Directed synthesis of isomerically pure platinum pyrazole complexes

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The complexes $K_2[PtCl_n]$ (n = 4 or 6) react with pyrazoles 3,5-MeRpzH (R = H or Me) in 0.1 *M* HCl at 20—25 °C to form the isomerically pure *cis*-$[PtCl_n(3,5\text{-}MeRpzH)_2]$ complexes (n = 2 or 4) (**1a,b** and **3a,b**), whereas a decrease in the acidity of the medium leads to a substantial decrease in selectivity of the reaction. Thermal isomerization of complexes **1a,b** and **3a,b** both in solution ($MeNO_2$) and in the solid state affords the *trans*-$[PtCl_n(3,5\text{-}MeRpzH)_2]$ complexes (n = 2 or 4) (**2a,b** and **4a,b**). Platinum(II) complexes **1a,b** and **2a,b** were also prepared by selective reduction of genetically related Pt^{IV} compounds (**3a,b** and **4a,b**) with the phosphorus ylide $Ph_3P{=}CHCO_2Me$ in chloroform. Platinum(IV) complexes (**3a,b** and **4a,b**) were synthesized by oxidation of the corresponding Pt^{II} complexes (**1a,b** and **2a,b**) with molecular chlorine. X-ray diffraction study demonstrated that coordination of 3(5)-MepzH to Pt^{IV} in complex **4a** stabilizes the sterically least hindered tautomer in the solid state.

Key words: pyrazoles, platinum complexes, isomerism, tautomerism.

Preparative coordination chemistry of pyrazoles is rather versatile due to the presence of two nucleophilic centers in these compounds and the possibility of easily changing the electronic and steric properties of the rings by introducing various substituents. The ability of pyrazoles to act as neutral and anionic monodentate and *exo*- or *endo*-bidentate ligands opens a route to numerous mono- or polynuclear complexes.[1—4] Many such compounds have ferromagnetic properties, serve as luminophores, and exhibit catalytic, antibacterial, antifungal, antiproliferative, antiviral, and antitumor activities (see the reviews[1—4] and references herein). These complexes are studied and used as light emitting diodes, pH sensors, anionic receptors, synthons in supramolecular and coordination chemistry, models of the active sites of metalloenzymes and metalloproteins, and models for studying homogeneous catalysis (see the reviews[1—4] and references herein). In particular, pyrazole-containing platinum(II) complexes are extensively studied and/or used as luminescence sensors,[5,6] reagents in preparative coordination chemistry,[7—10] and antitumor agents.[11—13]

In platinum chemistry, the geometric configuration of complexes is of particular importance for the prediction of their properties and, correspondingly, for the determination of the field of their application. This is associated with the difference in the reactivity and biological activity of *cis* and *trans* isomers.[14—17] Generally, platinum(II) complexes with N-donor ligands in the *cis* configuration exhibit much higher antitumor activity than their *trans* analogs.[18] At the same time, the molecular design and synthesis of some polynuclear complexes require the use of precursors in the *trans* form.[7] For pyrazole-containing complexes, this is true for the platinum(II) compound *cis*-$[PtCl_2(pzH)_2]$ (pzH is pyrazole), which displays considerable antitumor activity.[11] The *trans* isomer of this compound is a convenient synthon for the preparation of polynuclear complexes.[7]

In spite of the fact that the platinum(II) pyrazole complexes $[PtCl_2(R^1R^2pzH)_2]$ have been known for many years, the problems of their geometric isomerism and systematic synthesis of isomeric pairs remained to be solved, and most of the known methods for the synthesis of these complexes are characterized by relatively low selectivity and afford mixtures of *cis* and *trans* isomers.[19,20] In addition, methods for the synthesis of platinum(IV) pyrazole complexes have been applied only to the synthesis of the *cis*-$[PtCl_4(pzH)_2]$ compound.[21] Platinum(IV) pyrazole complexes, which can potentially possess such properties as antitumor activity,[22] are poorly known. The aim of the present study was to develop procedures for the directed synthesis of isomerically pure Pt^{II} and Pt^{IV} pyrazole complexes and examine the possible factors responsible for the formation of isomeric mixtures for some Pt^{II} pyrazole complexes synthesized earlier.

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Results and Discussion

To study the influence of substituents in ligands on the processes, we chose Pt^{II} and Pt^{IV} complexes with mono- and disubstituted pyrazoles (3(5)-MepzH and 3,5-Me_2pzH, respectively). Investigation of complexes with unsymmetrical pyrazole 3(5)-MepzH was of special interest because heterocycles characterized by this type of substitution are convenient models for studying stabilization of a particular tautomeric form of the ligand by a metal center. The isomeric compositions of all complexes were analyzed by ^{1}H NMR spectroscopy and TLC.

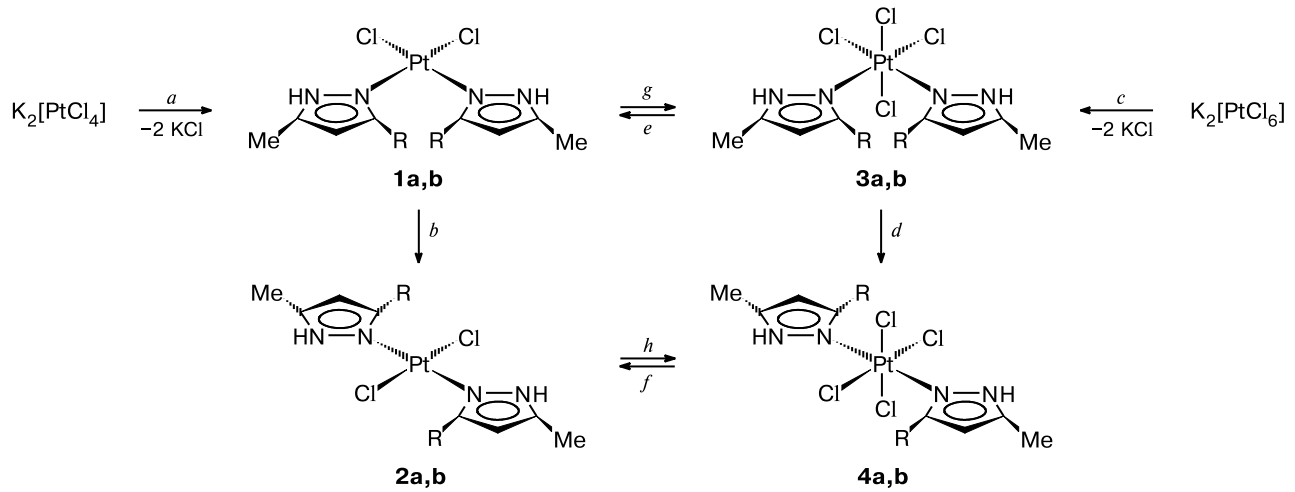
Earlier, the platinum(II) pyrazole complexes *cis*-[$PtCl_2$(3,5-R_2pzH)$_2$] (R = H,[11,20,23] Me,[11,19] Me_2CH,[11] or COOH/K [11]) were synthesized by the reaction of $K_2[PtCl_4]$ with pyrazoles 3,5-R_2pzH in 0.02,[11] 0.1,[11,19] or 1.5—2.0 *M* HCl (see Refs 20 and 23) or by the reaction of $K_2[PtCl_4]$ with $Me_2C(pz)_2$. The latter reaction was accompanied by splitting of $Me_2C(pz)_2$ and gave the *cis*-[$PtCl_2$(pzH)$_2$] complex.[20] The *cis*-[$PtCl_2$(pzH)$_2$] complex was also prepared by the reaction of $PtCl_2$ with pzH or $Me_2C(pz)_2$ in chloroform.[20] The syntheses in aqueous solutions required low pH to prevent the formation of [$PtCl_4$][Pt(3,5-R_2pzH)$_4$][23] and to avoid the formation of bridging pyrazolato or hydroxo complexes. The latter are generated due to deprotonation of the coordinated pyrazole and/or water molecules.[11] Scarce data published in the literature show that it is preferable to perform the reaction in 0.1 *M* HCl to achieve high selectivity and high yield of the target products.[11]

The platinum(II) *trans*-pyrazole complexes *trans*-[$PtCl_2$(3,5-R_2pzH)$_2$] (R = H [20,23] or Me [19]) were synthesized earlier by refluxing [Pt(pzH)$_4$]Cl_2 in concentrated HCl,[23] by the reaction of *trans*-[$PtCl_2$(PhCN)$_2$] with pzH,[20] and by the reaction of [$PtCl_2$(MeCN)$_2$] with 1-CH_2OH-3,5-Me_2pz (in the latter case, the ligand is generated *in situ* as a result of splitting of the latter reagent to form 3,5-Me_2pzH and CH_2O),[19] the reactions being performed under drastic conditions. All other known procedures for the synthesis of platinum(II) pyrazole complexes give isomeric mixtures of *cis*- and *trans*-[$PtCl_2$(3,5-R_2pzH)$_2$] (R = H [20] or Me [19]). The task of increasing the selectivity of the reactions and isomeric purity of the reaction products was beyond the scope of all the cited studies,[7,11,19,20,23] and conditions of the synthesis of Pt^{II} pyrazole complexes in the *cis* configuration were chosen without considering the possibility of isomerization of the resulting complexes in the reaction mixture.

Before the present study, the synthesis of only one platinum(IV) pyrazole complex [$PtCl_4$(pzH)$_2$] in the *cis* configuration has been documented. This complex was prepared by the reaction of $K_2[PtCl_6]$ with pzH in water at 70 °C. However, we have demonstrated earlier[24] that this method was accompanied by side reactions giving rise to the *trans*-[$PtCl_4$(pzH)$_2$] and [$PtCl_3$(pz)(pzH)$_2$]Cl compounds along with *cis*-[$PtCl_4$(pzH)$_2$]. Earlier, platinum(IV) pyrazole complexes in the *trans* configuration have remained unknown.

In the present study, we performed the directed synthesis of *cis*-platinum(II) complexes (**1a** and **1b**) and *cis*-platinum(IV) complexes (**3a** and **3b**) with pyrazoles characterized by different degrees of substitution by the reactions of $K_2[PtCl_n]$ (*n* = 4 or 6) with 3,5-MeRpzH (R = H or Me) in 0.1 *M* HCl at 20—25 °C (Scheme 1, paths *a* and *c*). The reaction *a* of unsymmetrical pyrazole 3(5)-MepzH (see Scheme 1) is complicated by the for-

Scheme 1



R = H (**a**), Me (**b**)

Reagents and conditions: *a*, *c*. 2 pzH, 0.1 *M* HCl; *b*, *d*. Δ; *e*, *f*. $Ph_3P{=}CHCO_2Me$; *g*, *h*. Cl_2.

mation of yet unidentified products, whose number and ratio substantially depend on pH of the solution and the reagent ratio. One of by-products, *viz.*, $[PtCl_4][Pt(5\text{-}MepzH)_4]$, which is generated upon the addition of 3(5)-MepzH to $K_2[PtCl_4]$ in one portion in a ratio of 1 : 2, was isolated and characterized by elemental analysis, ^1H NMR spectroscopy, and X-ray diffraction.[25] It was also found that the yield of product **1b** changes only slightly if the insoluble product *cis*-$[PtCl_2(3,5\text{-}Me_2pzH)_2]$ (**1b**) is removed from the reaction mixture from time to time, which method was recommended for the syntheses of *cis*-$[PtCl_2(pzH)_2]$ [11] and *cis*-$[PtCl_2(5\text{-}MepzH)_2]$. In addition, the synthesis of *cis*-platinum(IV) complexes (**3a** and **3b**) by the reaction of $K_2[PtCl_6]$ with 3,5-MeRpzH (R = H or Me) under the reaction conditions, which were used in the synthesis of platinum(II) complexes **1a** and **1b**, occurs with high selectivity and affords the target products in good yield. For example, the *cis*-platinum(IV) complexes (**3a** and **3b**) were prepared by the reaction of $K_2[PtCl_6]$ with 3,5-MeRpzH in 0.1 *M* HCl at 20—25 °C in 85% (**3a**) and 76% (**3b**) yields.

We synthesized the *trans*-Pt^{II} and *trans*-Pt^{IV} complexes $[PtCl_n(3,5\text{-}MeRpzH)_2]$ (n = 2 or 4; R = H or Me) (**2a**, **2b**, **4a**, and **4b**) from their *cis* analogs (**1a**, **1b**, **3a**, and **3b**, respectively) by refluxing in nitromethane or by heating in the solid state (see Scheme 1, paths *b* and *d*). These transformations are the first examples of thermal isomerization of platinum pyrazole complexes, which proceeds according to the rule for thermal isomerization.[26,27] The thermal transformation of the *cis*-Pt^{II} complexes occurs quantitatively both in solution and in the solid state. By contrast, although isomerization of Pt^{IV} complexes occurs almost quantitatively in solution, the solid-state isomerization of such complexes is accompanied by decomposition and, consequently, cannot be recommended as a preparative procedure.

One of the most convenient methods for the synthesis of Pt^{II} complexes is based on mild and selective reduction of genetically related Pt^{IV} complexes with the phosphorus ylide $Ph_3P{=}CHCO_2Me$ in nonaqueous media.[28] In the present study, we used this method for the synthesis of the *cis*-$[PtCl_2(3,5\text{-}MeRpzH)_2]$ (**1a,b**) and *trans*-$[PtCl_2(3,5\text{-}MeRpzH)_2]$ (**2a,b**) complexes from the corresponding platinum(IV) complexes **3a,b** and **4a,b** (see Scheme 1, paths *e* and *f*). In spite of relative instability on silica gel, we purified complexes **1a,b** and **2a,b** by flash chromatography on this sorbent.

On the contrary, the platinum(IV) complexes $[PtCl_4(pzH)_2]$ can be prepared by oxidation of the corresponding platinum(II) complexes $[PtCl_2(pzH)_2]$.[29] We synthesized the isomerically pure compounds *cis*-$[PtCl_4(MeRpzH)_2]$ (**3a,b**) and *trans*-$[PtCl_4(3,5\text{-}MeRpzH)_2]$ (**4a,b**) by the reactions of the corresponding platinum(II) complexes *cis*-$[PtCl_2(3,5\text{-}MeRpzH)_2]$ (**1a,b**) and *trans*-$[PtCl_2(3,5\text{-}MeRpzH)_2]$ (**2a,b**) with molecular chlorine (see Scheme 1, paths *g* and *h*) in chloroform. Both reactions gave the products in nearly 100% yields.

The purity, compositions, and structures of complexes **1a—4a** and **1b—4b** were established by elemental analysis, TLC, positive-ion FAB mass spectrometry, IR spectroscopy, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and X-ray diffraction (for compounds **2b**, **3b** · CH_2Cl_2, **3b** · $O{=}CMe_2$, and **4a**).

The elemental analysis data for all the reaction products are consistent with the calculated data. The FAB mass spectra of platinum(II) complexes **1a**,**b** and **2a**,**b** contain peaks, whose m/z and the isotopic pattern correspond to the molecular ion peak $[M]^+$. The peaks in the spectra of platinum(IV) complexes **3a,b** and **4a,b** correspond to the $[M - 2\ H]^+$ fragmentation. The TGA data for complexes **1a—4a** and **1b—4b** indicate that thermal stability of dimethyl-substituted platinum pyrazole complexes **1b—4b** is higher than that of monomethyl-substituted complexes **1a—4a**, thermal stability of *trans*-complexes **2a,b** and **4a,b** is higher than that of *cis*-complexes **1a,b** and **3a,b**, and platinum(IV) complexes **3a,b** and **4a,b** are thermally more stable than platinum(II) complexes **1a,b** and **2a,b**.

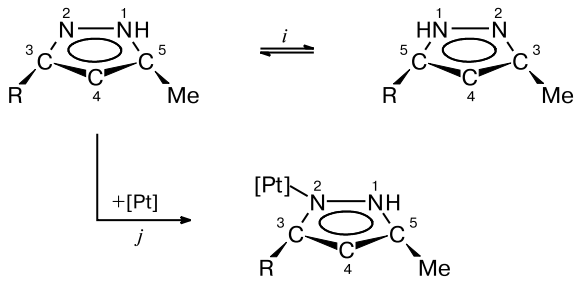
The number of peaks, their positions, and intensities in the IR spectra of all the complexes synthesized are similar to those in the spectra of free methylpyrazoles 3,5-MeRpzH (R = H or Me). The absorption bands were assigned based on the data published in the literature.[30,31] The IR spectra of free pyrazoles show intense broadened absorption bands at 3120 and 764 cm^{-1} for 3(5)-MepzH and at 3109 and 856 cm^{-1} for 3,5-Me_2pzH, which were assigned to the stretching (ν(C—H)) and out-of-plane bending (γ(C—H)) vibrations of the C—H bond of the ring. In the IR spectra of the platinum(II) complexes, these bands appear as narrow peaks of the same intensity at 3139—3113 and 792 cm^{-1} for **1a** and **2a** and at 3145 and 808—800 cm^{-1} for **1b** and **2b**, whereas these bands in the spectra of the platinum(IV) complexes appear at 3145—3130 and 788—787 cm^{-1} for **3a** and **4a** and 3149—3116 and 814 cm^{-1} for **3b** and **4b** and their intensities are substantially lower. Presumably, the intensity of absorption bands in the stretching and out-of-plane bending regions of the C—H bond of the ring can serve as an indicator for obtaining indirect data on the oxidation state of platinum in the $[PtCl_n(RMepzH)_2]$ complexes (n = 2 or 4; R = H or Me).

In the ^1H NMR spectra of complexes **1b** and **2a,b—4a,b**, all signals are shifted downfield relative to the corresponding signals in the spectra of free pyrazoles 3,5-MeRpzH (by 0.1—0.5 ppm for platinum(II) compounds **1a,b** and **2a,b** and by 0.3—0.6 ppm for platinum(IV) compounds **3a,b** and **4a,b**) due to coordination of pyrazole to the metal centers.[32] The only exception is the spectrum of compound **1a**, in which, like in the spectrum of the platinum(II) complex *cis*-$[PtCl_2(pzH)_2]$ synthesized ear-

lier,[20] the signal for the corresponding C(3)H proton of the pyrazole ring is shifted upfield (by 0.16 ppm).

In the ^{1}H NMR spectra of free pyrazoles 3,5-MeRpzH (R = H or Me), all signals are broadened due to the presence of a tautomeric equilibrium in solution (Scheme 2, path *i*).[33] In symmetrical 3,5-Me_2pzH, the protons of the Me groups are equivalent and, as a consequence, give one broadened signal. In the spectra of complexes **1a,b—4a,b**, all peaks are narrowed, whereas the spectra of the complexes with pyrazole 3,5-Me_2pzH (**1b—4b**) show two signals for the protons of the Me groups. The latter fact indicates that these protons are nonequivalent. Presumably, this change in the spectral pattern upon coordination of pyrazoles is evidence that one of tautomers is present in a substantially larger amount (see Scheme 2, path *j*).[33,34] This is consistent with the X-ray diffraction data. Only one of the possible tautomers, *viz.*, the sterically least hindered tautomer, was found in the crystals of the complex with unsymmetrical pyrazole 3(5)-MepzH (**4a**).

Scheme 2



All signals in the ^{13}C{^{1}H} NMR spectra of complexes **1a,b—4a,b**, like those in the ^{1}H NMR spectra, are shifted downfield relative to the corresponding signals in the spectra of free pyrazoles 3,5-MeRpzH, except for the peaks assigned to the carbon atoms of the Me groups. For example, the signal for the carbon atom of the Me group in the spectra of complexes **1a—4a** is shifted upfield relative to the corresponding signal in the spectrum of free pyrazole 3,5-MeRpzH. The ^{13}C{^{1}H} NMR spectra of compounds **1b—4b**, like the ^{1}H NMR spectra, show two resonances for the coordinated Me groups (these groups are equivalent in the free state), one of them being shifted downfield and another signal being shifted upfield (by 2.0 and 1.0 ppm, respectively) relative to their positions in free pyrazole 3,5-Me_2pzH. In the ^{13}C{^{1}H} NMR spectrum of free unsymmetrical pyrazole 3(5)-MepzH, the signal for the C(5) atom (for the tautomer of 3-MepzH) is substantially broadened due to exchange processes fast on the NMR time scale.[35] In the spectra of complexes **1a—4a**, no broadening is observed due, apparently, to stabilization of only one tautomer upon coordination to Pt^{II} and Pt^{IV} (see Scheme 2, path *j*).[34]

Compounds **2b**, **3b**·CH_2Cl_2, **3b**·O=CMe_2, and **4a** were structurally characterized by X-ray diffraction (Figs 1—4). The coordination polyhedron is a distorted planar square (**2b**) or an octahedron (**3b**·CH_2Cl_2, **3b**·O=CMe_2, and **4a**) formed by two N atoms and two (**2b**) or four (**3b**·CH_2Cl_2, **3b**·O=CMe_2, and **4a**) Cl atoms at the Pt atom. The N—N (1.35—1.37 Å), N—C (1.33—1.36 Å), and C—C (1.36—1.40 Å) bond lengths in the pyrazole rings of all four structures are typical of these heterocycles. In the structures of free pyrazoles 3,5-R_2pzH (R = H or Me), the N—N, N—C, and C—C distances in the rings are in the ranges of 1.33—1.36, 1.31—1.35, and 1.33—1.42 Å, respectively.[36,37] In the structures of the analogous pyrazole complexes *cis*-[$PtCl_n$(3,5-R_2pzH)$_2$] (*n* = 2 or 4; R = H or Me), the distances vary in ranges of 1.32—1.39, 1.29—1.39, and 1.29—1.43 Å, re-

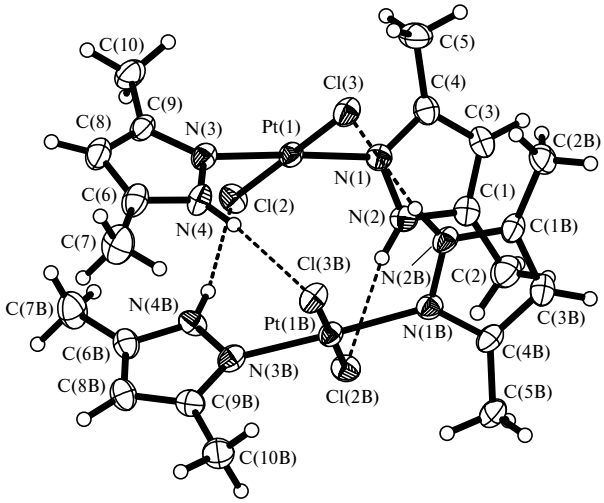


Fig. 1. Molecular dimeric structure of complex **2b**.

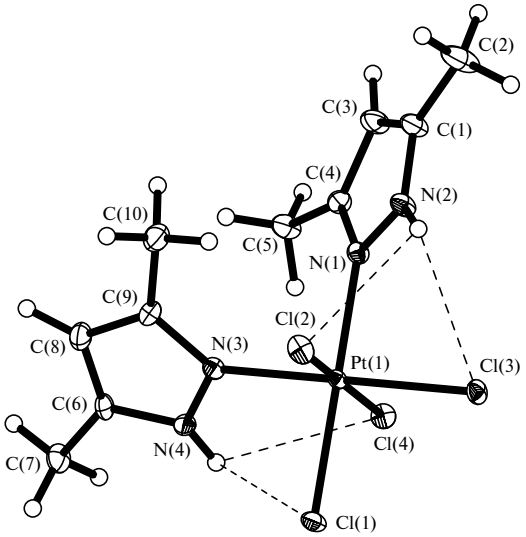


Fig. 2. Molecular structure of complex **3b**·CH_2Cl_2. The dichloromethane solvate molecule is omitted.

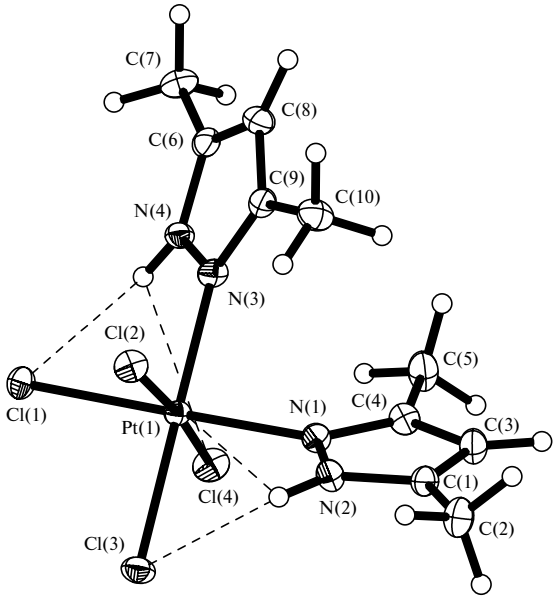


Fig. 3. Molecular structure of complex **3b** · O=CMe_2. The acetone solvate molecule is omitted.

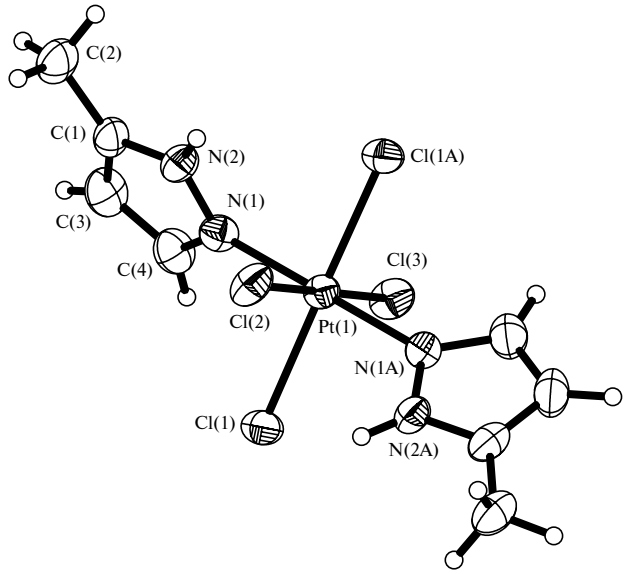


Fig. 4. Molecular structure of complex **4a**.

spectively.[19—21] The Pt—N (2.00—2.06 Å) and Pt—Cl (2.30—2.32 Å) bond lengths in compounds **2b**, **3b** · CH_2Cl_2, **3b** · O=CMe_2, and **4a** are comparable with those in the analogous complexes *cis*-[$PtCl_n$(3,5-R_2pzH)$_2$] (n = 2 or 4; R = H or Me) (1.93—2.04 Å and 2.28—2.32 Å, respectively).[19—21] For complex **4a** with pyrazole 3(5)-MepzH, like for analogous complexes with unsymmetrical pyrazoles 3(5)-RpzH (R = Me,[32,38] Ph,[39,40] or Bu^t [40,41]), the stable and sterically least hindered tautomer is that in which the heterocycle is coordinated to the metal center through the nitrogen atom most distant from the Me group.

Complex **2b** forms dimers through intermolecular hydrogen bonding between the NH groups of the pyrazole fragments of one molecule and the Cl atoms of the adjacent molecule. The N...Cl distances are in the range of 3.159(4)—3.215(5) Å (see Fig. 1). In compounds **3b** · CH_2Cl_2 and **3b** · O=CMe_2, there is an intramolecular hydrogen bond between the NH groups of the pyrazole fragments and two adjacent Cl atoms. The N...Cl distances are 3.158(3)—3.259(3) and 3.134(3)—3.232(2) Å, respectively (see Figs 2 and 3).

To summarize, we developed procedures for the directed synthesis of the isomerically pure complexes *cis*- and *trans*-[$PtCl_n$(3,5-MeRpzH)$_2$] (n = 2 or 4; R = H (**1a—4a**) or Me (**1b—4b**); see Scheme 1), prepared new platinum(II and IV) pyrazole complexes (**1a,b**, **3a,b**, and **4b**), studied their interconversions and thermal *cis—trans* isomerization, and revealed the possible factors responsible for the formation of isomeric mixtures for some already known platinum(II) pyrazole complexes. Owing to the harsh reaction conditions, the primary product in the *cis* configuration undergoes isomerization and is completely or partially transformed into the *trans* conformation, whereas the reactions performed under mild conditions and at optimal pH selectively afford *cis* isomers. This assumption accounts for the formation of both isomerically pure complexes *trans*-[$PtCl_2$(3,5-MeRpzH)$_2$][19,20] and isomeric mixtures of *cis*- and *trans*-[$PtCl_2$(3,5-Me_2pzH)$_2$] [19,20] in reactions, which have been performed earlier under drastic conditions. Coordination of pyrazoles to platinum(II or IV) leads to stabilization of one particular tautomer. Coordination of unsymmetrical pyrazole results in stabilization of the sterically least hindered tautomer (see Scheme 2).

Experimental

Thermogravimetric studies were carried out on a Mettler Toledo TGA85 derivatograph in aluminum crucibles at a heating rate of 8 K min^{-1} (temperature range was 20—1000 °C, the rate of air flow was 3 L h^{-1}, the weight of samples was 5—10 mg). The TLC analysis was performed on Merck 60 F_{254} plates. Positive-ion fast atom bombardment mass spectra were obtained on a Kratos MS-50C instrument using 3-nitrobenzyl alcohol as a matrix; samples were bombarded with 8-keV Xe atoms. The IR spectra were recorded in KBr pellets on a Bruker Vector 22 FTIR instrument in the 4000—400 cm^{-1} region. The ^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker DPX 300 spectrometer at room temperature.

Commercial solvents and reagents, *viz.*, 3(5)-methylpyrazole, 3,5-dimethylpyrazole (Aldrich), and the phosphorus ylide Ph_3P=$CHCO_2Me$ (Lancaster), were used without additional purification.

The *cis*-[$PtCl_n$(MeRpzH)$_2$] complexes (n = 2 or 4; R = H or Me) (**1a,b** and **3a,b**) were synthesized according to a modified procedure, which has been developed earlier for the synthesis of *cis*-[$PtCl_2$(pzH)$_2$].[11] Pyrazole 3,5-MeRpzH (1.00 mmol) was

added with stirring to a solution of $K_2[PtCl_4]$ (1.00 mmol) ($K_2[PtCl_6]$ in the case of **3a,b**) in 0.1 *M* HCl (5 mL). The reaction mixture was vigorously stirred at room temperature for 1 day, after which the beige precipitate (yellow precipitate in the case of **3a,b**) that formed was filtered off. Then an additional amount of 3,5-MeRpzH (1.00 mmol) was added to the filtrate. The reaction mixture was stirred for 5 days (7 days in the case of **3a,b**) at room temperature. The product that precipitated was filtered off every day until the precipitation ceased. All portions of the reaction product were combined, washed with distilled water (5 mL), rapidly washed with acetone (5 mL) at room temperature (washing with acetone was not required only for **3a,b**), and dried in air at 20—25 °C. The yields were 53% (**1a**), 47% (**1b**), 85% (**3a**), and 76% (**3b**).

The *trans*-$[PtCl_n(MeRpzH)_2]$ complexes (n = 2 or 4; R = H or Me) (**2a,b** and **4a,b**) were synthesized by refluxing *cis*-$[PtCl_n(MeRpzH)_2]$ (**1a**, **1b**, **3a**, or **3b**) (0.11 mmol) in nitromethane (5 mL) for 10, 30, 13, or 18 h, respectively, followed by removal of the solvent in an air flow and drying in air at room temperature for 1 day. The *trans*-$[PtCl_n(MeRpzH)_2]$ complexes (**2a**, **2b**, **4a**, and **4b**) were also synthesized by heating solid complexes **1a** and **1b** at 150 °C for 8 and 10 h, respectively, and complexes **3a** and **3b** at 170 °C for 23 and 35 h, respectively. The temperature mode of thermal isomerization of the complexes was chosen based on the TGA data for the starting compounds. Thermal isomerization was monitored by TLC (Merck 60 F_{254} plates; CH_2Cl_2—Me_2CO, 12 : 1, as the eluent). Both procedures gave the platinum(II) complexes in nearly quantitative yields. In the first case, the yields of the platinum(IV) complexes were 87% (**4a**) and 92% (**4b**). In the second case, the yields were 52% (**4a**) and 65% (**4b**). Complex **4a** (or **4b**) was separated from the starting compound **3a** (or **3b**) by flash chromatography (Fluka Silica gel 60; CH_2Cl_2—Et_2O, 5 : 1, as the eluent).

The *cis*-$[PtCl_2(MeRpzH)_2]$ compounds (R = H (**1a**) or Me (**1b**)) were prepared also by reduction of *cis*-$[PtCl_4(MeRpzH)_2]$ (R = H (**3a**) or Me (**3b**)) with the phosphorus ylide $Ph_3P{=}CHCO_2Me$. The latter reagent (0.040 g, 0.12 mmol) was added to a suspension of complex **3a** (or **3b**) (0.10 mmol) in chloroform (5 mL). The reaction mixture was vigorously stirred at room temperature for 30 min, after which product **1a** (or **1b**) was purified by flash chromatography (Fluka Silica gel 60; CH_2Cl_2—Et_2O, 5 : 1, as the eluent). Compound **1a** (or **1b**) was additionally purified, if necessary, by rapid washing of the precipitate with acetone. Analogously, the *trans*-$[PtCl_2(MeRpzH)_2]$ complexes (R = H (**2a**) and Me (**2b**)) were obtained without additional purification. The yields were 64% (**1a**), 85% (**1b**), 88% (**2a**), and 86% (**2b**).

The *cis*-$[PtCl_4(MeRpzH)_2]$ complexes (R = H (**3a**) or Me (**3b**)) were synthesized by oxidation of complex **1a** (or **1b**) (0.50 mmol) with molecular chlorine in chloroform (3 mL) at room temperature for 20 min. The solvent was removed from the resulting bright-yellow solution in an air flow. Compound **3a** (or **3b**) was dried in air at 20—25 °C for 1 day. Analogously, the *trans*-$[PtCl_4(MeRpzH)_2]$ complexes (R = H (**4a**) or Me (**4b**)) were prepared by chlorination of complex **2a** or **2b**. In both cases, the products were prepared in nearly quantitative yields.

***cis*-Dichloro[bis(5-methylpyrazole)]platinum(II), *cis*-$[PtCl_2(5\text{-}MepzH)_2]$ (1a).** DTA/TG: at 155 °C the gradual mass loss started; the mass loss was: 155—240 °C, 3.8%; 240—330 °C, 11.4%; 330—500 °C, 38.7%. R_f 0.59 (CH_2Cl_2—Me_2CO, 12 : 1, as the eluent). Found (%): C, 22.36; H, 2.85; N, 13.06. $C_8H_{12}N_4Cl_2Pt$. Calculated (%): C, 22.34; H, 2.81; N, 13.02. MS, *m/z*: 430 $[M]^+$, 358 $[M - 2\,Cl - H]^+$. IR, ν/cm^{-1}: 3209 (N—H); 3137, 3113 (C—H); 1571, 1536 (C=N + C=C). ^{1}H NMR (acetone-d_6), δ: 12.49 (s, 1 H, NH); 7.29 (d, 1 H, C(3)H, J = 2.2 Hz); 6.20 (d, 1 H, C(4)H, J = 2.2 Hz); 2.37 (s, 3 H, Me). ^{1}H NMR ($CDCl_3$), δ: 12.20 (s, 1 H, NH); 7.35 (d, 1 H, C(3)H, J = 2.2 Hz); 5.94 (d, 1 H, C(4)H, J = 2.2 Hz); 2.21 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 142.8 (C(5)Me); 141.6 (C(3)H); 106.0 (C(4)H); 11.2 (Me).

***cis*-Dichloro[bis(3,5-dimethylpyrazole)]platinum(II), *cis*-$[PtCl_2(3,5\text{-}Me_2pzH)_2]$ (1b).** DTA/TG: at 230 °C the gradual mass loss started; the mass loss was: 230—290 °C, 16.1%; 290—365 °C, 57.3%. R_f 0.60 (CH_2Cl_2—Me_2CO, 12 : 1, as the eluent). Found (%): C, 26.37; H, 3.49; N, 12.06. $C_{10}H_{16}N_4Cl_2Pt$. Calculated (%): C, 26.21; H, 3.52; N, 12.23. MS, *m/z*: 458 $[M]^+$, 423 $[M - Cl]^+$, 387 $[M - 2\,Cl]^+$. IR, ν/cm^{-1}: 3269 (N—H); 3145 (C—H); 1635, 1572 (C=N + C=C). ^{1}H NMR (acetone-d_6), δ: 12.18 (s, 1 H, NH); 5.99 (s, 1 H, C(4)H); 2.27 and 2.16 (both s, 3 H each, Me). ^{1}H NMR ($CDCl_3$), δ: 12.10 (s, 1 H, NH); 5.77 (s, 1 H, C(4)H); 2.40 and 2.14 (both s, 3 H each, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 150.1 (C(5)Me); 142.4 (C(3)Me); 105.2 (C(4)H); 13.8, 10.4 (Me).

***trans*-Dichloro[bis(5-methylpyrazole)]platinum(II), *trans*-$[PtCl_2(5\text{-}MepzH)_2]$ (2a).** DTA/TG: at 180 °C the gradual mass loss started; the mass loss was: 180—285 °C, 3.3%; 285—330 °C, 6.6%; 330—380 °C, 7.8%; 380—550 °C, 16.9%; 550—1000 °C, 11.5%. R_f 0.52 (CH_2Cl_2 as the eluent). Found (%): C, 22.58; H, 2.89; N, 12.97. $C_8H_{12}N_4Cl_2Pt$. Calculated (%): C, 22.34; H, 2.81; N, 13.02. MS, *m/z*: 430 $[M]^+$. IR, ν/cm^{-1}: 3245 (N—H); 3139, 3114 (C—H); 1570 (C=N + C=C). ^{1}H NMR (acetone-d_6), δ: 12.14 (s, 1 H, NH); 7.90 (d, 1 H, C(3)H, J = 2.2 Hz); 6.24 (d, 1 H, C(4)H, J = 2.2 Hz); 2.43 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: 141.8 (C(3)H); 107.0 (C(4)H); 10.8 (Me).

***trans*-Dichloro[bis(3,5-dimethylpyrazole)]platinum(II), *trans*-$[PtCl_2(3,5\text{-}Me_2pzH)_2]$ (2b).** DTA/TG: at 220 °C the gradual mass loss started; the mass loss was: 220—285 °C, 12.3%; 285—410 °C, 45.5%. R_f 0.37 (CH_2Cl_2 as the eluent). Found (%): C, 26.35; H, 3.56; N, 12.12. $C_{10}H_{16}N_4Cl_2Pt$. Calculated (%): C, 26.21; H, 3.52; N, 12.23. MS, *m/z*: 458 $[M]^+$, 387 $[M - 2\,Cl]^+$. IR, ν/cm^{-1}: 3211 (N—H); 3145 (C—H); 1618, 1577 (C=N + C=C). ^{1}H NMR (acetone-d_6), δ: 12.01 (s, 1 H, NH); 5.98 (s, 1 H, C(4)H); 2.59 and 2.17 (both s, 3 H each, Me). ^{1}H NMR ($CDCl_3$), δ: 11.81 (s, 1 H, NH); 5.75 (s, 1 H, C(4)H); 2.66 and 1.99 (both s, 3 H each, Me). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: 150.9 (C(5)Me); 142.5 (C(3)Me); 105.8 (C(4)H); 13.9, 9.9 (Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 150.8 (C(5)Me); 141.9 (C(3)Me); 105.0 (C(4)H); 14.2, 10.0 (Me).

***cis*-Tetrachloro[bis(5-methylpyrazole)]platinum(IV), *cis*-$[PtCl_4(5\text{-}MepzH)_2]$ (3a).** DTA/TG: at 160 °C the gradual mass loss started; the mass loss was: 160—280 °C, 13.9%; 280—305 °C, 3.9%; 305—560 °C, 24.8%; 560—1000 °C, 14.3%. R_f 0.40 (CH_2Cl_2—Me_2CO, 12 : 1, as the eluent). Found (%): C, 19.36; H, 2.47; N, 11.19. $C_8H_{12}N_4Cl_4Pt$. Calculated (%): C, 19.18; H, 2.41; N, 11.18. MS, *m/z*: 498 $[M - 2\,H]^+$, 463 $[M - Cl - 2\,H]^+$, 427 $[M - 2\,Cl - 3\,H]^+$. IR, ν/cm^{-1}: 3311 (N—H); 3130 (C—H); 1563, 1504 (C=N + C=C). ^{1}H NMR (acetone-d_6), δ: 12.50 (s, 1 H, NH); 7.79 (d, 1 H, C(3)H, J = 2.2 Hz); 6.47 (d, 1 H, C(4)H, J = 2.2 Hz); 2.54 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: 142.4 (C(3)H); 107.6 (C(4)H); 11.0 (Me).

***cis*-Tetrachloro[bis(3,5-dimethylpyrazole)]platinum(IV), *cis*-[$PtCl_4$(3,5-Me_2pzH)$_2$] (3b).** DTA/TG: at 190 °C the gradual mass loss started; the mass loss was: 190—250 °C, 11.43%; 250—350 °C, 7.1%; 350—780 °C, 45.2%. R_f 0.44 (CH_2Cl_2—Me_2CO, 12 : 1, as the eluent). Found (%): C, 22.94; H, 3.16; N, 10.25. $C_{10}H_{16}N_4Cl_4Pt$. Calculated (%): C, 22.77; H, 3.05; N, 10.59. MS, *m/z*: 491 [M – Cl – 2 H]$^+$, 456 [M – 2 Cl – 2 H]$^+$, 421 [M – 3 Cl – 2 H]$^+$, 385 [M – 4 Cl – 2 H]$^+$. IR, ν/cm^{-1}: 3325 (N—H); 3116 (C—H); 1619, 1573 (C=N + C=C). ^{1}H NMR (acetone-d_6), δ: 11.89 (s, 1 H, NH); 6.20 (s, 1 H, CH); 2.47 and 2.11 (both s, 3 H each, Me). ^{13}C{^{1}H} NMR (acetone-d_6), δ: 109.5 (C(4)H); 13.7, 10.9 (Me).

***trans*-Tetrachloro[bis(5-methylpyrazole)]platinum(IV), *trans*-[$PtCl_4$(5-MepzH)$_2$] (4a).** DTA/TG: at 200 °C the gradual mass loss started; the mass loss was: 200—260 °C, 13.3%; 260—285 °C, 5.3%; 285—520 °C, 39.1%. R_f 0.60 (CH_2Cl_2—Me_2CO, 12 : 1, as the eluent). Found (%): C, 19.38; H, 2.59; N, 11.18. $C_8H_{12}N_4Cl_4Pt$. Calculated (%): C, 19.18; H, 2.41; N, 11.18. MS, *m/z*: 498 [M – 2 H]$^+$, 463 [M – Cl – 2 H]$^+$, 428 [M – 2 Cl – 2 H]$^+$. IR, ν/cm^{-1}: 3315 (N—H); 3145 (C—H); 1565, 1529 (C=N + C=C). ^{1}H NMR (acetone-d_6), δ: 12.47 (s, 1 H, NH); 8.01 (d, 1 H, C(3)H, J = 2.2 Hz); 6.46 (d, 1 H, C(4)H, J = 2.2 Hz); 2.52 (s, 3 H, Me). ^{13}C{^{1}H} NMR (acetone-d_6), δ: 140.9 (C(3)H); 108.1 (C(4)H); 11.1 (Me).

***trans*-Tetrachloro[bis(3,5-dimethylpyrazole)]platinum(IV), *trans*-[$PtCl_4$(3,5-Me_2pzH)$_2$] (4b).** DTA/TG: at 240 °C the gradual mass loss started; the mass loss was: 240—260 °C, 9.4%; 260—310 °C, 6.6%; 310—480 °C, 44.2%. R_f 0.49 (CH_2Cl_2 as the eluent). Found (%): C, 22.87; H, 3.08; N, 10.42. $C_{10}H_{16}N_4Cl_4Pt$. Calculated (%): C, 22.70; H, 3.05; N, 10.59. MS, *m/z*: 493 [M – Cl]$^+$, 457 [M – 2 Cl – H]$^+$, 385 [M – 4 Cl – 2 H]$^+$. IR,

Table 1. Crystallographic data and details of structure refinement for complexes **2b**, **3b**·CH_2Cl_2, **3b**·O=CMe_2, and **4a**

Parameter	**2b**	**3b**·CH_2Cl_2	**3b**·O=CMe_2	**4a**
Molecular formula	$C_{10}H_{16}Cl_2N_4Pt$	$C_{11}H_{18}Cl_6N_4Pt$	$C_{13}H_{22}Cl_4N_4OPt$	$C_8H_{12}Cl_4N_4Pt$
Molecular weight	458.26	614.08	587.24	501.11
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	16.1467(9)	9.1204(3)	9.2420(6)	12.0969(9)
b/Å	10.9909(3)	9.9721(2)	9.8553(6)	11.0746(10)
c/Å	17.6103(9)	11.9160(3)	11.8541(8)	10.5266(6)
α/deg	90	111.3240(10)	111.436(5)	90
β/deg	111.981(2)	109.0570(10)	107.621(5)	99.049(5)
γ/deg	90	90.939(2)	90.735(7)	90
V/Å^3	2898.1(2)	942.93(4)	948.54(11)	1392.68(18)
Z	8	2	2	4
d_{calc}/mg m^{-3}	2.101	2.163	2.056	2.390
μ/mm^{-1}	10.037	8.290	7.967	10.825
Scan range/deg	2.72—27.45	3.00—26.36	2.50—27.50	3.92—25.98
Number of measured reflections	34664	13951	17459	5211
(R_{int})	(0.0463)	(0.0306)	(0.0383)	(0.0466)
R_1 ($I \geq 2\sigma$)	0.0309	0.0189	0.0237	0.0258
wR_2 ($I \geq 2\sigma$)	0.0643	0.0395	0.0349	0.0537

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complexes **2b**, **3b**·CH_2Cl_2, **3b**·O=CMe_2, and **4a**

Parameter	**2b**		**3b**·CH_2Cl_2	**3b**·O=CMe_2	**4a**
	A	**B**			
Bond			d/Å		
Pt(1)—Cl(1)	—	—	2.3035(7)	2.2958(8)	2.3153(12)
Pt(1)—Cl(2)	2.3070(13)	2.2989(13)	2.3133(7)	2.3152(8)	2.312(2)
Pt(1)—Cl(3)	2.3011(13)	2.3072(13)	2.3045(7)	2.2947(7)	2.310(2)
Pt(1)—Cl(4)	—	—	2.3226(7)	2.3039(8)	—
Pt(1)—N(1)	2.015(4)	2.004(4)	2.050(2)	2.044(3)	2.013(4)
Pt(1)—N(3)	2.013(4)	2.003(5)	2.055(3)	2.046(2)	—
N(1)—N(2)	1.361(6)	1.368(6)	1.360(4)	1.349(3)	1.352(6)
N(3)—N(4)	1.346(6)	1.355(6)	1.360(3)	1.350(3)	—
Angle			ω/deg		
Cl(1)—Pt(1)—Cl(4)	—	—	89.11(3)	88.26(3)	—
Cl(2)—Pt(1)—Cl(3)	178.80(5)	178.45(5)	88.04(3)	88.84(3)	180.0
N(1)—Pt(1)—N(3)	177.15(18)	177.73(18)	90.36(10)	90.38(10)	—

ν/cm^{-1}: 3332 (N—H); 3149 (C—H); 1621, 1574 (C=N + C=C). ^{1}H NMR (acetone-d_6), δ: 11.72 (s, 1 H, NH); 6.16 (s, 1 H, CH); 2.76 and 2.52 (both s, 3 H each, Me). ^{13}C{^{1}H} NMR (acetone-d_6), δ: 109.0 (C(4)H); 15.0, 10.4 (Me).

X-ray diffraction analysis. Single crystals of complexes **2b**, **3b**·O=CMe$_2$, and **4a** suitable for X-ray diffraction study were grown by slow evaporation of solutions of these compounds in acetone (crystals of **3b**·CH_2Cl_2 were grown from dichloromethane) at 20—25 °C. Before X-ray data collection, crystals of complexes **2b**, **3b**·O=CMe$_2$, **3b**·CH_2Cl_2, and **4a** were mounted in a nylon loop and soaked in a cryo protectant. X-ray diffraction data sets were collected on a Nonius KappaCCD diffractometer at 100(2) K (**3b**·CH_2Cl_2) or 120 K (**2b**, **3b**·O=CMe$_2$, and **4a**) (monochromator, Mo-Kα radiation, λ = 0.71073 Å). The unit cell parameters were refined and the X-ray data were merged using the Denzo-Scalepack[42] or EvalCCD[43] program packages. The structures were solved by direct methods with the use of the SIR97,[44] SIR2002,[45] and SHELXS97[46] program packages and the WinGX graphics interface.[47] Absorption corrections were applied based on the intensities of equivalent reflections with the use of the XPREP program from the SHELXTL v.6.14-1 program package[48] and the SADABS v.2.10 program[49] (T_{min}/T_{max} were 0.2842/0.3327, 0.2418/0.4900, 0.3045/0.4146, and 0.1380/0.6136 for **2b**, **3b**·CH_2Cl_2, **3b**·O=CMe$_2$, and **4a**, respectively). All structures were refined using the SHELXL97 program package.[50] The hydrogen atoms of the NH groups in complexes **3b**·CH_2Cl_2 and **3b**·O=CMe$_2$ were located from difference Fourier maps and were not refined. All other hydrogen atoms were placed in calculated positions. The atomic coordinates and complete tables of bond lengths and bond angles were deposited with the Cambridge Structural Database. Principal crystallographic parameters and details of structure refinement are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

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References

1. H. R. Bigmore, S. C. Lawrence, Ph. Mountford, and C. S. Tredget, *J. Chem. Soc.*, *Dalton Trans.*, 2005, 635.
2. S. Trofimenko, *Polyhedron*, 2004, **23**, 197.
3. R. Mukherjee, *Coord. Chem. Rev.*, 2000, **203**, 151.
4. A. P. Sadimenko and S. S. Basson, *Coord. Chem. Rev.*, 1996, **147**, 247.
5. S.-W. Lai, M. C. W. Chan, K.-K. Cheung, S.-M. Peng, and C.-M. Che, *Organometallics*, 1999, **18**, 3991.
6. S.-W. Lai, M. C. W. Chan, K.-K. Cheung, S.-M. Peng, and C.-M. Che, *Inorg. Chem.*, 1999, **38**, 4046.
7. K. Umakoshi, Y. Yamauchi, K. Nakamiya, T. Kojima, M. Yamasaki, H. Kawano, and M. Onishi, *Inorg. Chem.*, 2003, **42**, 3907.
8. R. Larry, J. Fornies, A. Martin, V. Sicilia, and P. Villarroya, *Organometallics*, 2002, **21**, 4604.
9. C. Pettinari, F. Marchetti, A. Cingolani, S. I. Troyanov, and A. Drozdov, *J. Chem. Soc., Dalton Trans.*, 1998, **19**, 3335.
10. C. Pettinari, *Main Group Met. Chem.*, 1995, **18**, 183.
11. K. Sakai, Y. Tomita, T. Ue, K. Goshima, M. Ohminato, T. Tsubomura, K. Matsumoto, K. Ohmura, and K. Kawakami, *Inorg. Chim. Acta*, 2000, **297**, 64.
12. S. Komeda, M. Lutz, A. L. Spek, M. Chikuma, and J. Reedijk, *Inorg. Chem.*, 2000, **39**, 4230.
13. E. Budzisz, U. Krajewska, M. Rozalski, A. Szulawska, M. Czyz, and B. Nawrot, *Eur. J. Pharmacol.*, 2004, **502**, 59.
14. V. Yu. Kukushkin, *Zh. Neorg. Khim.,* 1988, **33**, 1085 [*J. Inorg. Chem. USSR*, 1988, **33** (Engl. Transl.)].
15. V. Yu. Kukushkin, *Zh. Neorg. Khim.,* 1988, **33**, 1905 [*J. Inorg. Chem. USSR*, 1988, **33** (Engl. Transl.)].
16. V. B. Arion, E. Reisner, M. Fremuth, M. A. Jakupec, B. K. Keppler, V. Yu. Kukushkin, and A. J. L. Pombeiro, *Inorg. Chem.*, 2003, **42**, 6024.
17. A. H. Velders, H. Kooijman, A. L. Spek, J. G. Haasnoot, D. De Vos, and J. Reedijk, *Inorg. Chem.*, 2000, **39**, 2966.
18. M. J. Cleare and J. D. Hoeschele, *Bioinorg. Chem.*, 1974, **2**, 187.
19. A. Boixassa, J. Pons, X. Solans, M. Font-Bardia, and J. Ros, *Inorg. Chim. Acta*, 2003, **355**, 254.
20. M. A. Cinellu, S. Stoccoro, G. Minghetti, A. L. Bandini, G. Banditelli, and B. Bovio, *J. Organomet. Chem.*, 1989, **372**, 311.
21. L. Kh. Minacheva, T. N. Fedorova, and G. N. Kuznetsova, *Zh. Neorg. Khim.,* 2001, **46**, 240 [*Russ. J. Inorg. Chem.*, 2001, **46** (Engl. Transl.)].
22. E. G. Talman, W. Brüning, J. Reedijk, A. L. Spek, and N. Veldman, *Inorg. Chem.*, 1997, **36**, 854.
23. C. G. van Kralingen, J. K. de Ridder, and J. Reedijk, *Transition Met. Chem.*, 1980, **5**, 73.
24. A. V. Khripun, M. Haukka, D. N. Nikolaeva, and V. Yu. Kukushkin, *Acta Crystallogr., Sect. E*, 2005, **61**, m2069.
25. A. V. Khripun and V. Yu. Kukushkin, *Tez. dokl. Mezhdunar. Chugaevskoi konf. po koordinatsionnoi khimii* [*Abstrs. of Papers, Int. Chugaev Conf. on Coordination Chemistry*] *(June 20—24, 2005, Kishinev)*, Kishinev, Moldova, 2005, p. 204 (in Russian).
26. Yu. N. Kukushkin, *Khimiya koordinatsionnykh soedinenii* [*Chemistry Coordination Compounds*], Vysshaya shkola, Moscow, 1985, 455 pp. (in Russian).
27. A. J. L. Pombeiro and V. Yu. Kukushkin, *Comprehensive Coordination Chemistry*, 2nd ed., Elsevier, 2004, **1**, 639.
28. G. Wagner, T. B. Pakhomova, N. A. Bokach, J. J. R. Fraústo da Silva, J. Vicente, A. J. L. Pombeiro, and V. Yu. Kukushkin, *Inorg. Chem.*, 2001, **40**, 1683.
29. K. V. Luzyanin, M. Haukka, N. A. Bokach, M. L. Kuznetsov, V. Yu. Kukushkin, and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2002, 1882.
30. Ya. A. Shuster, V. A. Kozlova, and V. I. Seraya, *Khim. Geterotsikl. Soedin.*, 1974, **12**, 1655 [*Chem. Heterocycl. Compd.*, 1974, **12** (Engl. Transl.)].
31. D. Ya. Movshovich, V. N. Sheinker, T. A. Zayakina, A. D. Garnovskii, and O. A. Osipov, *Zh. Obshch. Khim.*, 1981, **51**, 636 [*J. Gen. Chem. USSR*, 1981, **51** (Engl. Transl.)].
32. F. Kratz, B. Nuber, J. Weiss, and B. K. Keppler, *Polyhedron*, 1992, **11**, 487.
33. M. Cano, J. A. Campo, J. V. Heras, J. Lafuente, C. Rivas, and E. Pinilla, 1995, **14**, 1139.
34. J. L. Atwood, K. R. Dixon, D. T. Eadie, S. R. Stobart, and M. J. Zaworotko, *Inorg. Chem.*, 1983, **22**, 774.

35. C. Lopez, R. M. Claramunt, S. Trofimenko, and J. Elguero, *Can. J. Chem.*, 1993, **71**, 678.
36. H. W. W. Ehrlich, *Acta Crystallogr.*, 1960, **13**, 46.
37. J. A. S. Smith, B. Wehrle, F. Aguilar-Parrilla, H.-H. Limbach, M. C. Foces-Foces, F. H. Cano, J. Elguero, A. Baldy, M. Pierrot, M. M. T. Khurshid, and J. B. Larcombe-McDouall, *J. Am. Chem. Soc.*, 1989, **111**, 7304.
38. S. A. Cotton, V. Franckevicius, and J. Fawcett, *Polyhedron*, 2002, **21**, 2055.
39. F. S. Keij, R. A. G. de Graaff, J. G. Haasnoot, J. Reedijk, and E. Pedersen, *Inorg. Chim. Acta*, 1989, **156**, 65.
40. Y.-J. Sun, X.-Y. Chen, P. Cheng, S.-P. Yan, D.-Z. Liao, Z.-H. Jiang, and P.-W. Shen, *J. Mol. Struct.*, 2002, **613**, 167.
41. X. Liu, C. A. Kilner, and M. A. Halcrow, *Chem. Commun.*, 2002, 704.
42. Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, in *Methods in Enzymology*, Vol. **276**, *Macromolecular Crystallography*, Part A, Eds C. W. Carter and R. M. Sweet, Academic Press, New York, 1997, pp. 307—326.
43. A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, and A. M. M. Schreurs, *J. Appl. Crystallogr.*, 2003, **36**, 220.
44. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
45. M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, and R. Spagna, *J. Appl. Crystallogr.*, 2003, **36**, 1103.
46. G. M. Sheldrick, *SHELXS97*, *Program for Crystal Structure Determination*, University of Göttingen, Göttingen (Germany), 1997.
47. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
48. G. M. Sheldrick, *SHELXTL v. 6.14-1*, Bruker AXS Inc., Madison (Wisconsin, USA), 2005.
49. G. M. Sheldrick, *SADABS — Bruker Nonius Scaling and Absorption Correction*, v. 2.10, Bruker AXS Inc., Madison (Wisconsin, USA), 2003.
50. G. M. Sheldrick, *SHELXL97*, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen (Germany), 1997.

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