*t*-BuCH$_2$CH$_2$NH-*t*-Bu)Cl$_2$(NCPh)] (3).

and angles are listed in Table V. The coordination of platinum is roughly planar and involves a chlorine atom and three nitrogen atoms, two from the chelating amino–amidine ligand, N(1) and N(2), and one from the benzamidate anion, N(4). Pt, Cl, N(1), N(2), and N(4) are displaced from the mean plane passing through them by -0.001 (3), -0.007 (3), -0.049 (8), 0.053 (8), and 0.057 (8) Å, respectively. Bond lengths and angles in the coordination sphere are quite regular and comparable with those found in other complexes of platinum.[19] The Pt–N(1) bond is slightly longer than Pt–N(2) and Pt–N(4) reflecting the different hybridization of the donor atoms. The "bite" angle of the chelating ligand, 89.1 (3)°, is considerably larger than those usually found in complexes with bidentate ligands and is very close to the expected value of 90°. This appears to be a characteristic of the seven-membered metallacycles[20] which are less strained than six- and five-membered rings.[21]

The rather short N(3)–C(3) bond [1.362 (13) Å] and the planarity of the aminic group at N(3) [deviations of N(3), C(2), C(3), and C(21) from the mean plane through them are -0.05 (1), 0.04 (1), 0.03 (1), and 0.05 (1) Å, respectively] suggest extensive electron delocalization within the amidine moiety.[22] Consequently, the N(2)C(3)N(3)C(2) torsion angle is of only 18 (1)° although this inevitably causes some sterical repulsion between the adjacent phenyl and *tert*-butyl groups. The electron delocalization does not involve the phenyl group which is slant [80.7 (5)°] against the amidine plane.

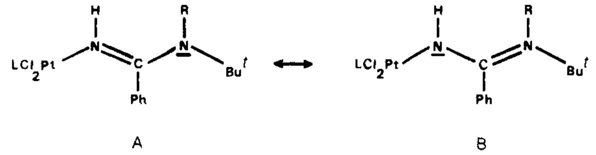
The conformation of the seven-membered chelate ring is determined by the requirements of planarity of the amidine moiety vis-à-vis the tetrahedral amine group. The substituents at the ethylene carbons [C(1) and C(2)] occupy eclipsed rather than staggered positions, and one hydrogen atom is held in near proximity of platinum [Pt···H(22) = 2.61 (15) Å]. The torsion angles around the bonds in the main chain of the chelating ligand [N(1)–C(1)–C(2)–N(3)–C(3)–N(2), Figure 1] are 34 (1), -105 (1), 46 (1), 18 (1), and 16 (2)°, respectively, and the conformation of the ring can be indicated as g$^+$, g$^-$, g$^+$, g$^+$, g$^+$.[23]

It is interesting to note that the *tert*-butyl group at N(1) and the chelate ring system are always on opposite sides with respect to the coordination plane. Therefore different absolute configuration at the coordinate nitrogen, *R* or *S*, is associated with opposite conformation of the ring, g$^+$, g$^-$, g$^+$, g$^+$, g$^+$ or g$^-$, g$^+$, g$^-$, g$^-$, g$^-$, respectively.

Table VI. Selected Bond Distances (Å) and Angles (deg) in Complex **3**

	Distances		
Pt–Cl(1)	2.296 (8)	C(17)–C(20)	1.55 (5)
Pt–Cl(2)	2.258 (6)	C(21)–C(22)	1.55 (4)
Pt–N(2)	2.03 (2)	C(21)–C(23)	1.60 (4)
Pt–N(4)	1.94 (2)	C(21)–C(24)	1.56 (4)
N(2)–C(3)	1.28 (3)	C(11)–C(12)	1.36 (4)
C(3)–N(3)	1.43 (3)	C(12)–C(13)	1.43 (4)
N(3)–C(2)	1.42 (3)	C(13)–C(14)	1.33 (5)
C(1)–C(2)	1.58 (4)	C(14)–C(15)	1.38 (5)
C(1)–N(1)	1.46 (4)	C(15)–C(16)	1.49 (4)
C(3)–C(11)	1.47 (3)	C(11)–C(16)	1.42 (4)
N(3)–C(21)	1.49 (3)	C(5)–C(6)	1.30 (4)
N(1)–C(17)	1.55 (3)	C(6)–C(7)	1.34 (4)
N(4)–C(4)	1.11 (3)	C(7)–C(8)	1.37 (4)
C(4)–C(5)	1.47 (4)	C(8)–C(9)	1.45 (5)
C(17)–C(18)	1.48 (5)	C(9)–C(10)	1.49 (4)
C(17)–C(19)	1.50 (5)	C(5)–C(10)	1.44 (4)
C(17)–C(20)	1.55 (5)		
	Angles		
Cl(1)–Pt–Cl(2)	91.3 (3)	C(2)–N(3)–C(3)	119 (2)
Cl(1)–Pt–N(4)	89.8 (6)	C(2)–N(3)–C(21)	120 (2)
N(2)–Pt–N(4)	90.1 (8)	C(3)–N(3)–C(21)	121 (2)
Cl(2)–Pt–N(2)	88.9 (6)	C(1)–C(2)–N(3)	116 (2)
Pt–N(2)–C(3)	127 (2)	N(1)–C(1)–C(2)	107 (2)
N(2)–C(3)–N(3)	117 (2)	C(17)–N(1)–C(1)	114 (2)
N(2)–C(3)–C(11)	119 (2)	Pt–N(4)–C(4)	174 (2)
N(3)–C(3)–C(11)	122 (2)	N(4)–C(4)–C(5)	175 (3)

Scheme II



The benzamidate anion is characterized by a rather large electron delocalization involving also the phenyl radical which makes an angle of 16.1 (4)° with the carboxamido group. On the other hand, the plane of carboxamido is not perpendicular to that of coordination, as expected on the basis of minimum sterical interaction with the cis ligands, but instead makes with it an angle of 19.7 (3)° which allows the formation of a rather strong intramolecular hydrogen bond with the cis amine group [N(1)···O = 2.789 (11) Å, N(1)–H(1)–O = 141 (12)°].

Description of the Structure of Compound 3. This complex was present in solution in two isomeric forms, the more abundant isomer appearing to have a different conformation of the amidine group than compounds **1** and **2**, that is the iminic proton trans to the phenyl group with respect to the azomethine double bond. Since the more stable conformation in solution could also be the preferred one in the solid state, we have undertaken a crystallographic investigation of this complex which could eventually support the given interpretation of the solution behavior. The results have been in accord with our expectations.

The molecular structure is shown in Figure 2 together with the atomic labeling scheme. Selected bond distances and angles are listed in Table VI.

The amino–amidine ligand is monocoordinated and bound to platinum through the iminic nitrogen, N(2). A nitrogen atom, N(4), from a benzonitrile molecule and two chlorine atoms complete the square-planar coordination of platinum [displacements of Pt, Cl(1), Cl(2), N(2), and N(4) from the mean plane through them are as follows: 0.003 (2), -0.020 (7), 0.004 (7), -0.15 (2), and 0.04 (2) Å, respectively].

The bond lengths and angles in the coordination sphere of platinum are regular and comparable with those found in compound **2**. The Pt–N bond distance of benzonitrile is slightly shorter

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[23] Dale, J. *Isr. J. Chem.* **1980**, *20*, 3–11. g$^+$ and g$^-$ indicate gauche conformations (torsion angles of 0° to +120° and 0° to -120°).

than that of the amino–amidine ligand also reflecting the different hybridization of the donor atoms.

Also in compound **3**, as already observed in **2**, the strict planarity of the aminic group at N(3) and the small value of the C(2)N(3)C(3)N(2) torsion angle [−26 (3)°] point to an extensive electron delocalization within the amidine group. Thus, according to the valence-bond theory, the amidine moiety can be described in terms of canonical forms A and B, Scheme II. In form B, which might also be stabilized by coordination to the metal, the N(2)–C(3) linkage has a single bond character which could account for the low energy of the cis–trans interconversion process. The phenyl group is slant [75 (1)°] against the amidine plane, probably because of steric interaction with the adjacent *tert*-butyl group, and does not contribute to the electron delocalization.

It is noteworthy that the free and coordinate ends of the amino–amidine ligand are linked together by a strong hydrogen bond [N(1)···N(2) = 2.80 (3) Å, N(2)–H(2)–N(1) = 167°] in such a way to form a pseudo-seven-membered ring which can be compared with the seven-membered metallacycle of compound **2** with a proton taking the place of platinum.

This finding gives a clue to the different isomerization about the C(3)=N(2) double bond observed in **3** as compared with **2**. In fact the two different conformations allow the platinum in **2** and the H(2) proton in **3** to come near to the aminic nitrogen [N(1)] and act as a ligating atom to close the seven-membered ring. This also indicates that the ligand molecule has a rather strong tendency to give such a cyclic structure which appears to be preferred either in the solid state or in solution.

The plane of the benzonitrile is nearly perpendicular to that of coordination [dihedral angle of 92 (1)°] as expected on the basis of steric interactions with cis ligands.

Conclusions

The reaction of a bidentate amine with *cis*- and *trans*-[$PtCl_2(NCPh)_2$] has shown that this very common substrate reacts readily with nucleophiles and the attack of one end of the diamine to a coordinate benzonitrile precedes the coordination of the second end to platinum. The monocoordinated amino–amidine ligand, formed in the first step of the reaction, undergoes cis–trans isomerization about the azomethine double bond and exhibits a strong tendency to form a seven-membered cyclic system either through formation of a strong hydrogen bond between the terminal aminic nitrogen and the platinum-bonded iminic nitrogen of amidine or through coordination of both ends to platinum.

Starting with *trans*-[$PtCl_2(NCPh)_2$] the formation of a chelating amino–amidine ligand leads to a cationic complex, still bearing a coordinate benzonitrile, which reacts readily with base to give a benzamidate species. The benzamidate anion forms a strong hydrogen bond with the cis aminic group and slants on the coordination plane.

Acknowledgment. This work has been supported by the Consiglio Nazionale delle Ricerche (C.N.R.) and Ministero della Pubblica Istruzione (M.P.I.) Rome and by the University of Parma.

Registry No. 1, 99727-69-2; **2**·CH_3OH, 99727-71-6; **3**·$^1/_2C_6H_5CH_3$, 99727-73-8; **4**, 89503-95-7; *trans*-[$PtCl_2(NCPh)_2$], 51921-56-3; *cis*-[$PtCl_2(NCPh)_2$], 15617-19-3; *t*-Bu_2en, 4062-60-6; benzonitrile, 100-47-0.

Supplementary Material Available: Listings of observed and calculated structure factors, hydrogen coordinates (Tables SI and SII), and thermal parameters (Tables SIII and SIV) (31 pages). Ordering information is given on any current masthead page.

Deprotonation and Anionic Rearrangements of Organometallic Compounds. 5. Kinetic vs. Thermodynamic Deprotonation in Reactions of Cyclopentadienylrhenium Acyl and Alkyl Complexes with Strong Bases

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Received August 5, 1985

Abstract: Reaction of (η^5-C_5H_5)Re(NO)(PPh_3)(COR) (**1a**, R = CH_3; **1b**, R = $CH_2C_6H_5$; **1c**, R = C_6H_5; **1d**, R = H) with $Li^{+}\,{}^{-}N(CH(CH_3)_2)_2$ (LDA; THF, −78 °C) and then CH_3I gives (η^5-C_5H_4COR)Re(NO)(PPh_3)(CH_3) (**2a–d**, 50–78%). Deuterium-labeling experiments indicate that **1** is initially deprotonated to (η^5-C_5H_4Li)Re(NO)(PPh_3)(COR) (**3**), and ^{31}P NMR shows a subsequent rapid rearrangement (**3a**: <3 min, −95 °C) to Li^+ [(η^5-C_5H_4COR)Re(NO)(PPh_3)]$^-$ (**4**). Crossover experiments show **3** → **4** to be intramolecular. Reaction of (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) with *n*-BuLi/TMEDA (−78 °C, 5 min) gives (η^5-C_5H_4Li)Re(NO)(PPh_3)($CH_2C_6H_5$) (**6**), which does not rearrange upon warming and yields (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)($CH_2C_6H_5$) (**7**, 74%) upon addition of CH_3I. When (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) ((+)-(*S*)-**8**, >98% ee) is treated with *n*-BuLi/TMEDA and then $(RCO)_2O$ (R = CH_3, $C_6H_5CH_2$, C_6H_5), (−)-(*S*)-**2a**, (−)-(*S*)-**2b**, and (−)-(*S*)-**2c**, all ≥98% ee, are obtained. Experiments with optically active **1** then show that **3a** → **4a** proceeds with >90% retention of configuration at rhenium and that **3b** → **4b** and **3c** → **4c** proceed with lesser degrees of retention and inversion, respectively. Pentamethylcyclopentadienyl complexes (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH_2R$) (**10a**, R = H; **10b**, R = C_6H_5) and *n*-BuLi react to give enolates Li^+(η^5-C_5Me_5)Re(NO)(PPh_3)(C(O^-)=CHR), which yield (η^5-C_5Me_5)Re(NO)(PPh_3)(COCH(R)CH_3) (72–82%) when treated with CH_3I. When **1b** is treated with the weaker base $Li^{+}\,{}^{-}N(Si(CH_3)_3)_2$, *E*-enolate Li^+(η^5-C_5H_5)-Re(NO)(PPh_3)(C(O^-)=CHC_6H_5 (**17**) forms and gives (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)(COCH(C_6H_5)CH_3) ((*SR,RS*)-**16**) with 96% diastereoselectivity when treated with CH_3I. The factors controlling the stereoselectivity and site of deprotonation in these reactions, and the relationship of **3** → **4** to anionic organic rearrangements, are discussed.

Carbanions generated by the deprotonation of ligands of organometallic complexes are seeing increased applications in organic and organometallic synthesis.[1-3] For example, over the last few years a number of research groups have reported the generation

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