Hetarylamidines derived from Pt^{IV}-mediated coupling of nitriles with aminoheterocycles

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The *trans*-$[PtCl_4(EtCN)_2]$ complex is involved in coupling reactions (CH_2Cl_2, 30—35 °C, 10—15 min) with 2-amino derivatives of heterocyclic compounds (2-NH_2Het, where Het is pyridyl, 4-methylpyridyl, 5-methylpyridyl, 6-methylpyridyl, or thiazolyl) to form the *trans*-$[PtCl_4\{\underline{N}(H)=C(Et)NHHet\}_2]$ complexes (**1—5**) with $\kappa^1(N)$-coordinated hetarylamidine ligands. The reaction with the use of 2-aminopyrimidine (2-NH_2Pym) produces the $[PtCl_4(2\text{-}NH_2Pym)_2]$ complex (**6**) as a result of complete replacement of the nitrile ligands in the $[PtCl_4(EtCN)_2]$ complex. The compositions and structures of compounds **1—6** were confirmed by elemental analysis (C, H, N), IR spectroscopy, ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectroscopy, and FAB mass spectrometry. Complex **1** was additionally characterized by X-ray diffraction.

Key words: coordinated nitriles, ligand reactivity, aminoazoles, aminoazines, amidines.

In the last two decades, the chemistry of complexes of virtually all metals with amidine ligands has attracted considerable interest.[1,2] First, this is associated with the diversity of coordination modes of amidines and amidinates, due to which their complexes are convenient models for solution of different structural and stereochemical problems. Second, these compounds can be employed as catalysts for olefin polymerization[3] and methyl methacrylate polymerization,[4] as well as in Suzuki—Miyaura cross-coupling reactions.[5]

There are two main procedures for the synthesis of amidine-containing coordination compounds.[1,2] One method is based on the direct reaction of a salt or a complex of a particular metal with the starting amidine ($R^1C(NHR^2)=NR^3$). This reaction most often produces amidinate complexes[2,6—8] and much more rarely affords nondeprotonated amidine metal derivatives.[1,9—13] Another approach to the synthesis of amidine complexes is based on the nucleophilic addition of various NH-containing compounds (for example, of primary or secondary amines, diamines, aziridine, amino alcohols, or amino acid esters[14—17]) to coordinated nitriles or generation of amidine ligands in the metal-mediated transformations involving the above-mentioned amino-containing nucleophiles in nitrile media. These reactions readily proceed if nitrile substrates are coordinated to metal centers, such as Co^{III},[18] Cu^{I},[19] Rh^{III},[20] W^{II},[21] Re^{IV},[22] Ir^{I},[23] Pt^{II}, or Pt^{IV}.[24—26]

Amino derivatives of heterocycles have found limited use in metal-mediated reactions.[27—30] This is apparently associated with the fact that most of reactions of metal salts with aminoheterocycles stop at complexes, in which amino ligands are coordinated by the endocyclic nitrogen atom.[31—34] The aim of the present study was to investigate the coupling between 2-aminoheterocycles and propionitriles activated through coordination to the Pt^{IV} center to form hetarylamidine ligands.

Results and Discussion

The reactions of metal salts (Cu^{II},[27] Co^{II},[28,29] Ni^{II},[28] and Pt^{II} (see Ref. 30)) at elevated temperatures and/or under microwave irradiation in nitrile media in the presence of various aminoheterocycles (2-amino-5,5-

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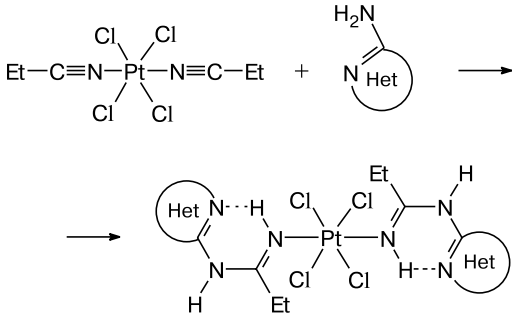
diphenylimidazolin-4-one,[27] 2,6-diaminopyridine,[28,29] 9-methyladenine,[30] or 1-methylcytosine[30]) afforded compounds of the general formula $[MX_2\{\underline{N}(H)=C(R)\underline{N}(H)Het\}]$ with *N,N*-bidentate hetarylamidine ligands. These complexes were isolated and structurally characterized. Even additional activation of the system with microwave irradiation did not lead to the formation of coupling products starting from monoamino derivatives of pyridines.[29] In the present study, we demonstrated that propiononitrile, which is electrophilically activated through coordination to Pt^{IV} in the *trans*-$[PtCl_4(EtCN)_2]$ complex under mild conditions (30—35 °C) in anhydrous (to prevent hydrolysis of the starting platinum complex) dichloromethane, is involved in nucleophilic addition reactions with a number of 2-aminoheterocyclic derivatives, including monoaminopyridines. These reactions produced the hetarylamidine complexes *trans*-$[PtCl_4\{\underline{N}H=C(Et)NHHet\}_2]$ (**1—5**) (Scheme 1). In all cases, the reaction time was 10—15 min, and the yields of compounds **1—5** were 52—67%. An attempt to perform the coupling reaction of propiononitrile with aminoheterocycles in the absence of a platinum center (refluxing of aminoheterocycles in propiononitrile for 48 h) failed. This is evidence for the metal-mediated character of the reaction.

Scheme 1



The reaction with 2-aminopyrimidine is accompanied by the replacement to form the $[PtCl_4(2\text{-}NH_2Pym)_2]$ complex (**6**), in which the heterocyclic ligand is coordinated at one of the nitrogen atoms of the pyrimidine ring.[31—33]

The elemental analysis data for compounds **1—5** are consistent with the calculated data for the complexes of composition $[PtCl_4\{\underline{N}(H)=C(Et)NHHet\}_2]$. The FAB mass spectra of compounds **1—5** show the $[M - nCl]^+$ fragmentation with successive elimination of chloride ions characteristic of $[PtCl_4L_2]$ derivatives.[35,36] Analysis of the IR spectra of complexes **1—5** revealed the absence of the $\nu_{C\equiv N}$ band at 2230 cm^{-1} and the presence of characteristic lines in the 3335—3290 cm^{-1} region, which can be assigned to NH stretching vibrations, two intense C=N stretching vibrations of the amidine fragment (1652—1633 cm^{-1}), and $\nu_{C=N}$ absorption bands (1613—1605 cm^{-1}) of the heterocycle. In the IR spectrum of complex **6**, the stretching frequencies of the amino group in the 3500—3300 cm^{-1} region are substantially lower than those in the spectrum of free 2-aminopyrimidine ($\Delta\nu$ = 40—120 cm^{-1}), which is apparently attributed not to coordination of the nitrogen atom of the NH_2 group to the metal center but to the involvement of the protons of this group in hydrogen bonding with the Cl atoms.[31]

The ^1H NMR spectra of compounds **1—5** show a triplet and a quartet for the protons of the Et group of the propiononitrile fragment at δ 1.29—1.33 and 2.95—3.10, respectively, of the methyl group at δ 2.33—2.40 (for compounds **2—4**), a multiplet for the protons of the pyridine ring at δ 6.8—8.2, and signals for the protons of two imino groups at δ 11.71—12.32 and 10.19—11.08 with the characteristic constants[26] $^2J_{Pt,H}$ and $^4J_{Pt,H}$. The $^{13}C\{^1H\}$ NMR spectra show signals for all carbon atoms involved in complexes **1—5**, including the carbon atom of the amidine group (*C*=NH), which gives a peak at δ 167—169. The $^{195}Pt\{^1H\}$ NMR spectra contain one broad singlet at δ 120—173, whose position is characteristic of Pt^{IV} complexes.[26] The ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectroscopic data are in complete agreement with the structure containing the hetarylamidine fragment as the ligand. This structure is additionally confirmed by X-ray diffraction study of complex **1**.

The structure of the coordination sphere in complex **1**·2DMSO (Fig. 1) can be described as a slightly distorted octahedron with four chlorine atoms and two nitrogen atoms at the vertices. The Pt—Cl bond lengths (2.3205(6) and 2.3231(6) Å) are virtually equal to those found earlier for Pt^{IV} complexes with an analogous atomic environment.[26,35] The Pt—N(1) and Pt—N(2) bond lengths (2.031(2) Å) are also in good agreement with the analogous distances in amidine platinum complexes.[24,25] The

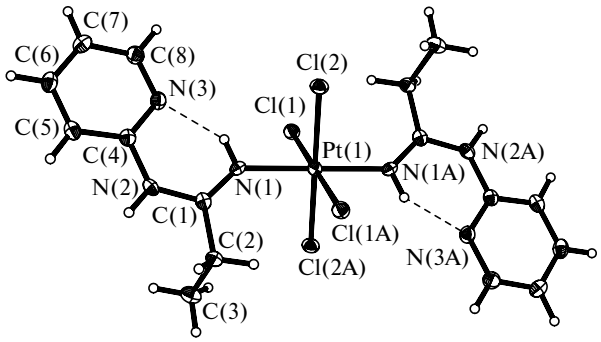


Fig. 1. Molecular structure of the complex **1**·2DMSO (DMSO solvent molecules are omitted). Selected bond lengths (Å) and bond angles (deg): Pt(1)—N(1), 2.031(2); Pt(1)—Cl(1), 2.3205(6); Pt(1)—Cl(2), 2.3231(6); N(2)—C(1), 1.366(3); N(2)—C(4), 1.404(3); N(1)—Pt(1)—Cl(1), 85.89(7); N(1)—Pt(1)—Cl(2), 86.47(6); Cl(1)—Pt(1)—Cl(2), 90.67(2).

HN=C(Et)NHPy ligands are in *trans* positions with respect to the metal center and adopt the *E* configuration stabilized by a hydrogen bond between the imine hydrogen atom and the nitrogen atom of the pyridine ring.

To conclude, we establish that hetarylamidine ligands can easily be generated by the metal-mediated reactions with 2-aminoheterocycles due to electrophilic activation of the carbon atom of nitrile through coordination. The use of 2-aminopyrimidine in this reaction is accompanied by the formation of the substitution product (the reaction of the amino group with the nitrile group is not observed), which is apparently accounted for by a decrease in the nucleophilicity of the NH_2 group in 2-aminopyrimidine.

Experimental

The starting *trans*-$[PtCl_4(EtCN)_2]$ complex was synthesized according to a known procedure.[37] Elemental analysis was carried out on a Carlo Erba Instruments TCM 480 instrument. The IR spectra (KBr pellets) were measured on a Nicolet Impact-400 instrument in the 4000—400 cm^{-1} region. The ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Varian UNITY-300 spectrometer in DMSO-d_6 at 20 °C. The melting points were measured on a Kofler table. The positive ion FAB mass spectra were obtained on a Kratos MS-50C instrument by bombarding a 3-nitrobenzyl alcohol matrix with Xe atoms (8 KeV).

Addition of 2-aminoheterocycles to propiononitrile coordinated to Pt^{IV}; synthesis of the *trans*-$[PtCl_4\{\underline{N}(H)=C(Et)NHHet\}_2]$ complexes (1—5) (general procedure). A solution containing the corresponding heterocycle (2-aminopyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, or 2-aminothiazole) (0.1 mmol) in CH_2Cl_2 (2 mL) at 30—35 °C was added to a suspension of the *trans*-$[PtCl_4(EtCN)_2]$ complex (0.022 mg, 0.05 mmol) in dichloromethane (2 mL) at the same temperature. The reaction mixture was kept at room temperature for 20 min. The solvent was removed under a stream of dry nitrogen at 20—25 °C. The resulting yellow crystalline products were washed with hot acetone (3×5 mL) and diethyl ether (5 mL) and dried *in vacuo*. The yields were 52—67%.

***trans*-Tetrachlorobis{κ^1*N*-[*N*-(2-pyridyl)propionamidine]}platinum(IV), *trans*-$[PtCl_4\{N(H)=C(Et)(NHC_5H_4N)\}_2]$ (1).** The yield was 54%, m.p. 201—202 °C (decomp.). Found (%): C, 30.09; H, 3.27; N, 13.14. $C_{16}H_{22}Cl_4N_6Pt$. Calculated (%): C, 30.33; H, 3.50; N, 13.27. MS (FAB), *m/z*: 529 $[M - 3Cl]^+$, 493 $[M - 4Cl + H]^+$. IR (KBr), ν/cm^{-1}: 3331 m (NH); 1636 s (C=N); 1604 s (C=N); 1543 s (C=C). ^1H NMR (DMSO-d_6), δ: 1.32 (t, 3 H, Me, $^3J_{H,H}$ = 7.5 Hz); 3.00 (q, 2 H, CH_2, $^3J_{H,H}$ = 7.5 Hz); 7.16—8.25 (m, 4 H, Py); 10.51 (s+d, 1 H, NH, $^4J_{Pt,H}$ = 9.9 Hz); 11.83 (s+d, 1 H, NH, $^2J_{Pt,H}$ = 35.2 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 13.8, 27.1 (CH_2Me); 113.4 (C(4)); 119.4 (C(5)); 139.1 (C(3)); 145.6 ($C_{uncoord}$); 153.9 (C(6)); 168.5 (C=NH). $^{195}Pt\{^1H\}$ NMR (DMSO-d_6), δ: 173 ($\Delta_{1/2}$ = 241 Hz).

***trans*-Tetrachlorobis{κ^1*N*-[*N*-(4-methyl-2-pyridyl)propionamidine]}platinum(IV), *trans*-$[PtCl_4\{N(H)=C(Et)NH(4\text{-}MeC_5H_3N)\}_2]$ (2).** The yield was 67%, m.p. 211—212 °C (decomp.). Found (%): C, 32.14; H, 3.88; N, 12.52. $C_{18}H_{26}Cl_4N_6Pt$. Calculated (%): C, 32.67; H, 3.96; N, 12.70. MS (FAB), *m/z*: 555 $[M - 3Cl]^+$, 520 $[M - 4Cl + H]^+$. IR (KBr), ν/cm^{-1}: 3335 m (NH); 1636 s (C=N); 1613 s (C=N); 1541 s (C=C). ^1H NMR (DMSO-d_6), δ: 1.30 (t, 3 H, Me, $^3J_{H,H}$ = 7.5 Hz); 2.97 (q, 2 H, CH_2, $^3J_{H,H}$ = 7.5 Hz); 2.33 (c, 3 H, Me); 6.97—8.10 (m, 3 H, Py); 10.37 (s+d, 1 H, NH, $^4J_{Pt,H}$ = 9.6 Hz); 11.81 (s+d, 1 H, NH, $^2J_{Pt,H}$ = 36.6 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 13.8, 27.7 (CH_2Me); 20.8 (Me); 113.2 (C(4)); 120.6 (C(5)); 145.3 (C(3)); 149.9 ($C_{uncoord}$); 153.9 (C(6)), 168.5 (C=NH). $^{195}Pt\{^1H\}$ NMR (DMSO-d_6), δ: 120 (295 Hz).

***trans*-Tetrachlorobis{κ^1*N*-[*N*-(5-methyl-2-pyridyl)propionamidine]}platinum(IV), *trans*-$[PtCl_4\{N(H)=C(Et)NH(5\text{-}MeC_5H_3N)\}_2]$ (3).** The yield was 64%, m.p. 207—208 °C (decomp.). Found (%): C, 32.31; H, 3.74; N, 12.50. $C_{18}H_{26}Cl_4N_6Pt$. Calculated (%): C, 32.67; H, 3.96; N, 12.70. MS (FAB), *m/z*: 592 $[M - 2Cl]^+$, 520 $[M - 4Cl + H]^+$. IR (KBr), ν/cm^{-1}: 3322 s (N—H); 1636 s (C=N); 1605 s (C=N); 1542 s (C=C). ^1H NMR (DMSO-d_6), δ: 1.35 (t, 3 H, Me, $^3J_{H,H}$ = 7.4 Hz); 3.00 (q, 2 H, CH_2, $^3J_{H,H}$ = 7.4 Hz); 2.35 (s, 3 H, Me); 7.00—8.20 (m, 3 H, Py); 10.19 (s+d, 1 H, NH, $^4J_{Pt,H}$ = 9.8 Hz); 11.71 (s+d, 1 H, NH, $^2J_{Pt,H}$ = 35.8 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 13.8, 27.7 (CH_2Me); 113.2 (C(4)); 120.6 (C(5)); 145.3 (C(3)); 149.9 ($C_{uncoord}$); 153.9 (C(6)); 168.5 (C=NH). $^{195}Pt\{^1H\}$ NMR (DMSO-d_6), δ: 119.5 (295 Hz).

***trans*-Tetrachlorobis{κ^1*N*-[*N*-(6-methyl-2-pyridyl)propionamidine]}platinum(IV), *trans*-$[PtCl_4\{N(H)=C(Et)NH(6\text{-}MeC_5H_3N)\}_2]$ (4).** The yield was 58%, m.p. 196—197 °C (decomp.). Found (%): C, 31.98; H, 3.29; N, 12.49. $C_{18}H_{26}Cl_4N_6Pt$. Calculated (%) C, 32,67; H, 3.96; N, 12.70. MS (FAB), *m/z*: 628 $[M - Cl]^+$, 555 $[M - 3Cl]^+$. IR (KBr), ν/cm^{-1}: 3328 s (N—H); 1652 s (C=N); 1638 s (C=N); 1541 s (C=C). ^1H NMR (DMSO-d_6), δ: 1.29 (t, 3 H, Me, $^3J_{H,H}$ = 7.5 Hz); 3.10 (q, 2 H, CH_2, $^3J_{H,H}$ = 7.5 Hz); 2.40 (s, 3 H, Me); 6.90—7.80 (m, 3 H, Py); 10.19 (s+d, 1 H, NH, $^4J_{Pt,H}$ = 9.6 Hz); 12.32 (s+d, 1 H, NH, $^2J_{Pt,H}$ = 36.1 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 13.9, 27.4 (CH_2Me); 114.2 (C(4)); 120.1 (C(5)); 145.8 (C(3)); 149.9 ($C_{uncoord}$); 154.6 (C(6)); 167.6 (C=NH). $^{195}Pt\{^1H\}$ NMR (DMSO-d_6), δ: 117.5 (292 Hz).

***trans*-Tetrachlorobis{κ^1*N*-[*N*-(2-thiazolyl)propionamidine]}platinum(IV), *trans*-$[PtCl_4\{N(H)=C(Et)NH(C_3H_2NS)\}_2]$ (5).** The yield was 52%, m.p. 188—189 °C (decomp.). Found (%): C, 21.93; H, 2.76; N, 12.83. $C_{12}H_{18}Cl_4N_6PtS_2$. Calculated (%): C, 22.33; H, 2.82; N, 12.83. MS (FAB), *m/z*: 575 $[M - 2Cl + H]^+$, 541 $[M - 3Cl + H]^+$, 503 $[M - 4Cl - H]^+$. IR (KBr), ν/cm^{-1}: 3292 s (N—H); 1633 s (C=N); 1567 s (C=C). ^1H NMR (DMSO-d_6), δ: 1.29 (t, 3 H, Me, $^3J_{H,H}$ = 7.8 Hz); 3.00 (q, 2 H, CH_2, $^3J_{H,H}$ = 7.8 Hz); 7.37—7.56 (m, 2 H, C_3H_2NS); 11.08 (s+d, 1 H, NH, $^4J_{Pt,H}$ = 10.17 Hz); 11.75 (s+d, 1 H, NH, $^2J_{Pt,H}$ = 35.3 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 13.4, 26.6 (CH_2CH_3); 114.1 (C(4)); 138.1 (C(5)); 161.5 ($C_{uncoord}$); 167.1 (C=NH). $^{195}Pt\{^1H\}$ NMR (DMSO-d_6), δ: 118.7 (294 Hz).

Synthesis of *trans*-tetrachloro[bis(2-aminopyrimidine)]platinum(IV), *trans*-$[PtCl_4(2\text{-}NH_2Pym)_2]$. Solid 2-aminopyrimidine, 2-NH_2Pym, (9.5 mg, 0.10 mmol) was added to a suspension of $[PtCl_4(EtCN)_2]$ (22 mg, 0.05 mmol) in dichloromethane at 35 °C. The orange crystalline product that formed virtually immediately was filtered off, washed with diethyl ether (3×3 mL), and dried in air.

Tetrachloro[bis(2-aminopyrimidine)]platinum(IV) $[PtCl_4(2\text{-}NH_2C_4H_3N)_2]$ (6). The yield was 92%, m.p. 214—215 °C (decomp.). Found (%): C, 18.76; H, 1.86; N, 15.79. $C_8H_{10}Cl_4N_6Pt$. Calculated (%): C, 18.29; H, 1.92; N, 16.01. MS (FAB), *m/z*: 527 $[M - H]^+$. IR (KBr), ν/cm^{-1}: 3409 m ($\nu_{as}(NH_2)$); 3307 m ($\nu_s(NH_2)$); 1649 s (C=N); 1595 s (C=C);

Table 1. Crystallographic data for the complex **1**·2DMSO

Parameter	**1**·2DMSO
Molecular formula	$C_{20}H_{34}Cl_4N_6O_2PtS_2$
Molecular weight	791.54
Space group	$P\bar{1}$
a/Å	9.2643(4)
b/Å	9.4112(3)
c/Å	10.1875(3)
α/deg	64.364(2)
β/deg	69.466(2)
γ/deg	85.133(2)
V/Å^3	747.56(5)
Z	1
ρ_{calc}/g cm^{-3}	1.758
μ(Mo-Kα)/mm^{-1}	5.218
Number of measured reflections	8663
Number of independent reflections with $I > 2\sigma(I)$	3398
Final R factors with $I > 2\sigma(I)$	
R_1	0.0228
wR_2	0.0483
Total R factors	
R_1	0.0235
wR_2	0.0485
GOOF	1.067
θ_{max}/deg	27.44

Note. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]]^{1/2}$.

1557 s (NH_2). ^{1}H NMR (DMSO-d_6), δ: 6.72 (s, 2 H, NH_2); 7.79—8.36 (m, 3 H, Pym). ^{13}C{^{1}H} NMR (DMSO-d_6), δ: 157.8 (C(4), C(6)); 110.0 (C(5)). ^{195}Pt{^{1}H} NMR (DMSO-d_6), δ: 717 (310 Hz).

X-ray diffraction study. Single crystals of the complex **1**·2DMSO were grown by vapor diffusion of ethanol into a solution of **1** in DMSO. X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer (Mo-Kα, λ = 0.71073 Å, T = 120(2) K) with the use of the Denzo-Scalepack program package[38] for the determination and refinement of the unit cell parameters. The structure of the complex was solved by direct methods using the SIR2002 program.[39] A semiempirical absorption correction was applied (T_{min}/T_{max} = 0.5617/0.8104).[40] The structure was refined with the use of the SHELXLS-97 [41] and WinGX [42] program packages. The hydrogen atoms of the NH groups were located in difference Fourier maps and refined using a riding model. The other H atoms were generated geometrically and also refined using a riding model (d(C—H) = 0.95—0.99 Å and $U_{iso} = (1.2—1.25)U_{eq}$(X), where X is the adjacent atom). The crystallographic parameters of the compound **1**·2DMSO and principal details of structure refinement are given in Table 1.

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