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Unusual Reaction between (Nitrile)Pt Complexes and Pyrazoles: Substitution Proceeds via Metal-Mediated Nitrile–Pyrazole Coupling Followed by Elimination of the Nitrile

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The reaction of platinum(IV) complex *trans*-$[PtCl_4(EtCN)_2]$ with pyrazoles 3,5-RR′pzH (R/R′ = H/H, Me/H, Me/Me) leads to the formation of the *trans*-$[PtCl_4\{NH{=}C(Et)(3,5\text{-}RR'pz)\}_2]$ (**1**–**3**) species due to the metal-mediated nitrile–pyrazole coupling. Pyrazolylimino complexes **1**–**3** (i) completely convert to pyrazole complexes *cis*-$[PtCl_4(3,5\text{-}RR'pzH)_2]$ by elimination of EtCN upon reflux in a CH_2Cl_2 solution or upon heating in the solid state; (ii) undergo exchange at the imino C atom with another pyrazole different from that contained in the pyrazolylimino ligand. The reaction of *trans*-$[Pt^{II}Cl_2(EtCN)_2]$ and 3,5-RR′pzH, conducted under conditions similar to those for *trans*-$[Pt^{IV}Cl_4(EtCN)_2]$, is much less selective, and the composition of the products strongly depends on the pyrazole employed: (a) with pzH, the reaction gives a mixture of three products, i.e., $[PtCl_2\{NH{=}C(Et)pz\text{-}\kappa^2N,N\}]$ (**4**), $[PtCl(pzH)\{NH{=}C(Et)\text{-}pz\text{-}\kappa^2N,N\}]Cl$ (**5**), and $[Pt(pzH)_2\{NH{=}C(Et)pz\text{-}\kappa^2N,N\}]Cl_2$ (**6**) (complexes **5** and **6** are rather unstable and gradually transform to *trans*-$[PtCl_2(pzH)_2]$ and $[Pt(pzH)_4]Cl_2$ and free EtCN); (b) with 3,5-Me_2pzH, the reaction leads to the formation of $[PtCl_2\{NH{=}C(Et)(3,5\text{-}Me_2pz)\text{-}\kappa^2N,N\}]$ (**7**) and $[PtCl(3,5\text{-}Me_2pzH)_3]Cl$ (**8**); (c) in the case of asymmetric pyrazole 3(5)-MepzH, which can be added to EtCN and/or bind metal centers by any of the two nonequivalent nitrogen sites, a broad mixture of currently unidentified products is formed. The reduction of **1**–**3** with $Ph_3P{=}CHCO_2Me$ in $CHCl_3$ allows for the formation of corresponding platinum(II) compounds *trans*-$[PtCl_2\{NH{=}C(Et)(3,5\text{-}RR'pz)\}_2]$ (**9**–**11**). Ligands NH=C(Et)(3,5-RR′pz) (**12**–**14**) were almost quantitatively liberated from **9**–**11** with 2 equiv of 1,2-bis-(diphenylphosphino)ethane in $CDCl_3$, giving free imines **12**–**14** in solution and the precipitate of *trans*-$[Pt(dppe)_2](Cl)_2$. Pyrazolylimines **12**–**14** undergo splitting in $CDCl_3$ solution at 20–25 °C for ca. 20 h to furnish the parent propiononitrile and the pyrazole 3,5-RR′pzH, but they can be synthetically utilized immediately after the liberation.

Introduction

The activation of organonitriles by metal centers toward nucleophilic[1−5] or electrophilic additions[1,2,6] or 1,3-dipolar cycloaddition[1,7,8] is a frontier area of research targeted on further exploration of the synthetic potential of RCN species.

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The application of nitrile transition-metal complexes for these purposes has been surveyed in a number of reviews,[1−5] including the ones written by two of us.[1−4]

As far as nucleophilic addition is concerned, literature up to this date clearly shows that in the vast majority of cases, the coordination of organonitriles to metal centers makes their reactions with nucleophilic reagents favorable, resulting in versatile imino compounds with new C−N, C−O, C−C, C−P, and C−S bonds. The largest number of these studies is devoted to the creation of a C−N bond by the addition of protic HN nucleophiles, where the N atom is in sp^3 hybridization (i.e., ammonia,[9] primary and secondary amines,[10] hydrazines,[11] hydroxylamines[12]) and is relevant to hydrolytic amidation of RCN species (e.g., for metal-catalyzed formation of amides from nitriles[1,13]).

Despite the wealth of examples of metal-mediated RCN−(sp^3)-amine integration, only a limited number of works deals with the nitrile coupling with the imines HN=ERR′,[14,15] in which the nucleophilic N atom is in sp^2 hybridization. In addition to the reactions with the imines, one of the recently emerged and intriguing themes is the application of azaheterocyclic systems for the additions to metal-activated RCN. It is worth mentioning that the significant difference between the azaheterocycles and the imines is the possible involvement of the azoheterocycle's electron pair in aromatization. Thus, the reported studies include some examples of the metal-mediated additions of pyrazoles to organonitriles[16−24] (Figure 1, **A**) and three instances of the coupling between 1*H*-indazole and RCN at a Ru^{II} center[25] (**B**), 7-azaindole and nitriles mediated by an Os_6 cluster[26] (**C**), and between amino-alkylated adenines and RCN at a Re^{IV} center[27] (**D**). With a rare exception,[24,25] coupling with the azaheterocycles has not been investigated systematically and data on the reactivity of newly formed ligands **A**−**D** (Figure 1) has not been obtained. However, the listed reports give collateral evidence that the probability of metal-mediated nitrile−azaheterocycle integration is rather high for the pyrazole-type systems.

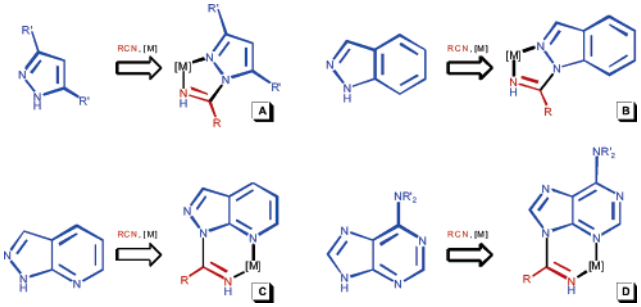

Figure 1. Examples of metal-mediated additions of pyrazoles to organonitriles (**A**), coupling between 1*H*-indazole and RCN at a Ru^{II} center (**B**), 7-azaindole and nitriles mediated by an Os_6 cluster (**C**), and between amino-alkylated adenines and RCN at a Re^{IV} center (**D**).

With an interest in the amplification of our works[1,2] on the reactions of (nitrile)[M] complexes and various protic HN nucleophiles to more-complicated and much less studied heterocyclic systems, we focused our attention on the reactions between (nitrile)Pt compounds and pyrazoles. Our aim was (i) to get an easy entry to the seldom-explored pyrazolylimino moieties; (ii) to clarify the effects of the oxidation state of the platinum center on the coupling reaction by comparing our results obtained for Pt^{II} and for the corresponding Pt^{IV} systems; (iii) to investigate the reactivity of the iminoacylated pyrazole functionality.

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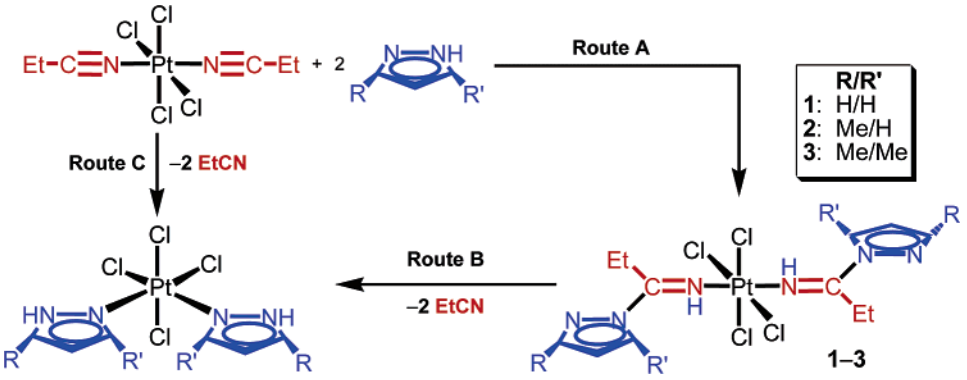
Scheme 1



We report herein on the reaction of (nitrile)Pt(IV) and (nitrile)Pt(II) complexes with pyrazoles and provide evidence that substitution of RCN ligands might proceed in an unusual way via metal-mediated nitrile−pyrazole coupling followed by elimination of RCN to furnish (pyrazole)Pt species.

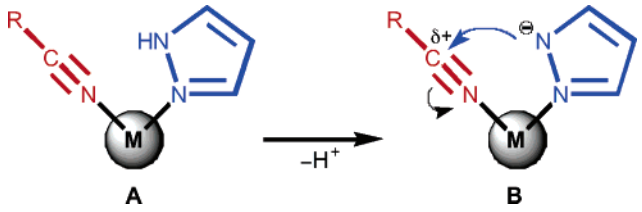
Results and Discussion

Although a great amount of works have dealt with nucleophilic additions to organonitriles bound to Pt^{II} centers,[1−4] only recently has it been established that a Pt^{IV} center provides a substantially stronger activation of RCN species, making reactions that cannot occur at Pt^{II}, as well as a great variety of other metal centers, feasible. In fact, platinum(IV) is currently recognized as being one of the strongest electrophilic activators of RCN substrates, which allow the performance of a facile coupling or [2+3] cycloadditions.[1−4] For this work, we addressed the kinetically inert (relative to other nitrile metal compounds) (nitrile)Pt(IV) and (nitrile)-Pt(II) complexes $[PtCl_n(EtCN)_2]$ (n = 4, 2), which proved to be superior models for investigations of the additions to nitriles; on the other hand, we studied pyrazoles 3,5-RR′pzH (R/R′ = H/H, Me/H, Me/Me) with various degrees of substitution to investigate the influence of the substituent on the proceeding reactions. The choice of propiononitrile complexes is explained by the fact that the Et group in $[PtCl_4(EtCN)_2]$ provides a rather good solubility of the platinum(IV) complex in nonpolar solvents, contrary to the poorly soluble, although more common, $[PtCl_4(RCN)_2]$ (R = Me, Ph).

Pyrazole−Nitrile Coupling at a Pt(IV) Center. The reaction of *trans*-$[PtCl_4(EtCN)_2]$ and pyrazoles 3,5-RR′pzH in a CH_2Cl_2 suspension occurs for 2 h at room temperature and leads to the formation of the *trans*-$[PtCl_4\{NH{=}C(Et)(3,5\text{-}RR'pz)\}_2]$ (**1**−**3**) species (Scheme 1, Route A).

Increasing the reaction time between *trans*-$[PtCl_4(EtCN)_2]$ and 3,5-RR′pzH (42, 122, or 22 h for R/R′ = H/H, Me/H, or Me/Me, respectively; the reaction time depends mostly on the solubilities of the complexes) or carrying out the reaction under harsh conditions (reflux for 2−45 h) or under treatment with focused 200 W microwave irradiation for 0.5−12 h leads to the formation of *cis*-$[PtCl_4(3,5\text{-}RR'pzH)_2]$ (Route C) with no traces of **1**−**3**. However, the resulting *cis*-$[PtCl_4(3,5\text{-}RR'pzH)_2]$ complex is contaminated with the appropriate *trans*-$[PtCl_4(3,5\text{-}RR'pzH)_2]$ (ca. 10:1 ratio by ^1H NMR integration); the latter complex presumably formed as a result of a partial thermal isomerization of the former one, in accord with our earlier data on these complexes.[28,29] Moreover, we also found that imino complexes **1**−**3** completely convert to known pyrazole complexes *cis*-$[PtCl_4(3,5\text{-}RR'pzH)_2]$ (R/R′ = H/H, Me/H, Me/Me) by elimination of EtCN (detected by ^1H and $^{13}C\{^1H\}$ NMR, e.g., $^{13}C\{^1H\}$ NMR, δ: 121.1 (*E*t*C*N)) upon reflux on stirring for 1−44 h (or within 20−120 h at room temperature) in a CH_2Cl_2 solution (Scheme 1, Route B).

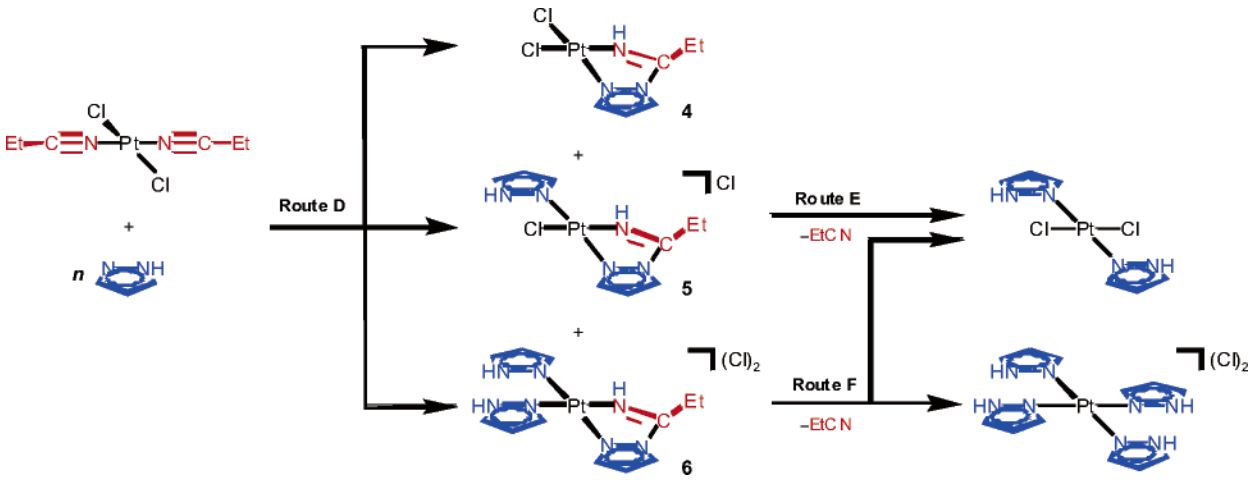
Scheme 2



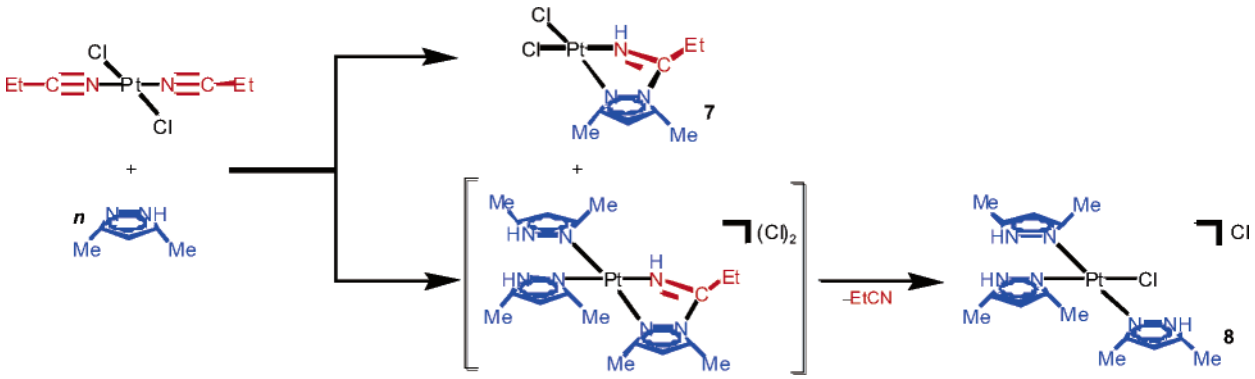
Although nitrile−pyrazole type heterocycle coupling has been reported in a number of papers,[16−25] in most of these works, their authors exclusively described synthetic experiments and only a few attempts were made to suggest a plausible mechanism of this unusual conversion. Thus, all documented examples of the coupling include the formation of solely chelated complexes (Figure 1, **A** and **B**) and this fact allowed the assumption[18,24] of an intramolecular mechanism of the reaction when a pyrazole coordinates (via the pyridine N atom) to a metal center in the adjacent position to a metal-bound nitrile (Scheme 2, A) followed by the coupling between the electrophilically activated RCN and the NH pyrrole site of the heterocycle. This approach has certain conceptual problems insofar as the pyrrole NH moiety does not exhibit nucleophilic properties because of the involvement of the electron pair at the N atom in the aromatic system. To avoid these difficulties, another group of authors[25] suggested that deprotonation of the pyrrole group, leading to the appearance of the nucleophilic site, advanced the coupling (Scheme 2, B).

Our experiments with the (nitrile)Pt^{IV} complex indicate that the coupling might proceed in an intermolecular way to form open-chain species **1**−**3**. Indeed, the formation of the chelated NH═C(R)pz-κ^2N,N ligand followed by the ring-opening is hardly probable at a very kinetically inert Pt^{IV} center. On the basis of these and the previous[16−25] observa-

Scheme 3



Scheme 4



tions, we assume that both intra- and intermolecular paths for the reaction are possible and that their occurrence depends on the electronic configuration of the metal center employed and its kinetic lability/inertness. We suggest that, in the case of the Pt^{IV} system, the reaction with the pyrazoles proceeds via the nucleophilic attack of the pyridine N atom followed by H-transfer (either from the pyrrole NH site or by the solvent-assisted path) to the Pt-bound iminato group formed upon the addition.

Pyrazole−Nitrile Coupling at a Pt(II) Center. The reaction of the platinum(II) complex *trans*-$[PtCl_2(EtCN)_2]$ and pyrazoles 3,5-RR′pzH was carried out under conditions (CH_2Cl_2, 20−25 °C, 2 h) similar to those described above for the platinum(IV) complex *trans*-$[PtCl_4(EtCN)_2]$. It appears that being conducted at the more kinetically labile Pt^{II} center (relative to the Pt^{IV} center) makes the reaction much less selective; in addition, the composition of products strongly depends on the pyrazole employed.

In the case of the unsubstituted pyrazole, the reaction between *trans*-$[PtCl_2(EtCN)_2]$ and pzH in a 1:1 molar ratio gives a mixture of three products, i.e., $[PtCl_2\{NH{=}C(Et)pz\text{-}\kappa^2N,N\}]$ (**4**), $[PtCl(pzH)\{NH{=}C(Et)pz\text{-}\kappa^2N,N\}]Cl$ (**5**), and $[Pt(pzH)_2\{NH{=}C(Et)pz\text{-}\kappa^2N,N\}]Cl_2$ (**6**) (Scheme 3, Route D); variation of the molar ratio of the reactants does not improve the selectivity of the coupling/substitution. Complexes **5** and **6** are rather unstable and gradually transform (2 days in acetone or MeOH solutions, respectively) to the pyrazole compounds depicted in Scheme 3 (routes E and F). In acetone-d_6 (reaction E) and in CD_3OD (reaction F), we also succeeded to detect EtCN by the NMR method.

Earlier, Cinellu et al.[22] reported that the interplay between pzH and $[PtCl_2(PhCN)_2]$ leads to a mixture of known *trans*-$[PtCl_2(pzH)_2]$[30] and the coupling product $[PtCl_2\{NH{=}C(Ph)pz\text{-}\kappa^2N,N\}]$, which was characterized by spectroscopic methods. By investigation of a similar system but with a less-electron-deficient nitrile (EtCN), we succeeded in identifying other products of the reaction and confirming unambiguously, by X-ray diffraction (see later), the formulation of $[PtCl_2\{NH{=}C(R)pz\text{-}\kappa^2N,N\}]$. All the more important that we observed that pyrazole complexes *trans*-$[PtCl_2(pzH)_2]$ and $[Pt(pzH)_4]Cl_2$[28,29,31] might originate from the elimination of EtCN from the initially formed imino compounds; this elimination will be discussed later in this article.

Furthermore, treatment of *trans*-$[PtCl_2(EtCN)_2]$ with the most sterically demanding pyrazole (3,5-Me_2pzH) leads to the formation of two complexes, $[PtCl_2\{NH{=}C(Et)(3,5\text{-}Me_2pz)\text{-}\kappa^2N,N\}]$ (**7**) and $[PtCl(3,5\text{-}Me_2pzH)_3]Cl$ (**8**) (Scheme 4). The latter presumably formed as a result of the decomposition of $[Pt(3,5\text{-}Me_2pzH)_2\{NH{=}C(Et)(3,5\text{-}Me_2pz)$-

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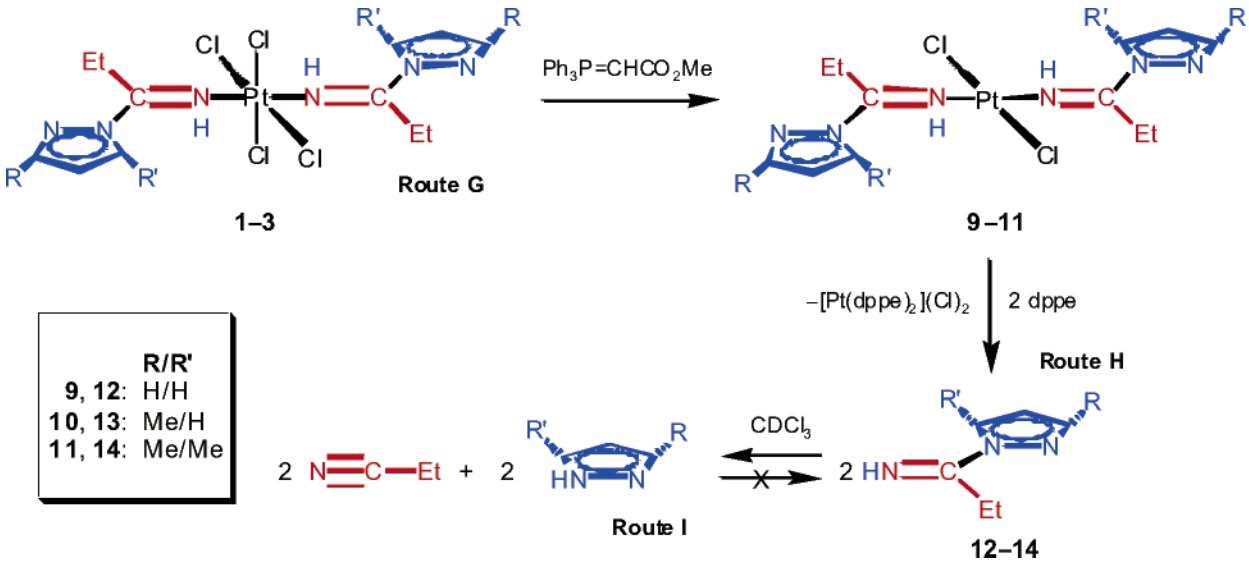
Scheme 5



κ^2N,N}](Cl)$_2$, which is, unlike analogous compound **6**, substantially less stable, probably because of the steric hindrance of the ligands. Finally, in the case of asymmetric pyrazole 3(5)-MepzH, which can be added to EtCN and/or can bind metal centers by any of the two nonequivalent nitrogen sites, a broad mixture of yet unidentified products is formed.

Thus, the described results from this and from the previous section show that the coordination mode of the pyrazolylimino species depends on the oxidation state of the Pt centers. In the case of Pt^{II} complexes, contrary to in Pt^{IV} systems, there appears to be an explicit tendency toward the bidentate coordination mode; earlier, we observed this tendency for other systems.[14,32]

Liberation of the Imino Ligands from the Platinum Complexes. Although metal-mediated coupling between azaheterocycles and nitriles has already been observed,[16−27] in all the reported instances, the reaction results in the formation of the chelated pyrazolylimino species (Figure 1); these should be rather inert toward substitution (see, for example, ref 33), and no attempts for liberation of NH═C(Et)(3,5-RR′pz) were undertaken. In our case, the formation of open-chain rather than chelated ligands gives better potential opportunities for their substitution, and we decided to explore this route for the preparation of these yet unknown compounds by the displacement of NH═C(Et)(3,5-RR′pz) from their Pt(IV) and Pt(II) complexes.

The endeavor of the liberation of imines NH═C(Et)(3,5-RR′pz) from Pt^{IV} complexes **1**−**3** with an excess of pyridine in $CHCl_3$, by the known method,[34] was not successful insofar as the treatment of **1**−**3** with C_5H_5N results in a broad mixture of unidentified species. However, we succeeded in performing the liberation starting from the corresponding Pt^{II} complexes *trans*-[$PtCl_2${NH═C(Et)(3,5-RR′pz)}$_2$].

Thus, in the first step, the reduction of **1**−**3** with a 1.2-fold excess of Ph_3P═$CHCO_2Me$ at room temperature in $CHCl_3$ (by the previously reported procedure[35]) allows for the formation of the corresponding platinum(II) compounds *trans*-[$PtCl_2${NH═C(Et)(3,5-RR′pz)}$_2$] (**9**−**11**) (Scheme 5, Route G) along with phosphorus-containing species. The latter were separated and, consequently, **9**−**11** were purified by fast washing with cold MeOH and the complexes were obtained in 65−85% isolated yields. These complexes are rather stable; only on being kept in $CDCl_3$ or acetone-d_6 solution for 1 day (**11**) or 1 or 2 months (**9** and **10**, respectively) at 20−25 °C do they gradually decompose to give a mixture of *trans*-[$PtCl_2(EtCN)_2$], the free pyrazole, and the chelated compounds (**4**, **7** for R/R′ = H/H, Me/Me), or compounds similar to those depicted in Schemes 3 and 4.

In the second step, ligands NH═C(Et)(3,5-RR′pz) (**12**−**14**) were almost quantitatively liberated from complexes **9**−**11** with 2 equiv of 1,2-bis-(diphenylphosphino)ethane (dppe) in $CDCl_3$ (Scheme 5, Route H), giving free imines **12**−**14** in solution and the precipitate of well-known *trans*-[Pt(dppe)$_2$](Cl)$_2$ ($^{31}P\{^1H\}$ NMR in $CDCl_3$, ppm: 48.4, J_{Pt-P} = 2348.5 Hz;[36] 45.7, J_{Pt-P} = 2360.5 Hz); the latter complex is separated from the reaction mixture by filtration. Identification of **12**−**14** (IUPAC name: 1-(3,5-RR′-1*H*-pyrazol-1-yl)propan-1-imine) in solution was done by both ^1H and $^{13}C\{^1H\}$ NMR (see Experimental Section).

The latter methods also indicate that free imines NH═C(Et)(3,5-RR′pz), having a restricted lifetime, undergo the splitting in a $CDCl_3$ solution at 20−25 °C for ca. 20 h to furnish the parent propiononitrile and pyrazole 3,5-RR′pzH (Scheme 5, Route I). An additional ^1H NMR experiment shows that EtCN does not react with the pyrazoles under the reaction conditions or under even more drastic conditions

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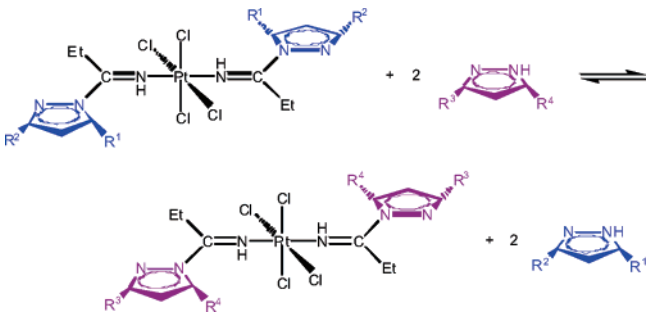
Scheme 6



(45 °C, 7 days) and all these observations together support the idea that the coupling between the nitrile and the pyrazoles is metal-mediated.

Reactivity of the Pyrazolylimine Ligands. We have described above that Pt^{IV} and Pt^{II} complexes bearing the pyrazolylimino ligands undergo further conversion to the (pyrazole)Pt compounds and EtCN (Schemes 1, 3, and 4) in solution. We also found that this type of conversion occurs in the solid state. Thus, TG/DTA measurements of imino complexes **1**−**3** and **9**−**11** display a mass-loss (see Experimental Section) that corresponds to the elimination of 2 equiv of EtCN per molecule; occurrence of the elimination was proved by condensation of the evolving gaseous products, followed by NMR monitoring of the condensate. In synthetic experiments, heating of platinum(IV) complexes **1**−**3** in the solid phase at 150−170 °C leads to the quantitative formation of the known[28,29] *cis*-[$PtCl_4$(3,5-RR′pzH)$_2$] species, which, on further heating, isomerize to the trans isomers. In the case of platinum(II) complexes **9**−**11**, formation of [$PtCl_2$(3,5-RR′pzH)$_2$],[28,29] which was identified by both TLC and NMR methods, proceeds concurrently with the complex's decomposition to give a mixture of products.

A relevant observation was made when we treated a suspension of **1**−**3** in $CDCl_3$ with excess of another pyrazole (other than that contained in the pyrazolylimino ligand) and observed an exchange of the pyrazole group as depicted in Scheme 6. This exchange at the imino C atom resembles that observed earlier at Fischer type carbene ligands.[37] Unfortunately, poor solubility of the Pt^{IV} complexes prevents us from performing a qualitative study of this kind of exchange.

It is worth noting that our observations match well with those reported by Oro et al.,[24] who investigated polynuclear Ir/Ag complexes with pyrazolylimino ligand NH═C(Me)(pz) and found that the imino moiety in CD_3CN exhibits an exchange to give the metal-bound NH═C(CD_3)(pz). The latter data, along with the experiments disclosed in this article, indicate a substantial lability of the NH═C(R″)(RR′pz) moiety and that the formation of pyrazole complexes [$PtCl_4$(3,5-RR′pzH)$_2$] in the reaction between *trans*-[$PtCl_4$(EtCN)$_2$] and 3,5-RR′pzH (Scheme 1, Route C) might proceed via the formation of imino complexes **1**−**3** (Route A) followed by elimination of EtCN (Route B).

Characterization of the Coupling Products. The structures of platinum(IV) (**2**) (Figure 2) and platinum(II) (**4**, **9**, and **10**) complexes (Figures 3−5) were determined by X-ray single-crystal diffraction; one should notice that structures **2**, **9**, and **10** are the first examples of complexes with open-chain ligands HN═C(Et)(3-Rpz), whereas structure **4** represents the first structurally characterized platinum complex with chelating ligand NH═C(Et)pz-κ^2N,N.

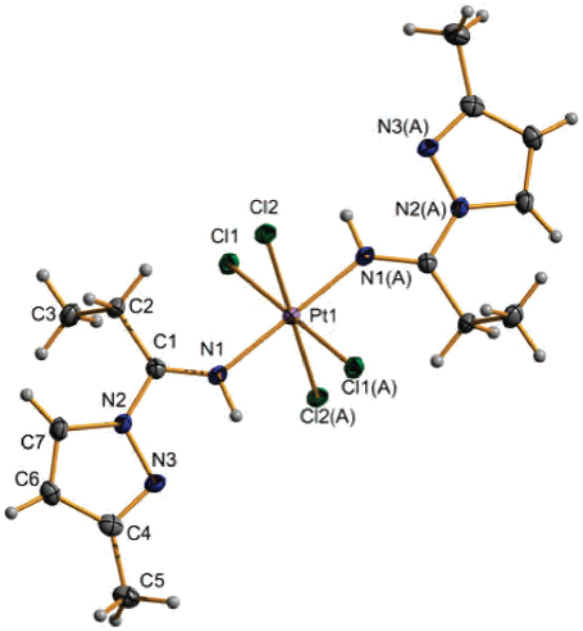


Figure 2. Thermal ellipsoid view of **2** with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt1−Cl1 2.3035(7), Pt1−Cl2 2.3133(7), Pt1−Cl3 2.3045(7), Pt1−Cl4 2.3226(7), Pt1−N1 2.050(2), Pt1−N3 2.055(3), N1−C1 1.343(4), N1−N2 1.360(4), N3−C6 1.339(4), N3−N4 1.360(3); N1−Pt1−N3 90.36(10), Cl1−Pt1−Cl3 90.68(3), Cl2−Pt1−Cl4 175.21(3), N1−Pt1−N1# 180.0. Symmetry transformations used to generate equivalent atoms: # $-x+1, -y+1, -z+1$.

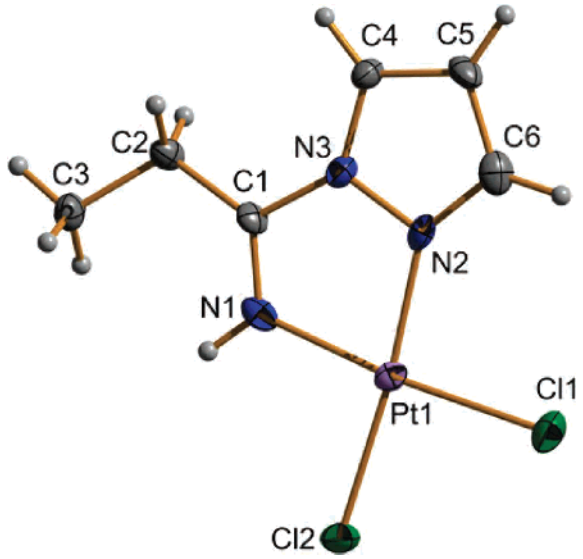


Figure 3. Thermal ellipsoid view of **4** with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt(1)−Cl(1) 2.306(2), Pt(1)−Cl(2) 2.298(2), Pt(1)−N(2) 1.985(6), Pt(1)−N(1) 1.996(6), N(2)−N(3) 1.369(8), N(1)−C(1) 1.279(9), N(3)−C(1) 1.405(9), C(1)−C(2) 1.469(10); N(2)−Pt(1)−N(1) 79.0(2), Cl(2)−Pt(1)−Cl(1) 90.63(7), N(2)−N(3)−C(1) 117.2(6), N(1)−C(1)−N(3) 113.0(6), N(1)−C(1)−C(2) 129.0(7).

The coordination polyhedra of the complexes are slightly distorted octahedra and square planes. In complexes **2**, **9**,

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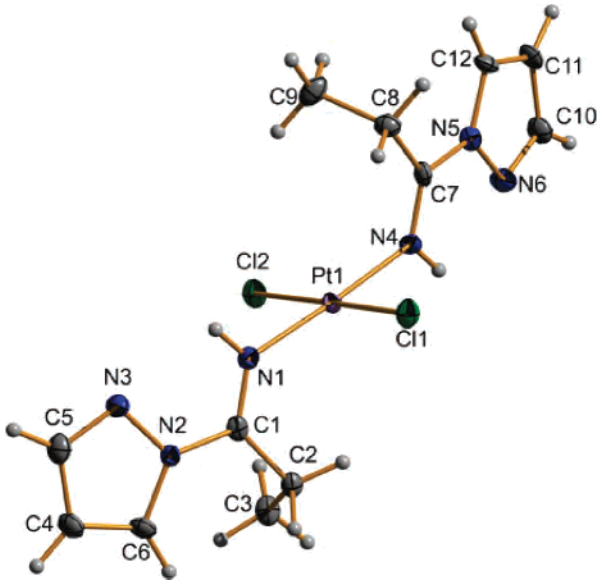

Figure 4. Thermal ellipsoid view of **9** with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) (there are 2.5 Pt molecules in the asymmetric unit (labels A, B, and C, respectively): Pt1−N1 2.011(4), Pt1−N4 2.016(4), Pt1−Cl1 2.3021(13), Pt1−Cl2 2.3096(13), Pt1(B)−N4(B) 2.009(4), Pt1(B)−N1(B) 2.020(4), Pt1(B)−Cl1(B) 2.3019(13), Pt1(B)−Cl2(B) 2.3103(13), Pt1(C)−N1(C) 2.005(4), Pt1(C)−Cl1(C) 2.3083(13), Pt1(D)−N1(D) 2.021(4), Pt1(D)−Cl1(D) 2.3047(13); N1−Pt1−N4 176.86(16), Cl1−Pt1−Cl2 179.17(5), N1−C1−N2 119.8(4), N4B−Pt1B−N1B 177.44(16), Cl1B−Pt1B−Cl2B 178.31(5), N1B−C1B−N2B 119.9(4), N1C−Pt1C−N1C#1 180.0, Cl1C−Pt1C−Cl1C#1 180.0, N1C−C1C−N2C 119.8(4). Symmetry transformations used to generate equivalent atoms: # $-x+1, -y, -z+1$.

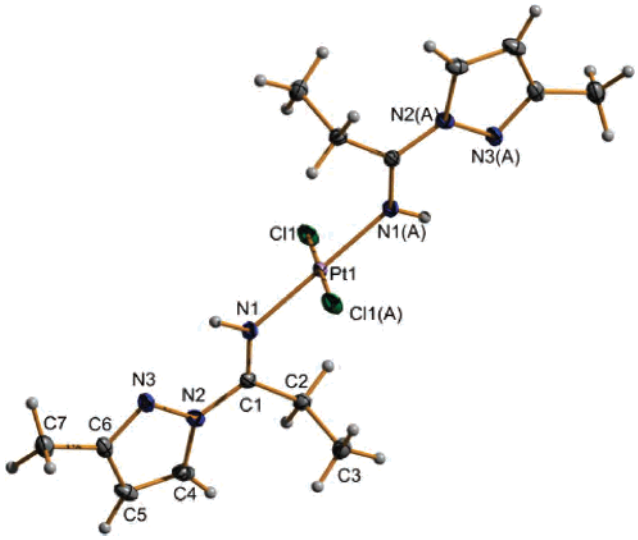

Figure 5. Thermal ellipsoid view of **10** with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.011(2), Pt(1)−Cl(1) 2.3072(7), N(1)−C(1) 1.275(3), C(1)−C(2) 1.491(4), C(1)−N(2) 1.396(3); N(1)−Pt(1)−Cl(1) 91.74(6), Cl(1)−Pt(1)−Cl(1A) 180.0, C(1)−N(1)−Pt(1) 128.6(2), N1−Pt1−N1# 180.0. Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z+1$.

and **10**, the two open-chain imino ligands are mutually trans and in the *E* configuration. In **4**, two Cl atoms occupy the cis positions and the other two coordination positions are filled with N atoms from the imine and pyrazole moieties of the chelating NH═C(Et)pz-κ^2N,N ligand. In the structurally characterized complexes, the values of all bond distances

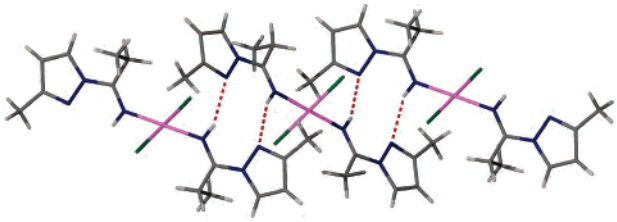

Figure 6. Intermolecular hydrogen bonding in **10**. N1−H1 = 0.88 Å, H1···N3# = 2.25 Å, N1···N3# = 3.063(3) Å, N1−H1···N3# = 152.6°.

and angles around the Pt center are normal[38] and in a good agreement with those previously found in platinum(IV) and platinum(II) compounds of type $[PtCl_n\{NH{=}C(R)R'\}_2]$ (n = 4, 2).[14,32,39] The C═N bond lengths (1.27−1.29 Å) in all complexes correspond to the mean value of the C═N double bonds (1.279 Å[40]). It should be noted that in **2** and **10**, the asymmetric pyrazole 3(5)-MepzH adds to the nitrile N≡C group through the *N* atom that is the most remote from the methyl group of the heterocycle; the addition via this atom matches well with the coordination of 3(5)-MepzH via the same site to a variety of metal centers.[29,41]

The arrangement of the Pt^{II} complexes (**9** and **10**) deserves separate comments. Thus, in **10** (Figure 6), the nearest molecules are linked by complementary N−H···N interactions between the N*H* imine moiety of one molecule and the N pyrazole atom of the neighboring molecule with a distance of 3.063(3) Å, forming sinusoid infinite chains. In the other Pt^{II} complex (**9**), the intermolecular N−H···N interactions are weaker, with N···N distances of 3.342(5)−3.593(5) (see the Supporting Information, Figure S1), but give the same chainlike array. It is curious that in the related Pt^{IV} complex **2**, two additional Cl atoms destroy this H-bonding scheme (see the Supporting Information, Figure S2).

It is worthwhile to mention that currently there is an intense interest in the formation of array systems containing transition-metal centers linked by hydrogen bonding from metal-bound species. The real challenge in this field is the design of synthons having a number of well-oriented hydrogen-bond donors and acceptors within one molecule.[28,42] From this viewpoint, in **9** and **10**, Pt^{II}-bound iminoacylated pyrazoles bearing one imino H atom and one

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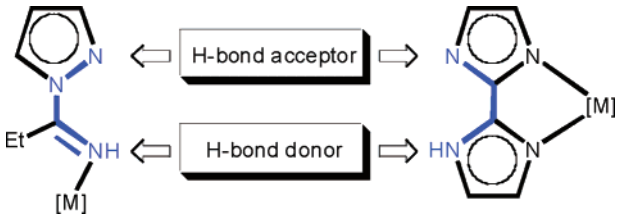

Figure 7. Self-assembly of a 2,2′-biimidazolate transition-metal complex.

pyridine type −N═ atom provide a novel and useful system for self-assembly that resembles those of 2,2′-biimidazolate transition-metal complexes (Figure 7), which were successfully employed as excellent building blocks for crystal-engineering purposes.[43]

In addition to the X-ray structural data, formulation of complexes {NH═C(Et)(3,5-RR′pz}Pt(IV) and {NH═C(Et)-(3,5-RR′pz}Pt(II) (**1**−**4**, **6**, **7**, and **9**−**11**) was supported by the satisfactory C, H, and N elemental analyses and the expected molecular ion and fragmentation patterns in FAB^+ mass spectra for complexes **1**−**7** and **9**−**11**. In the IR spectra, the absence of C≡N stretching vibrations, the presence of ν(N−H) bands (3296−3232 cm^{-1}) from the imino group, and characteristic strong vibrations of ν(C═N) (1650−1627 cm^{-1}) were recognized. The fingerprint areas for all 10 compounds, in number of peaks, their position, and intensity, are similar to those of noncoordinated 3,5-RR′pzH in these ranges.

NMR data confirmed the formation of the coupling products formed via the addition of the pyrazole to the nitrile N≡C group. The ^{1}H NMR spectra of **1**−**7** and **9**−**11** show a broad signal, displayed in the range from 9.5 to 11.0 ppm, attributable to the imino N*H* proton presumably involved in H-bonding in solution.[44] Compared to the ^{1}H NMR spectra of the starting reactants (3,5-RR′pzH and $[PtCl_4(EtCN)_2]$), most of signals, especially those that correspond to the pyrazole fragment, in the spectra of **1**−**7** and **9**−**11** display a low-field shift, which increases from the open-chain Pt^{II} (**9**−**11**) to the open-chain Pt^{IV} complexes (**1**−**3**); the largest shift was observed for the platinum(II) chelates (**4**−**7**). In the ^{1}H NMR spectra of free pyrazoles, H^3 and H^5 protons (for pzH) and protons from the Me groups (for 3,5-Me_2pzH) are equivalent because of the tautomeric exchange of the NH proton[28,45] in solution. However, these protons become nonequivalent upon coupling of the azaheterocycles with the organonitrile, and the complexes display two peaks from these distinct hydrogens. The assignment of signals of the pyrazole fragments in all complexes was made by analogy with the spectra of the free pyrazoles and their Pt(IV) and Pt(II) complexes[28,29] and on the basis of the multiplicity. ^{13}C{^{1}H} and ^{195}Pt NMR spectra of platinum(IV) compounds **1**−**3** and platinum(II) chelates **4**, **5**, and **7** were not measured because of their low solubility and instability due to the elimination of EtCN in the most-common organic solvents. However, platinum(II) complexes **9**−**11** bearing open-chain ligands and chelate **6** exhibit higher solubility. Signals of the imino carbons were detected in the range of 164−165 ppm for compounds **9**−**11** (171.3 ppm in the case of chelate **6**); the assignment of signals was made through HSQC experiments. In the ^{195}Pt NMR spectra, all Pt^{II} complexes **6** and **9**−**11** exhibit only one signal in the range (−2355 for **6** and from −2105 to −2073 ppm for **9**−**11**) specific for Pt^{II} species.

Final Remarks. The results from this work may be considered from a few perspectives. First, the reactions described here provide a convenient method for the synthesis of pyrazolylimino species, which, to the best of our knowledge, were previously known only for RN═C(Ar)-(3,5-RR″pz),[46] although *O*-acyl pyrazoles are quite common[47,48] and efficiently applied as useful synthons in organic synthesis.

Second, we found explicit evidence that platinum centers provide stabilization of the potentially unstable pyrazolylimines and these ligands can be "stored" without changes in the coordinated form in **1**−**3** and **9**−**11** at normal conditions for a prolonged time and then substituted when necessary. Thus liberated reactive imines NH═C(Et)(3,5-RR′pz), which are rather unstable and gradually split to EtCN and 3,5-RR′pzH, can be, in principle, immediately used in situ for further reactions; we felt this methodology warrants investigation. An example of this strategy for synthetic utilization of imines upon their liberation was given by us earlier.[15]

Third, from the work reported herein it is clear that the coordination mode of the pyrazolylimine species formed during the Pt-mediated nitrile-pyrazole coupling depends on the oxidation state of the metal. In the case of Pt^{II} complexes, there appears to be an explicit tendency toward the bidentate coordination mode; this tendency we observed earlier for

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other systems.[14,32] In addition, the monodentate coordination at a Pt^{IV} center, when all conditions for the formation of the stable 5-membered rings are favorable, seems to be a general phenomenon for platinum(IV) complexes. We anticipate that the stability of the Pt^{IV} complex with two monodentate pyrazolylimines is greater than that with the chelated NH═C(Et)(3,5-RR′pz)-κ^2*N*,*N* ligand containing only one imino group and than that with two of such chelated ligands (dicationic complex).

Forth, nitrile transition-metal complexes are common and useful starting materials for preparation of other metal-containing compounds by substitution.[49] In particular, (RCN)-[M] species are often employed for the preparation of (pyrazole)[M] complexes[50] (in general) and (pyrazole)Pt^{II} complexes[51] (in particular). It is clear from the results of this work that the substitution of nitriles with pyrazoles might proceed in a nonconventional way via metal-mediated RCN-3,5-RR′pzH coupling followed by elimination of RCN from the initially formed metal-bound imines. Hence, previous works on the synthesis of pyrazole complexes by the displacement of RCN ligands should be thoroughly revisited and the possibility of the consecutive coupling and elimination should be taken into account upon further studies.

Experimental Section

Materials and Instrumentation. Solvents, pyrazoles, 1,2-bis-(diphenylphosphino)ethane (Aldrich), and Ph_3P═$CHCO_2Me$ (Lancaster) were obtained from commercial sources and used as received. Complexes *trans*-[$PtCl_n(EtCN)_2$] (n = 2, 4) were prepared as previously described.[52] C, H, and N elemental analyses were performed at the Analytical Chemistry Laboratories at the St. Petersburg State University. TG/DTA studies were performed using a Mettler Toledo TGA850 instrument (temperature range from 20 to 1000 °C with a heating rate of 8 °C/min, air flow of 3 L/h, and a sample mass of 5−10 mg in an aluminum crucible; the buoyancy correction for the TGA was done by measuring a blank). For TLC, Merck UV 254 SiO_2 plates have been used. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrixes of the samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a Vector 22 (Bruker) FTIR device at 298 K in KBr pellets. ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectra were measured on a Bruker-DPX 300 spectrometer at ambient temperature. ^{195}Pt chemical shifts are relative to $Na_2[PtCl_6]$ (by using $K_2[PtCl_4]$ (δ = −1630 ppm) as a standard), and the half-height line width is given in parentheses. The microwave irradiation experiments were undertaken in a focused microwave Minotavr 2 (LUMEX, St.Petersburg) reactor (power 200 W) fitted with a rotational system.

Synthetic Work. Coupling of Pyrazoles and the Ligated Nitriles in *trans*-[$PtCl_4(EtCN)_2$]. A solution of *trans*-[$PtCl_4(EtCN)_2$] (31 mg, 0.07 mmol) and any of the pyrazoles 3,5-RR′pzH (0.14 mmol) in CH_2Cl_2 (5 mL) is vigorously stirred at room temperature for 2 h, whereupon the yellow precipitate formed is filtered off, washed with three 3 mL portions of Me_2CO and three 3 mL portions of Et_2O, and dried in vacuo at room temperature. The yield of **1**−**3** is 70−96%. On heating in the solid state complexes, **1**−**3** change their colors from pale yellow to dark yellow at 140−170 °C. TG curves: (**1**) mass loss is 20.1% at 152 °C (calcd mass loss for −2EtCN is 18.9%), (**2**) mass loss is 19.7% at 168 °C (calcd mass loss for −2EtCN is 18.0%), (**3**) mass loss is 18.3% at 139 °C (calcd mass loss for −2EtCN is 17.2%). The solubility and stability of **1**−**3** in the most common deuterated solvents is insufficient to measure their $^{13}C\{^1H\}$ and ^{195}Pt NMR spectra.

***trans*-[$PtCl_4${NH═C(Et)pz}$_2$] (1).** Yield: 83%. Anal. Calcd for $C_{12}H_{18}N_6Cl_4Pt$: C, 24.71; H, 3.11; N, 14.41. Found: C, 24.96; H, 3.19; N, 14.48. FAB^+-MS, *m*/*z*: 579 $[M - 2H]^+$, 543 $[M - Cl - 4H]^+$, 443 $[M - 4Cl + 2H]^+$. IR (selected bands, cm^{-1}): 3245 w [ν(N−H)], 1638 and 1539 s [ν(C═N + C═C)]. ^1H NMR ($CDCl_3$, δ): 1.58 (t, J = 7.5 Hz, 3H) and 3.64 (q, J = 7.5 Hz, 2H) (Et), 6.60 (dd, J = 1.8 and 3.0 Hz, 1H, ^{4}CH), 7.88 (d, J = 1.8 Hz, 1H, ^{3}CH), 7.94 (d, J = 3.0 Hz, 1H, ^{5}CH), 10.02 (br, 1H, NH). ^1H NMR ($(CD_3)_2CO$, δ): 1.51 (t, J = 7.5 Hz, 3H) and 3.73 (q, J = 7.5 Hz, 2H) (Et), 6.78 (dd, J = 1.8 and 3.0 Hz, 1H, ^{4}CH), 8.06 (d, J = 1.8 Hz, 1H, ^{3}CH), 8.62 (d, J = 3.0 Hz, 1H, ^{5}CH), 9.99 (br, 1H, NH).^1H NMR ($(CD_3)_2SO$, δ): 1.37 (t, J = 7.5 Hz, 3H) and 3.61 (q, J = 7.5 Hz, 2H) (Et), 6.83 (dd, J = 1.8 and 3.0 Hz, 1H, ^{4}CH), 8.18 (d, J = 1.8 Hz, 1H, ^{3}CH), 8.71 (d, J = 3.0 Hz, 1H, ^{5}CH), 9.71 (br, 1H, NH).

***trans*-[$PtCl_4${NH═C(Et)(3-Mepz)}$_2$] (2).** Yield: 96%. Anal. Calcd for $C_{14}H_{22}N_6Cl_4Pt$: C, 27.51; H, 3.63; N, 13.75. Found: C, 27.66; H, 3.69; N, 13.44. FAB^+-MS, *m*/*z*: 613 $[M + 3H]^+$, 541 $[M - 2Cl + H]^+$, 506 $[M - 3Cl + H]^+$, 468 $[M - 4Cl - H]^+$. IR (selected bands, cm^{-1}): 3247 w [ν(N−H)], 1628 and 1561 s [ν(C═N + C═C)]. ^1H NMR ($CDCl_3$, δ): 1.54 (t, J = 7.4 Hz, 3H) and 3.56 (q, J = 7.4 Hz, 2H) (Et), 2.38 (s, 3H, Me), 6.37 (d, H, J = 2.8 Hz, 1H, ^{4}CH), 7.80 (d, J = 2.8 Hz, 1H, ^{5}CH) and 9.84 (br, 1H, NH). ^1H NMR ($(CD_3)_2SO$, δ): 1.35 (t, J = 7.4 Hz, 3H) and 3.55 (q, J = 7.4 Hz, 2H) (Et), 2.35 (s, 3H, Me), 6.66 (d, H, J = 2.8 Hz, 1H, ^{4}CH), 8.57 (d, J = 2.8 Hz, 1H, ^{5}CH) and 9.47 (br, 1H, NH).

***trans*-[$PtCl_4${NH═C(Et)(3,5-Me_2pz)}$_2$] (3).** Yield: 70%. Anal. Calcd for $C_{16}H_{26}N_6Cl_4Pt\cdot 0.5CH_2Cl_2$: C, 29.07; H, 3.99; N, 12.33. Found: C, 29.39; H, 3.95; N, 12.37. FAB^+-MS, *m*/*z*: 603 $[M - Cl]^+$, 568 $[M - 2Cl]^+$, 495 $[M - 4Cl - 2H]^+$. IR (selected bands, cm^{-1}): 3232 w [ν(N−H)], 1627 and 1580 s [ν(C═N + C═C)]. ^1H NMR ($CDCl_3$, δ): 1.43 (t, J = 7.4 Hz, 3H) and 3.59 (q, J = 7.4 Hz, 2H) (Et), 2.29 and 2.59 (s, 3H, Me), 6.09 (s, 1H, ^{4}CH) and 9.57 (br, 1H, NH). ^1H NMR ($(CD_3)_2CO$, δ): 1.33 (t, J = 7.4 Hz, 3H) and 3.47 (q, J = 7.4 Hz, 2H) (Et), 2.25 and 2.69 (s, 3H, Me), 6.30 (s, H, ^{4}CH).

Coupling of Pyrazoles and Ligated Nitriles in *trans*-[$PtCl_2(EtCN)_2$]. A solution of *trans*-[$PtCl_2(EtCN)_2$] (139 mg, 0.37 mmol) and any of the pyrazoles 3,5-RR′pzH (0.74 mmol) in CH_2Cl_2 (4 mL) is vigorously stirred at room temperature for 2 h, whereupon the yellow precipitate formed is filtered off, washed fast with 3 mL portions of CH_2Cl_2, and dried in vacuo at room temperature. The precipitate presented a mixture of three products, [$PtCl_2${NH═

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C(Et)pz-κ^2N,N}] (**4**), [PtCl(pzH){NH=C(Et)pz-κ^2N,N}]Cl (**5**), and [Pt(pzH)$_2$}{NH=C(Et)pz-κ^2N,N}]Cl$_2$ (**6**) (for pzH), or two products, [PtCl$_2${NH=C(Et)(3,5-Me$_2$pz)-κ^2N,N}] (**7**) and [PtCl(3,5-Me$_2$pzH)$_3$]-Cl (**8**) (for 3,5-Me$_2$pzH). In the case of 3(5)-MepzH, the precipitation was not observed; analysis of the residue that formed after evaporation of the solvent in a flow of N_2 to dryness by the ^{1}H NMR method shows the presence of some yet unidentified pyrazole-containing complexes.

Complexes **4**−**6** can be separated by fractional washing with CH_2Cl_2 and Me_2CO, i.e., the precipitate is first washed with three 5 mL portions of CH_2Cl_2 to separate **5**, and three 5 mL portions of Me_2CO can then be used to separate **4**. The remaining insoluble colorless powder is **6**. The **4**:**5**:**6** molar ratio of released products is ca. 3:1:10. Complex **7** can be separated from [PtCl(3,5-Me$_2$pzH)$_3$]-Cl by washing with three 5 mL portions of H_2O. Solubility and stability of complexes **4**, **5**, and **7** in the most common deuterated solvents is insufficient to measure their ^{13}C{^{1}H} and ^{195}Pt NMR spectra.

[PtCl$_2${NH=C(Et)pz-κ^2N,N}] (4). Anal. Calcd for $C_6H_9N_3Cl_2Pt$: C, 18.52; H, 2.33; N, 10.80. Found: C, 18.64; H, 2.65; N, 10.79. TLC: R_f = 0.32 (eluent, 3:1 CH_2Cl_2:Me_2CO). FAB$^+$-MS, *m*/*z*: 385 [M − 4H]$^+$, 354 [M − Cl]$^+$, 317 [M − 2Cl − H]$^+$. IR (selected bands, cm^{-1}): 3122 s [ν(N−H)], 1635 s and 1525 w [ν(C=N + C=C)]. ^{1}H NMR ((CD$_3$)$_2$CO, δ): 1.49 (t, J = 7.6 Hz, 3H) and 3.19 (q, J = 7.6 Hz, 2H) (Et), 7.03 (pseudo-t, J = 2.6 Hz, 1H, ^{4}CH), 8.20 (d, J = 1.8 Hz, J_{PtH} = 17.0 Hz, 1H, ^{3}CH), 8.89 (d, J = 3.2 Hz, 1H, ^{5}CH), 10.93 (br, 1H, NH).

[PtCl{NH=C(Et)pz-κ^2N,N}(pzH)]Cl (5). This complex is unstable in dichloromethane solution and rapidly decomposes further. However, we succeeded to characterize it by ^{1}H NMR and FAB$^+$-MS from a mixture with **4**. FAB$^+$-MS, *m*/*z*: 420 [M − Cl− 2H]$^+$. ^{1}H NMR ((CD$_3$)$_2$CO, δ): 1.53 (t, J = 7.6 Hz, 3H) and 3.32 (q, J = 7.6 Hz, 2H) (Et), 7.07 (pseudo-t, J = 2.6 Hz, 1H, ^{4}CH), 8.01 (d, J = 1.8 Hz, J_{PtH} = 11.4 Hz, 1H, ^{3}CH) and 8.95 (d, J = 3.2 Hz, 1H, ^{5}CH), 10.91 (br, 1H, NH) (κN(2)pz), 6.55 (pseudo-t, J = 2.6 Hz, 1H, ^{4}CH), 8.36 (d, J = 1.8 Hz, 1H, ^{5}CH), 8.38 (d, J = 3.2 Hz, J_{PtH} = 18.0 Hz, 1H, ^{3}CH), 12.56 (br, 1H, NH) (pzH).

[Pt{NH=C(Et)pz-κ^2N,N}(pzH)$_2$]Cl$_2$ (6). Anal. Calcd for $C_{12}H_{17}N_7Cl_2Pt$: C, 27.44; H, 3.26; N, 18.67. Found: C, 27.69; H, 3.29; N, 18.55. FAB$^+$-MS, *m*/*z*: 525 [M]$^+$, 422 [M − Cl − pzH]$^+$, 385 [M − 2Cl − pzH − H]$^+$. IR (selected bands, cm^{-1}): 3119 s [ν(N−H)], 1634 s and 1527 w [ν(C=N + C=C)]. ^{1}H NMR (D$_2$O, δ): 1.30 (t, J = 7.6 Hz, 3H) and 3.06 (q, J = 7.6 Hz, 2H) (Et), 6.84 (pseudo-t, J = 2.6 Hz, 1H, ^{4}CH), 8.50 (d, J = 3.3 Hz, 1H, ^{3}CH) and 8.54 (d, J = 1.4 Hz, 1H, ^{5}CH) (κN(2)pz), 6.39 (pseudo-t, J = 2.5 Hz, 1H, ^{4}CH), 7.37 (d, J = 2.5 Hz, 1H, ^{3}CH) and 7.75 (d, J = 2.5 Hz, 1H, ^{5}CH) (2pzH). ^{13}C{^{1}H} NMR (D$_2$O, δ): 10.1 (CH$_3$) and 24.1 (CH$_2$) (Et), 112.1 (^{4}CH), 135.2 (^{5}CH), and 149.1 (^{3}CH)($\kappa N(2)$pz), 171.3 (C=N), 108.1 (^{4}CH), 133.8 (^{5}CH) and 142.4 (^{3}CH) (2pzH). ^{195}Pt NMR (D$_2$O, δ): −2355 (1800 Hz).

[PtCl$_2${NH=C(Et)(3,5-Me$_2$pz)-κ^2N,N}] (7). Anal. Calcd for $C_8H_{13}N_3Cl_2Pt$: C, 23.03; H, 3.14; N, 10.07. Found: C, 23.05; H, 3.35; N, 9.98. TLC: R_f = 0.42 (eluent, 6:1 CH_2Cl_2:Me_2CO). FAB$^+$-MS, *m*/*z*: 417 [M]$^+$, 344 [M − 2Cl − 2H]$^+$. IR (selected bands, cm^{-1}): 3262 and 3231 m [ν(N−H)], 1631 and 1573 s [ν(C=N + C=C)]. ^{1}H NMR ((CD$_3$)$_2$CO, δ): 1.48 (t, J = 7.4 Hz, 3H) and 3.17 (q, J = 7.4 Hz, 2H) (Et), 2.60 and 2.76 (s, 3H, Me), 6.55 (s, 1H, J_{PtH} = 10.2 Hz, ^{4}CH) and 10.20 (br, 1H, NH).

[PtCl(3,5-Me$_2$pzH)$_3$]Cl (8). Anal. Calcd for $C_{15}H_{24}N_6Cl_2Pt$: C, 32.50; H, 4.36; N, 15.16. Found: C, 32.51; H, 4.32; N, 15.08. FAB$^+$-MS, *m*/*z*: 555 [M + H]$^+$. IR (selected bands, cm^{-1}): 3075 s [ν(N−H)], 1577 and 1551 s [ν(C=N + C=C)]. ^{1}H NMR (D$_2$O, δ): 1.87 (s, Me, 3H), 1.95 (s, Me, 6H), 2.08 (s, Me, 3H), 2.20 (s, Me, 6H), 5.93 (s, 3H, ^{4}CH).

Reduction of the Platinum(IV) Complexes *trans*-[PtCl$_4${NH=C(Et)(3,5-RR′pz)}$_2$]. The carbonyl-stabilized phosphorus ylide Ph_3P=$CHCO_2Me$ (40 mg, 0.12 mmol) is added at room temperature to a solution of complexes **1**−**3** (0.10 mmol) in $CHCl_3$ (4 mL). The reaction mixture is vigorously stirred at 20−25 °C for 2 h and then left to stand for 30 min, whereupon the solvent is evaporated in a flow of N_2 to dryness; the residue formed is washed fast with three 1 mL portions of ice-cold MeOH and dried in vacuo at room temperature. The yield of **9**−**11** is 65−85%. On heating in the solid state, complexes **9**−**11** change their colors from pale yellow to dark yellow at 130−150 °C. TG curves for complexes **9**−**11**: (**9**) mass loss is 20.3% at 148 °C (calcd mass loss for −2EtCN is 21.5%), (**10**) mass loss is 18.2% at 142 °C (calcd mass loss for −2EtCN is 20.4%), (**11**) mass loss is 17.1% at 135 °C (calcd mass loss for −2EtCN is 19.4%).

***trans*-[PtCl$_2${NH=C(Et)pz}$_2$] (9).** Yield: 85%. Anal. Calcd for $C_{12}H_{18}N_6Cl_2Pt$: C, 28.14; H, 3.54; N, 16.41. Found: C, 28.64; H, 3.58; N, 16.34. TLC: R_f = 0.58 (eluent, 9:1 CH_2Cl_2:Me_2CO). FAB$^+$-MS, *m*/*z*: 511 [M]$^+$, 441 [M − 2Cl]$^+$, 385 [M − L − 4H]$^+$. IR (selected bands, cm^{-1}): 3258 s and 3210 w [ν(N−H)], 1649 s and 1532 m [ν(C=N + C=C)]. ^{1}H NMR (CDCl$_3$, δ): 1.67 (t, J = 7.6 Hz, 3H) and 3.61 (q, J = 7.6 Hz, 2H) (Et), 6.51 (dd, J = 1.5 and 3.0 Hz, 1H, ^{4}CH), 7.79 (d, J = 1.5 Hz, 1H, ^{3}CH), 7.85 (d, J = 3.0 Hz, 1H, ^{5}CH) and 9.45 (br, 1H, NH). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 12.2 (CH$_3$) and 26.9 (CH$_2$) (Et), 110.6 (^{4}CH), 128.2 (^{5}CH), 144.7 (^{3}CH) and 164.6 (C=N). ^{195}Pt NMR (CDCl$_3$, δ): −2105 (1024 Hz).

***trans*-[PtCl$_2${NH=C(Et)(3-Mepz)}$_2$] (10).** Yield: 80%. Anal. Calcd for $C_{14}H_{22}N_6Cl_2Pt$: C, 31.12; H, 4.10; N, 15.55. Found: C, 31.29; H, 4.15; N, 15.51. TLC: R_f = 0.57 (eluent CH_2Cl_2: Me_2CO = 15:1). FAB$^+$-MS, *m*/*z*: 535 [M − 5H]$^+$, 469 [M − 2Cl]$^+$. IR (selected bands, cm^{-1}): 3296 s and 3197 w [ν(N−H)], 1650 s and 1556 m [ν(C=N + C=C)]. ^{1}H NMR (CDCl$_3$, δ): 1.64 (t, J = 7.5 Hz, 3H) and 3.52 (q, J = 7.5 Hz, 2H) (Et), 2.33 (s, 3H, Me), 6.28 (d, J = 2.6 Hz, 1H, ^{4}CH), 7.70 (d, J = 2.6 Hz, 1H, ^{5}CH) and 9.22 (br, 1H, NH). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 12.3 (CH$_3$) and 26.5 (CH$_2$) (Et), 13.8 (Me), 111.1 (^{4}CH), 128.6 (^{5}CH), 154.9 (^{3}CH) and 164.0 (C=N). ^{195}Pt NMR (CDCl$_3$, δ): −2101 (995 Hz).

***trans*-[PtCl$_2${NH=C(Et)(3,5-Me$_2$pz)}$_2$] (11).** Yield: 65%. Anal. Calcd for $C_{16}H_{26}N_6Cl_2Pt$: C, 33.81; H, 4.61; N, 14.79. Found: C, 33.75; H, 4.78; N, 14.95. TLC: R_f = 0.65 (eluent, 15:1 CH_2Cl_2: Me_2CO). FAB$^+$-MS, *m*/*z*: 569 [M + H]$^+$, 496 [M − 2Cl − H]$^+$, 417 [M − L]$^+$. IR (selected bands, cm^{-1}): 3278 s [ν(N−H)], 1640 and 1577 s [ν(C=N + C=C)]. ^{1}H NMR (CDCl$_3$, δ): 1.58 (t, J = 7.5 Hz, 3H) and 3.65 (q, J = 7.5 Hz, 2H) (Et), 2.22 and 2.52 (s, 3H, Me), 6.00 (s, H, ^{4}CH) and 9.03 (br, 1H, NH). ^{1}H NMR ((CD$_3$)$_2$-CO, δ): 1.45 (t, J = 7.6 Hz, 3H) and 3.66 (q, J = 7.6 Hz, 2H) (Et), 2.19 and 2.57 (s, 3H, Me), 6.17 (s, H, ^{4}CH) and 9.30 (br, 1H, NH). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 12.1 (CH$_3$) and 27.9 (CH$_2$) (Et), 13.9 and 14.6 (Me), 113.2 (^{4}CH), 141.0 (^{5}CMe), 153.3 (^{5}CMe) and 167.2 (C=N). ^{195}Pt NMR (1:1 CDCl$_3$:(CD$_3$)$_2$CO, δ): −2073 (774 Hz).

Liberation of Ligands 12−14 from Complexes 9−11. Dppe (16 mg, 0.04 mmol) was added at room temperature to a solution of any of complexes **9**−**11** (0.02 mmol) in $CDCl_3$ (2 mL). After 20 min, the reaction mixture is cooled to 0 °C for 10 min, whereupon the released solid [Pt(dppe)$_2$](Cl)$_2$ is separated by filtration and the free ligand is characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

NH=C(Et)pz (12). ^{1}H NMR (CDCl$_3$, δ): 1.31 (t, J = 7.4 Hz, 3H) and 2.97 (q, J = 7.4 Hz, 2H) (Et), 6.41 (dd, J = 1.7 and 2.6

Table 1. Crystallographic Data

	2	**4**·(H_2O)	**9**·($CHCl_3$)	**10**·(CH_2Cl_2)
empirical formula	$C_{11}H_{18}Cl_6N_4Pt$	$C_6H_{11}Cl_2N_3OPt$	$C_{13}H_{19}Cl_5N_6Pt$	$C_{15}H_{24}Cl_4N_6Pt$
fw	614.08	407.17	631.68	625.29
T (K)	173(2)	120(2)	120(2)	120(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$C2/c$
a (Å)	9.1204(3)	7.3045(6)	12.3022(4)	17.2725(6)
b (Å)	9.9721(2)	10.5777(11)	32.8307(11)	11.9158(4)
c (Å)	11.9160(3)	13.5023(14)	15.0957(5)	13.2018(3)
α (deg)	111.3240(10)	90	90	90
β (deg)	109.0570(10)	94.288(6)	96.7710(10)	128.227(2)
γ (deg)	90.939(2)	90	90	90
V (Å^3)	942.93(4)	1040.33(18)	6054.5(3)	2134.49(11)
Z	2	4	12	4
ρ_{calcd} (Mg/m^3)	2.163	2.600	2.079	1.946
μ(Mo Kα) (mm^{-1})	8.290	13.966	7.625	7.087
R1[a] ($I \geq 2\sigma$)	0.0189	0.0326	0.0360	0.0198
wR2[b] ($I \geq 2\ \sigma$)	0.0395	0.0571	0.0694	0.0405

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Hz, 1H, ^{4}CH), 7.63 (d, J = 2.6 Hz, 1H, ^{3}CH) and 7.67 (d, J = 1.7 Hz, 1H, ^{5}CH), 8.27 (br, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 9.7 (CH_3) and 26.6 (CH_2) (Et), 108.2 (^{4}CH), 127.0 (^{5}CH) and 142.0 (^{3}CH).

NH═C(Et)(3-Mepz) (13). ^{1}H NMR ($CDCl_3$, δ): 1.30 (t, J = 7.4 Hz, 3H) and 2.90 (q, J = 7.4 Hz, 2H) (Et), 2.33 (s, 3H, Me), 6.20 (d, J = 2.6 Hz, 1H, ^{4}CH), 7.70 (d, J = 2.6 Hz, 1H, ^{5}CH) and 8.10 (br, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 9.8(CH_3) and 26.4 (CH_2) (Et), 13.8 (Me), 108.5 (^{4}CH) and 127.6 (^{5}CH).

NH═C(Et)(3,5-Me$_2$pz) (14). ^{1}H NMR ($CDCl_3$, δ): 1.22 (t, J = 7.3 Hz, 3H) and 2.97 (q, J = 7.3 Hz, 2H) (Et), 2.24 and 2.58 (s, 3H, Me), 5.95 (s, 1H, ^{4}CH) and 9.01 (br, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 10.1 (CH_3) and 29.0 (CH_2) (Et), 14.0 and 15.7 (Me) 110.1 (^{4}CH), 129.5 (^{5}CH) and 142.9 (^{3}CH), 149.7 (C═N).

X-ray Crystallography. The crystals were immersed in perfluoropolyether, mounted in cryoloops, and measured at 120 or 150 K. The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The Denzo-Scalepack[53] program package was used for cell refinements and data reductions. Both structures were solved by direct methods using the SHELXS-97 or SIR2002 programs[54,55] with the WinGX graphical user interface.[56] An empirical absorption correction on the basis of equivalent reflections was applied to all data (XPREP in SHELXTL version 6.14).[57] The maximum/minimum transmission factors were **2** = 0.11156/0.16778, **4** = 0.1575/0.7042, **9** = 0.09048/0.18463, and **10** = 0.37549/0.47563, respectively. Structural refinements were carried out with SHELXL-97.[58] The NH hydrogens in **2** and H_2O hydrogens in **4** were located from the difference Fourier map. The former was refined isotropically, whereas the latter ones were constrained to ride on their parent atom (U_{iso} = 1.5U_{eq} (parent atom)). Other hydrogens were positioned geometrically and allowed to ride on their parent atoms, with N−H = 0.88 Å and U_{iso} = 1.2U_{eq} (parent atom), C−H = 0.95−0.99 Å and U_{iso} = 1.2−1.5U_{eq} (parent atom). The asymmetric unit of **9** contained 2.5 independent Pt molecules. The crystallographic data are summarized in Table 1. Selected bond lengths and angles are shown in the figure captions.

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Supporting Information Available: Crystallographic data in CIF format; figures of the intermolecular contacts in **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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