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Pt^{II}-Mediated Nitrile–Tetramethylguanidine Coupling as a Key Step for a Novel Synthesis of 1,6-Dihydro-1,3,5-triazines○

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The coupling between tetramethylguanidine, $HN{=}C(NMe_2)_2$, and coordinated organonitriles in the platinum(II) complexes *cis/trans*-$[PtCl_2(RCN)_2]$ (R = Me, Et, Ph) proceeds rapidly under mild conditions to afford the diimino compounds containing two *N*-bound monodentate 1,3-diaza-1,3-diene ligands $[PtCl_2\{NH{=}C(R)N{=}C(NMe_2)_2\}_2]$ (R = Et, *trans*-**1**; R = Ph, *trans*-**2**; R = Me, *cis*-**3**; R = Et, *cis*-**4**), and this reaction is the first observation of metal-mediated nucleophilic addition of a guanidine to ligated nitrile. Complexes **1**–**4** were characterized by elemental analyses (C, H, N), X-ray diffraction, FAB mass spectrometry, IR, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopies; assignment of signals from *E/Z*-forms of 1,3-diaza-1,3-diene ligands and verification of routes for their $Z \rightleftharpoons E$ isomerization in solution were performed using 2D $^1H,^1H$-COSY, $^1H,^{13}C$-HETCOR, and 1D NOE NMR experiments. The newly formed and previously unknown 1,3-diaza-1,3-dienes $NH{=}C(R)N{=}C(NMe_2)_2$ were liberated from the platinum(II) complexes $[PtCl_2\{NH{=}C(R)N{=}C(NMe_2)_2\}_2]$ (**1**–**3**) by substitution with 2 equiv of 1,2-bis-(diphenylphosphino)ethane (dppe) to give the uncomplexed $HN{=}C(R)N{=}C(NMe_2)_2$ species (**5**–**7**) in solution and the solid $[Pt(dppe)_2](Cl)_2$. The former were utilized in situ, after filtration of the latter, in the reaction with 1,3-di-*p*-tolylcarbodiimide, (*p*-tol)N=C=N(tol-*p*), in $CDCl_3$ to generate (6*E*)-*N*,*N*-dimethyl-1-(4-methylphenyl)-6-[(4-methylphenyl)imino]-1,6-dihydro-1,3,5-triazin-2-amines) (**8**–**10**) due to the [4 + 2]-cycloaddition accompanying elimination of $HNMe_2$. The formulation of **8**–**10** is based on ESI-MS, ^1H, $^{13}C\{^1H\}$ NMR, and X-ray crystal structures determined for **9** and **10**. The reaction of 1,3-diaza-1,3-dienes with 1,3-di-*p*-tolylcarbodiimide, described in this article, constitutes a novel synthetic approach to a useful class of heterocyclic species like 1,6-dihydro-1,3,5-triazines.

Introduction

The versatility of reactivity modes of imines RR′C=NR″ and the overall chemical instability of these species are mostly associated with the availability of the nitrogen lone pair, whose activity can be modified by alteration of donor/acceptor properties of substituents at the azomethine group.[1] Donor substituents increase basicity of the N center, and this results in a substantial activation of the imines toward di-, tri-, and polymerizations and various redox-type conversions. In particular, the imines $R_2C{=}NH$ with two donor substituents are usually so reactive in hydrolysis and trimerizations that some of these compounds are commonly treated as *elusive*.[2−4] The too high reactivity of such imines strongly restricts their synthetic utilization.

Recently we[5,6] and others[7] found that platinum group metal centers provide enormous stabilization of the potentially unstable imines $R_2C{=}NH$ due to an efficient blocking of the electron pair by coordination. Respectively, these ligands can be "stored" without changes in the complexed form at normal conditions for a prolonged time. We also reported[8a] that the combination of the inertness of *coordinated* imines $R_2C{=}NH$ with their high reactivity in the *uncomplexed state*

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○ Dedicated to Professor Mikhail G. Voronkov on the occasion of his 85th birthday.

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could have some intrinsic practical implications. Indeed, if the imine ligand is displaced under mild conditions from its complex, the liberated reactive $R_2C{=}NH$ species can be immediately used in situ for further reactions. We felt that this "pop-the-cork" strategy[8] warrants additional investigation and can be applied to a metal-mediated synthesis and stabilization of unusual 1,3-diaza-1,3-dienes followed by their further exploitation (after liberation) in metal-free synthetic transformations.

Thus, within our ongoing project on the metal-mediated nitrile−imine coupling,[8−14] we attempted to extend our previous studies on reactions between platinum-bound RCN species and $HN{=}ER_n$ (ER_n = CPh_2,[9] C(Alkyl)(OAlkyl),[8] C(Ar)(NHAr),[10] SAr_2,[11,12] PPh_3[13]) to such specific imines as guanidines (ER_n = $C(NR_2)_2$) to perform nitrile−guanidine coupling and apply thus formed 1,3-diaza-1,3-dienes in further reactions.

The scenario of this work was the following. (i) To use a metal center as the promoter for formation of 1,3-diaza-1,3-dienes derived from the previously unknown nucleophilic addition of guanidines to (RCN)[M] species. For this part of the study we addressed *cis/trans*-$[PtCl_2(RCN)_2]$ (R = Me,[15] Et,[16] Ph[17]) compounds insofar as it has been demonstrated that the Pt^{II} center provides sufficient activation of RCN ligands to achieve the metal-mediated nitrile−imine integration.[8−14] Tetramethylguanidine ($HN{=}C(NMe_2)_2$; TMG), commercially available and very soluble in organic solvents, was used as a nucleophile for the addition. (ii) To perform the liberation of the ligated 1,3-diaza-1,3-dienes $HN{=}C(R)N{=}C(NMe_2)_2$, stabilized by coordination, and characterize them in the free form. Despite the general inertness of the imino complexes toward ligand displacement, some substitution methods have been previously developed,[6,18,19] and it was anticipated to apply them for the liberation. (iii) To utilize the released 1,3-diaza-1,3-dienes $HN{=}C(R)N{=}C(NMe_2)_2$ species in situ for further reactions by studying their interplay with the carbodiimide (*p*-tol)N=C=N(tol-*p*), which is a highly reactive reagent toward various N-donor nucleophiles.[20] All these results—showing the first example of nitrile−guanidine coupling and application of the latter reaction as the key step to achieve useful class of heterocycles, i.e., 1,6-dihydro-1,3,5-triazine-2-amines—are reported herein.

Results and Discussion

Nitrile−Guanidine Coupling at a Pt(II) Center. The coupling between platinum(II)-bound nitriles in complexes $[PtCl_2(RCN)_2]$ and tetramethylguanidine (TMG) proceeds in a molar ratio of 1:2 at 20−25 °C in MeCN (R = Me), EtCN (R = Et), or CH_2Cl_2 (R = Ph) and results in formation of diimino complexes containing two *N*-bound monodentate 1,3-diaza-1,3-diene ligands $[PtCl_2\{NH{=}C(R)N{=}C(NMe_2)_2\}_2]$. It was proved that TMG does not react with RCN (R = Et, Ph) under the coupling conditions, and this implies that the nitrile−TMG coupling is Pt^{II} mediated. We believe that the (1,3-diaza-1,3-diene)Pt^{II} complexes are presumably formed by nucleophilic attack of the imine N atom on the electrophilically activated carbon atom of the nitrile.

Treatment of *trans*-$[PtCl_2(RCN)_2]$ (R = Et, Ph) with TMG allows isolation of the *trans*-$[PtCl_2\{NH{=}C(R)N{=}C(NMe_2)_2\}_2]$ (**1** and **2**) complexes (route A in Scheme 1). Reaction between *cis*-$[PtCl_2(RCN)_2]$ (R = Me, Et) and TMG leads to

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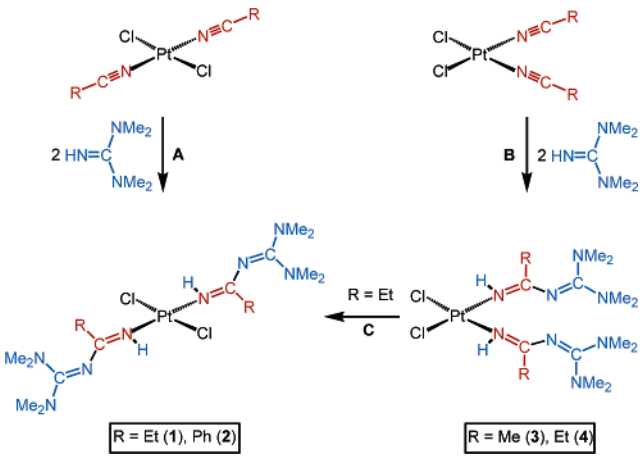
Scheme 1



formation of *cis*-[$PtCl_2${NH═C(R)N═C(NMe_2)$_2$}$_2$] (**3** and **4**) (route B in Scheme 1). Complexes *cis*-[$PtCl_2$(RCN)$_2$] contain admixtures of trans isomers[15,16] (see Experimental Section); consequently, the isolated *cis*-[$PtCl_2${NH═C(R)N═C(NMe_2)$_2$}$_2$] was contaminated with the appropriate trans form; the latter can be removed by washing of solid residues obtained upon complete evaporation of the reaction mixtures (see Experimental Section).

The possibility of geometric cis/trans isomerization has been verified for the isomeric pair **1**/**4**. Thus, heating **1** either in the solid state (100 °C, 6 h) or in solution (EtCN, 70 °C, 14 h) with TLC monitoring of the process shows no cis/trans isomerization but gradual overall degradation of the complex. In contrast, heating **4** under the same conditions gives some quantities of **1** (route C, Scheme 1) along with yet unidentified decomposition products. Heating **4** in the solid state (110 °C, 17 h) with TLC monitoring of the process shows no cis/trans isomerization but gradual overall degradation of **4**. Hence, the geometric cis/trans isomers exhibit significant stability and do not isomerize under normal conditions.

Characterization of 1,3-Diaza-1,3-diene Complexes 1−4. Complexes **1**−**4** have been characterized by elemental analysis, FAB^+ mass spectrometry, infrared, and NMR (^{1}H, ^{13}C{^{1}H}) spectroscopies. The compounds give satisfactory C, H, and N elemental analyses for the proposed formulation. In the FAB^+ mass spectra, **1**−**4** give the expected molecular ion $[M]^+$ along with some fragmentation peaks.

The IR spectroscopic data additionally confirm the nucleophilic addition of TMG to the RCN ligands and rule out the possibility of displacement of nitriles by TMG. Thus, comparison of the IR spectra of **1**−**4** with the spectra of the starting complexes shows the absence of the ν(C≡N) absorption band in the typical range of 2350−2300 cm^{-1} and the presence of intense stretching bands ν(C═N) at lower frequencies (1566−1525 cm^{-1}). The latter stretches correspond well to the ν(C═N) values (1540−1522 cm^{-1}) for Pt^{II}- or Pt^{IV}-bound heterodiazadiene[11,12,14] or diazadiene species (1561−1540 cm^{-1}) for the previously reported Pt^{II} complexes in which the imidoylamidinato ligand is chelated.[10] In addition, weaker bands due to ν(N−H) are seen for **1**−**4** in the region between 3510 and 3249 cm^{-1}.

In the ^{1}H NMR spectra recorded at room temperature, the signal of the proton from the imino group C═N*H* (δ 6.90−5.42 ppm) is shifted upfield compared to those observed in NMR spectra of other platinum imine complexes (δ 8−9 ppm).[22] In the latter, the hydrogen bonding involving the imine C═N*H* proton was unambiguously recognized, while in our case the position of the signal at such a high field gives indirect evidence that the proton of the C═N*H* group is not involved in the hydrogen bonding in solution.[9,14] The ^{13}C{^{1}H} NMR spectra show two signals of the *C*═N bonds in the range from 177.5 to 162.4 ppm, which corresponds to the characteristic *C*═N resonances in platinum imine complexes.[14,18,22,23] In the ^{13}C{^{1}H} and ^{1}H NMR spectra, the resonances from the dimethylamino N*Me*$_2$ carbons and protons appear at δ 40.6−39.2 and 3.14−2.73 ppm, respectively.

In the ^{1}H NMR spectra measured in $CDCl_3$, **1**−**4** typically display three or four sets of signals, which can be rationalized by formation of complexes in *EE*-, *EZ*-, and *ZZ*-configurations of the 1,3-diaza-1,3-diene ligands due to *cis*- (for the *E*-form) and *trans*-addition (for the *Z*-form) of TMG to the triple C≡N bond and/or slow dynamic noncatalyzed *Z*−*E* isomerization of the ligated diazadiene species similar to those observed recently for other Pt^{IV}-bound diazadiene systems.[10,12] The difference in chemical shifts between *E*- and *Z*-forms of the ligated imines (0.2−0.8 ppm for N*H* protons and 0.2−0.4 ppm for N*Me*$_2$ protons) in our case agrees well with those previously reported for the Pt^{IV}-complexed imino esters NH═C(R)OR′ (0.3−0.4 ppm; a slightly smaller value (0.1 ppm) was reported for R = Et[6]) and the (imino ester)Pt^{II} complexes (0.6−0.7 ppm).[24,25]

Assignment of signals from *E*/*Z*-forms and verification of routes for their *Z* ⇌ *E* isomerization have been performed using 2D ^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HETCOR, and 1D NOE NMR experiments. Thus, addition of TMG to the coordinated nitriles in *trans*-[$PtCl_2$(EtCN)$_2$] leads to formation of *trans*-[$PtCl_2${(*Z*)-HN═C(Et)N═C(NMe_2)$_2$}$_2$] as the main product. Upon dissolution in $CDCl_3$, the latter complex is subject to a slow dynamic *Z* ⇌ *E* isomerization giving *trans*-[$PtCl_2$-{(*E*)-HN═C(Et)N═C(NMe_2)$_2$}$_2$] through the intermediate formation of *trans*-[$PtCl_2${(*Z*)-HN═C(Et)N═C(NMe_2)$_2$}{(*E*)-HN═C(Et)N═C(NMe_2)$_2$}]; all species were identified by 1D NOE NMR. After 1 day, all forms exist in an equilibrium and the *ZZ*:*EZ*:*EE* isomeric ratio, obtained by ^{1}H NMR integration, is ca. 1:2:1. Reaction between TMG and *trans*-[$PtCl_2$(PhCN)$_2$] allows isolation of *trans*-[$PtCl_2${(*Z*)-HN═C(Ph)N═C(NMe_2)$_2$}$_2$] as the main solid product along with *EE*- and *EZ*-forms of *trans*-[$PtCl_2${HN═C(Ph)N═C(NMe_2)$_2$}$_2$] as minor species that remain in solution. In the case of *trans*-[$PtCl_2${HN═C(Ph)N═C(NMe_2)$_2$}$_2$], the rate of the *Z* ⇌ *E*

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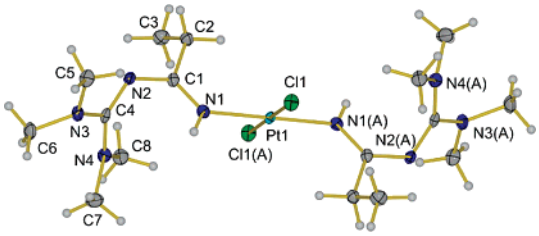

Figure 1. Thermal ellipsoid view of **1** with atom-numbering scheme. Thermal ellipsoids are drawn with 50% probability.

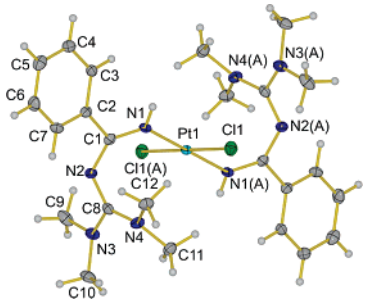

Figure 2. Thermal ellipsoid view of complex **2** with atom-numbering scheme. Thermal ellipsoids are drawn with 50% probability.

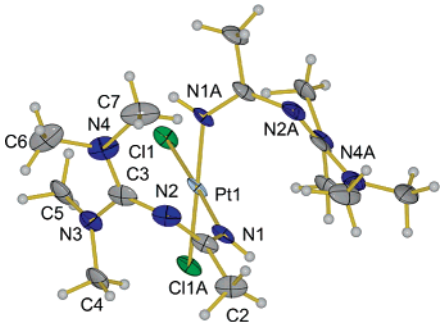

Figure 3. Thermal ellipsoid view of complex **3** with atom-numbering scheme. Thermal ellipsoids are drawn with 30% probability.

isomerization is rather low and after 1 week at 20−25 °C only 10% of the starting *ZZ*-isomer was isomerized to the other forms.

The selectivity in formation of the *E*- or *Z*-form is less noticeable for the *cis*-[$PtCl_2$(1,3-diaza-1,3-diene)$_2$] species than for the appropriate trans complexes. Thus, the reaction of *cis*-[$PtCl_2(NCR)_2$] (R = Me, Et) with TMG in the corresponding nitriles, used as solvents, gives *cis*-[$PtCl_2$-{HN=C(R)N=C(NMe_2)$_2$}$_2$], whose ^{1}H NMR spectrum, measured right after completion of the coupling, shows the simultaneous presence of the *EE*-, *EZ*-, and *ZZ*-isomers in ca. 1:2:2 (R = Me) and ca. 1:3:4 (R = Et) ratios.

X-ray Structure Determinations of Pt Complexes. The structures of **1**−**4** were determined by X-ray single-crystal diffraction. In **1**, **2**, and **2b**, two new 1,3-diaza-1,3-diene ligands are in the mutually trans position, and they are both in the *E*- (**1**; Figure 1) and *Z*-configuration (**2** and **2b**; Figure 2 for **2**; for **2b** see Figure S1 in Supporting Information). In **3** (Figure 3) and **4** (Figure 4), two new diazadiene ligands are in the *Z*-configuration and cis to each other; the adjacent molecules are linked by weak (NH···Cl)$_2$ interactions [2.71 Å for **3** and 2.67 Å for **4**] (Figure S4, Table S2 and Figure S5, Table S3, respectively).

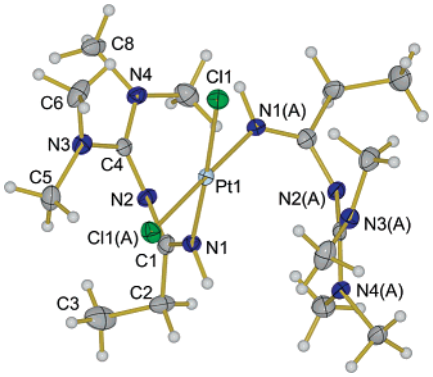

Figure 4. Thermal ellipsoid view of complex **4** with atom-numbering scheme. Thermal ellipsoids are drawn with 50% probability.

The values of the Pt−Cl bond distances (2.30−2.32 Å) agree well with previously characterized platinum(II) chloride compounds.[11,25,26] The N(1)−C(1) bond lengths in **1**−**4** and N(2)−C(3) in **3** [1.296(3), 1.305(4), 1.300(5), 1.300(5), 1.308(7) Å, respectively] correspond, within 3σ, to the typical C=N double bond [mean value 1.279(8) Å in compounds with C_{Ar}−C=N−C moiety[27]]. The bond lengths N(2)−C(1) in **1** and **2** [1.357(3) and 1.346(4) Å, respectively] have values closer to a C−N single bond [Nsp^2−Csp^2 in amides 1.346(11) Å[27]]. N(2)−C(4) in **1** [1.326(3) Å], N(2)−C(8) [1.324(4) Å] in **2**, N(2)−C(1) [1.332(7) Å] in **3**, and N(2)−C(1) [1.334(5) Å] and N(2)−C(4) [1.317(5) Å] in **4** bond lengths are intermediate between those values. These observations demonstrate the presence of electron delocalization for N(2)−C(4) bonds in **1** and **4** and N(2)−C(8) in **2** of the TMG moiety of the Pt(II)-bound 1,3-diaza-1,3-diene species, which is relevant to that observed for the N(1)−C(1) bond length [1.3292(17) Å] of NH=C(NMe_2)$_2$·HCl (Figure S3) and at any of the uncomplexed substituted guanidinium species [C−(NH_2)$_3$]$^+$ [av. Nsp^2−Csp^2 is 1.328(15) Å[27]].

However, in general, the data demonstrate the absence of electron delocalization in the 1,3-diaza-1,3-diene ligand. A similar phenomenon has been observed in the imidoylamidine NH=C(NEt_2)N=C(Ph)NHPh[10] and the diazadiene NH=C(Et)N=CPh_2[9] species monodentately coordinated to a Pt^{IV} center, where the imine ligands have distinct single and double CN bonds with no electron delocalization. The N−C bond lengths N(3)−C(4) [1.361(3) Å] and N(4)−C(4) [1.358(3) Å] in **1**, N(3)−C(8) [1.346(4) Å] and N(4)−C(8) [1.355(4) Å] in **2**, N(3)−C(3) [1.361(7) Å] and N(4)−C(3) [1.350(7) Å] in **3**, and N(3)−C(4) [1.352(5) Å] and N(4)−C(4) [1.347(5) Å] in **4** of =C−(NMe_2)$_2$ fragments correspond, within 3σ, to N(2)−C(1) [1.3395(16) Å] or N(3)−C(1) [1.3453(16) Å] bond lengths of NH=C(NMe_2)$_2$·HCl (Figure S3) and also to the typical Nsp^2−Csp^2 single bond [av. 1.355(14) in C=C−N−(Csp^3)$_2$ (Nsp^2 planar)[27]].

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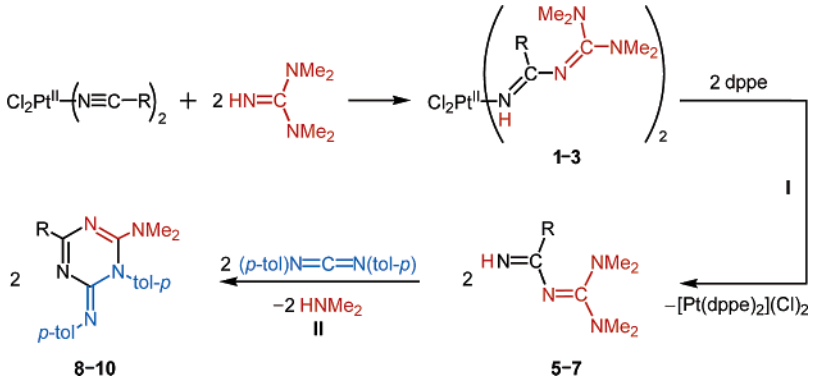
Scheme 2



Liberation of the 1,3-Diaza-1,3-dienes. Insofar as 1,3-diaza-1,3-dienes are useful synthons for many organic transformations[28,29] and their formation easily occurs at the Pt^{II} center, we suggest an efficient route for liberation of the NH═C(R)N═C(NMe$_2$)$_2$ species from **1**−**3** by substitution with 1,2-bis-(diphenylphosphino)ethane (dppe) in accord with previous reports.[6,8,9] Displacement in $CDCl_3$ resulted in precipitation of the known[6,8,9,14] highly insoluble complex [Pt(dppe)$_2$](Cl)$_2$ (identified by $^{31}P\{^1H\}$ NMR), which was separated by filtration from the solution containing the free diazadiene NH═C(R)N═C(NMe$_2$)$_2$ (**5**−**7**) (route I, Scheme 2); the latter (IUPAC name[30] *N*-[bis(dimethylamino)methylene]carboximidamide) were characterized by ESI-MS and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (see Experimental Section).

It was previously reported that although *N*-unsubstituted-1,3-diaza-1,3-dienes are rather unstable, they have acceptable stability under normal conditions depending on donor/acceptor properties of substituents at the C^2 atoms being more stable with electron-withdrawing groups.[1] We observed that, accordingly, **5** and **7** containing donor groups (Me and Et, respectively) are rather unstable in $CDCl_3$ and decompose after 6−12 h at room temperature, whereas phenyl-containing **6** is stable for at least 5 days under the same conditions.

The known synthetic pathways[29] to achieve 1,3-diaza-1,3-dienes do not include direct interaction between organonitriles and imines. In particular, the 1,3-diaza-1,3-dienes [Me$_2$N═C(R)N═C(NMe$_2$)$_2$](ClO$_4$), which are the most relevant to our systems, were obtained by treatment of [(Me)$_2$N═C(Cl)Ph](Cl) (R = Ph)[31] or [Me$_2$N═C(OMe)Me]-(MeSO$_4$) (R = Me)[32] with TMG. Thus, the nitrile−TMG coupling reported herein constitutes a potential *alternative* pathway to the synthesis of 1,3-diaza-1,3-dienes and a consequence of the metal-mediated coupling, and the liberation allows the facile synthesis of the previously unknown *N*-unsubstituted 1,3-diaza-1,3-dienes HN═C(R)N═(NMe$_2$)$_2$.

In Situ Conversion of the Diazadienes to 1,6-Dihydro-1,3,5-triazine-2-amines. In organic chemistry, 1,3-diaza-1,3-dienes are useful for syntheses of six-membered nitrogen-containing heterocycles, and their involvement in [4 + 2] cycloadditions to give these systems was a subject of rapt attention.[28] We attempted to utilize the novel HN═C(R)N═C-(NMe$_2$)$_2$ species for cycloaddition and used diazadienes **5**−**7** in situ in the reaction with 1,3-di-*p*-tolylcarbodiimide (reactions of this reagent with various *N*-nucleophiles and dipoles are well-known[20,21]) and observed that they readily react with (*p*-tol)N═C═N(tol-*p*) in $CDCl_3$ to generate 1,6-dihydro-1,3,5-triazine derivatives (IUPAC name[30] (6*E*)-*N*,*N*-dimethyl-1-(4-methylphenyl)-6-[(4-methylphenyl)imino]-1,6-dihydro-1,3,5-triazin-2-amines) (**8**−**10**) (route II, Scheme **2**) due to the [4 + 2]-cycloaddition accompanying elimination of HNMe$_2$ (the latter was detected by ^1H NMR, 2.42, and $^{13}C\{^1H\}$ NMR, 39.0 ppm); elimination of dimethylamine from pyrimidine or pyrimido[4,5-*d*]pyrimidine derivatives upon cycloaddition has several precedents in the past.[33]

The ^1H NMR spectra of **8**−**10** display two *p*-C*H*$_3$Ph singlets in the range from 2.41 to 2.27 ppm and two N*Me*$_2$ singlets at 3.18−3.08 and 2.87−2.74 ppm, respectively, in a ratio of 1:5 obtained by integration. The $^{13}C\{^1H\}$ NMR spectra of **8**−**10** and the X-ray structures of **9** and **10** confirmed the formulation. $^{13}C\{^1H\}$ NMR spectra of **8**−**10** display three characteristic signals at 175.1−150.6 ppm, four (**8** and **9**) or five (**10**) characteristic signals at 146.6−131.4 ppm, two characteristic signals at 41.5−40.4 ppm, and two characteristic signals at 21.6−21.3 ppm assigned to *C*═N, C_{ipso}, N*Me*$_2$, and *C*H$_3$Ph carbons, correspondingly.

In **9** (Figure 5) and **10** (Figure 6), characterized by X-ray crystallography, the N(1)−C(18), N(1)−C(1), N(2)−C(1), N(2)−C(8), and N(3)−C(8) bond lengths [1.370(2), 1.312-(2), 1.349(2), 1.330(2), 1.378(2), and 1.3714(17), 1.3154-(18), 1.3471(18), 1.3329(18), 1.3777(18) Å, respectively] agree well with the mean value reported for C═N delocalized double bonds in pyrimidine (overall) [1.336(14) Å[27]]. However, the N(1)−C(1) bond lengths [1.312(2) and 1.3154-(18) Å, respectively] have values closer to the C═N double bond [av. 1.313(11) Å in the −N═C−N fragment of

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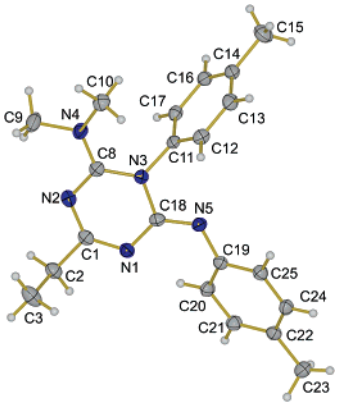

Figure 5. Thermal ellipsoid view of **9** with atom-numbering scheme. Thermal ellipsoids are drawn with 50% probability.

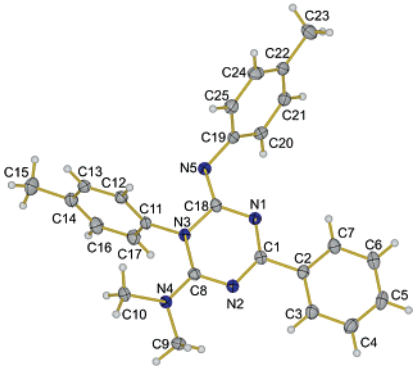

Figure 6. Thermal ellipsoid view of **10** with atom-numbering scheme. Thermal ellipsoids are drawn with 50% probability.

imidazole, av. 1.314(9) Å in the O−N═C−Csp^2 moiety of isoxazole[27]], whereas N(1)−C(18), N(2)−C(1) bond lengths [1.370(2), 1.349(2), and 1.3714(17), 1.3471(18) Å, correspondingly] have values closer to Csp^2−Nsp^2 single bond [av. 1.376(11) Å in ═N−C═C moiety of imidazole[27]].

The N−C bond lengths N(2)−C(8) in **9** and **10** [1.330(2) and 1.3329(18) Å, respectively] correspond, within 3σ, to the N(1)−C(1) bond length [1.3292(17) Å] of NH═C(NMe$_2$)$_2$•HCl (Figure S3) and also to the typical N−C single bond in substituted guanidinium species [C−(NH$_2$)$_3$]$^+$ [av. Nsp^2−Csp^2 is 1.328(15) Å[27]]. This indicates the presence of electron delocalization for the N═C double bond, apparently induced by the neighboring NMe$_2$ and N(*p*-(MeC$_6$H$_4$) groups, i.e., analogous to substituted guanidinium species [C−(NH$_2$)$_3$]$^+$ [av. Nsp^2−Csp^2 is 1.328(15) Å[27]]. The N−C bond lengths N(4)−C(8) in **9** and **10** [1.345(2) and 1.3403(18) Å, respectively] correspond, within 3σ, to the typical Nsp^2−Csp^2 single bond [av. 1.355(14) in C═C−N−(Csp^3)$_2$ (Nsp^2 planar)[27]]. The N(5)−C(18) bond lengths [1.290(2) and 1.2811(18) Å, respectively] agree well, within 3σ, with the typical C═N double bond [mean value 1.279(8) Å in compounds with the C$_{Ar}$−C═N−C moiety[27]]. N(3)−C(18) and N(3)−C(8) in **9** and **10** [1.429(2), 1.378(2) and 1.4332(17), 1.3777(18), respectively] correspond, within 3σ, to the typical Nsp^2−Csp^2 single bond [av. 1.409(20) Å in imides [Csp^2−C(═O)]$_2$−N−Csp^2 (Nsp^2 planar)[27]]. N(3)−C(11) in **9** and **10** [1.450(2) and 1.4443(17) Å, respectively] corresponds, within 3σ, to the typical C$_{Ar}$−N single bond [av. 1.390(30) Å in compounds with fragment C$_{Ar}$−N−(Csp^3)$_2$[27]]. In **9** and **10**, six-membered rings N(1)C(1)N(2)C(8)N(3)C(18) are planar [rms of the deviations of atoms from the plane N(1)C(1)N(2)C(8)N(3)C(18) are 0.048(1) (**9**) and 0.063(1) Å (**10**)].

Thus, all data combined together indicate that 1,3-diaza-1,3-dienes **5**−**7** undergo [4 + 2] cycloaddition with 1,3-di-*p*-tolylcarbodiimide with concomitant loss of HNMe$_2$, thus converting into cycloadducts **8**−**10**.

Dihydrotriazines are the known class of six-membered heterocycles, and some of these compounds possess antibacterial (e.g., against such bacteria as wild-type *Plasmodium falciparum* dihydrofolate reductase, *Escherichia coli* and *Staphilococcus aureus*, *Plasmodium berghei* in mice, *Plasmodium gallinaceum* in hens),[34−37] anti-diabetic,[38] herbicidal,[39,40] and antitumor activities[41] and also show hypoglycemic properties.[42] Other successful applications of the dihydrotriazines include controlling leukocytozoon disease in chickens,[43] use as insecticides,[44,45] antithyroidal,[46] antimalarial,[47−51] or anti-inflammatory agents,[52] as well as use as corrosion inhibitors.[53]

Dihydrotriazines are commonly prepared by (i) acid-catalyzed cyclocondensation between biguanidines,[35−38,54−56] cyanoguanidines, amines,[40,45,48,50,56−58] *N*′-amidinothioureas,[55] and carbonyl compounds, (ii) cyclocondensation of RCN with carbonyl compound and NH$_3$ in alcohols under harsh conditions,[59,60] (iii) cyclization of thiourea derivative[52] or polymer-bound guanidines (solid-phase synthesis)[61] with chlorcarbonylisocyanate and cyclization of two *N*′-(aminocarbonyl)imidocarbamates,[62] (iv) cyclization of imidothiocarbamate derivative[63] or guanidine[64] with isothiocyanate derivative and cyclization of amidines with imidoylisothiocyanates,[65]and (v) trimerization of RCN induced by alkyllithium

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derivatives[66] or sodium.[67] Hence, the [4 + 2]-cycloaddition of 1,3-diaza-1,3-diene to carbodiimides, described in this section, constitutes a novel synthetic approach to this useful class of heterocyclic species.

Final Remarks

The results from this work may be considered from three perspectives. First, it was observed that addition of HN═C(NMe$_2$)$_2$ to coordinated organonitriles is Pt^{II} mediated and results in the previously unknown ligated HN-unsubstituted 1,3-diaza-1,3-dienes HN═C(R)N═C(NMe$_2$)$_2$, and the reaction represents the first example of nitrile−guanidine coupling. The Pt^{II} center plays a dual role in the synthesis of the 1,3-diaza-1,3-dienes, i.e., it activates the organonitriles toward the nucleophilic addition of TMG and stabilizes the formed ligands (especially those with donor groups) by complexation. We are continuing to explore the metal-mediated nitrile−guanidine integration and apply for that purpose various guanidines including more reactive species HN═C(NHR)$_2$ with partially substituted (R = alkyl, aryl) or unsubstituted (R = H) amido groups. Second, the consequence of the platinum(II)-mediated reactions followed by ligand liberation provide a novel and facile route to the previously unreported 1,3-diaza-1,3-dienes HN═C(R)N═C(NMe$_2$)$_2$. Third, we found that [4 + 2]-cycloaddition of the 1,3-diaza-1,3-dienes to carbodiimides—performed in situ within the "pop-the-cork strategy"[8]—constitutes a novel synthetic approach to this useful class of heterocycles, 1,6-dihydro-1,3,5-triazines.

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Experimental Section

Materials and Instrumentation. Guanidine HN═C(NMe$_2$)$_2$, 1,3-di-*p*-tolylcarbodiimide (*p*-tol)N═C═N(tol-*p*) (Aldrich), and solvents were obtained from commercial sources and used as received. Complexes *cis*-[PtCl$_2$(RCN)$_2$] (R = Me,[15] Et[16]) were prepared in accord with the published methods. These compounds contain admixtures of the trans isomers (isomeric cis:trans ratio obtained by NMR integration is ca. 5:1 for R = Me,[15] ca. 6:1 for R = Et[16]). The isomerically pure complexes *trans*-[PtCl$_2$(RCN)$_2$] (R = Et,[16] Ph[17]) were obtained as previously described.

TLC was done on Merck 60 F_{254} SiO_2 plates. Elemental analyses were obtained on a Hewlett-Packard 185B Carbon Hydrogen Nitrogen Analyzer at the Department of Organic Chemistry, St. Petersburg State University. Positive-ion FAB mass spectra were obtained on a Kratos MS-50C instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with Xe atoms. Electrospray ionization mass spectra of **5**−**10** were recorded on a Bruker *esquire*$_{3000}$ ion trap mass spectrometer in positive-ion mode equipped with an orthogonal electrospray interface (Bruker Daltonics, Bremen, Germany). The sample solution in methanol was delivered at a flow rate of 3 μL/min using a syringe pump 74900 from Cole-Parmer Instrument Co. (Vernon Hills, IL), and N_2 was used as drying and nebulizing gas (flow rates 5 L/min). Expected and experimental isotope distributions were compared. Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets.

1D ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, NOE; 2D ^{1}H,^{1}H-COSY, and ^{1}H,^{13}C-HETCOR NMR spectra were measured on a Bruker DPX 300 spectrometer at ambient temperature. Assignment of ^{1}H chemical shifts for the CH_2 and CH_3 protons from the Et group for all isomers of both **1** and **4** was based on 2D ^{1}H,^{1}H-COSY NMR experiments. The description of the NMR spectra given in the synthetic part contains symbols {*E*} and {*Z*}, which designate the appropriate *E*- and *Z*-forms, e.g., "{*Z*}-*EZ*" denote a ligand in the Z-form for the *EZ* isomer.

Synthetic Work. Reaction of *trans*-[PtCl$_2$(RCN)$_2$] and TMG. HN═C(NMe$_2$)$_2$ (48 μL; 0.38 mmol) was added to a yellow solution of *trans*-[PtCl$_2$(RCN)$_2$] (0.19 mmol) in EtCN (1.5 mL) (R = Et) or CH_2Cl_2 (1.5 mL) (R = Ph) and left to stand for 1 h (R = Et) or 5 min (R = Ph) at 20−25 °C. In both cases, the greenish-yellow solution formed was evaporated to dryness, and the yellow residue was crystallized under a layer of Et_2O (1 mL) to form yellow powders which were washed with two 1-mL portions of acetone and one 1-mL portion of Et_2O (R = Ph) or two 1-mL portions of acetone:Et_2O = 1:1 mixture (R = Et), and both were dried in air at room temperature. Yields are 88 mg (77% (R = Et)) and 110 mg (83% (R = Ph)).

***trans*-[PtCl$_2${NH═C(Et)N═C(NMe$_2$)$_2$}$_2$] (1).** Anal. Calcd for $C_{16}H_{36}N_8Cl_2Pt$: C, 31.68; H, 5.94; N, 18.48. Found: C, 31.78; H, 6.05; N, 18.83. FAB$^+$-MS, *m/z*: 606 [M]$^+$, 171 [NH═C(Et)N═C(NMe$_2$)$_2$ + H]$^+$. TLC: R_f = 0.56 (eluent MeOH:$CHCl_3$ = 1:10). IR (KBr, selected bands) cm^{-1}: 3448 (br, w), 3327 (m-w), 3249 (w), ν(N−H); 2978 (m-w), 2925 (m-w), 2871 (m-w), ν(C−H from Et and N*Me*$_2$); 1566 (s), 1525 (s), ν(C═N); 1477 (s), 1448 (s), 1392 (s), δ(C−H from Et and N*Me*$_2$). ^{1}H NMR ($CDCl_3$), δ: 5.84 (s, br, {*Z*}-*ZZ*), 5.64 (s, br, {*Z*}-*EZ*), 5.42 (s, br, {*E*}-*EZ*), 5.40 (s, br, {*E*}-*EE*) (2H, N*H*), 3.08, 2.84, and 2.82 (m, 24H, N*Me*$_2$), 3.01 (q, 7.32 Hz, {*Z*}-*ZZ*), 2.93 (q, 7.32 Hz, {*Z*}-*EZ*), 2.39 (q, 7.32 Hz, {*E*}-*EZ*), 2.33 (q, 7.32 Hz, {*E*}-*EE*) (4H, C*H*$_2$ from Et), 1.34 (t, 7.32 Hz, {*Z*}-*ZZ*), 1.24 (t, 7.32 Hz, {*Z*}-*EZ*), 1.14 (t, 7.32 Hz, {*E*}-*EZ*), 1.09 (t, 7.32 Hz, {*E*}-*EE*) (6H, C*H*$_3$ from Et). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 178.2, 178.0, 176.0, 175.2, 163.2, 163.0, 162.9, 162.7

(*C*═N), 40.6, 40.4, 40.3, 40.3 (N*Me*$_2$), 35.0, 34.5, 31.7, 31.2 (*C*H$_2$ from Et), 12.5, 12.4, 12.1, 11.9 (*C*H$_3$ from Et). Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a hexane:chloroform (1:1, v/v) solution of **1**.

***trans*-[PtCl$_2${NH═C(Ph)N═C(NMe$_2$)$_2$}$_2$] (2).** Anal. Calcd for $C_{24}H_{36}N_8Cl_2Pt$: C, 41.02; H, 5.13; N, 15.95. Found: C, 40.79; H, 5.28; N, 15.75. FAB$^+$-MS, *m/z*: 703 [M + H]$^+$, 666 [M − Cl]$^+$, 630 [M − HCl − Cl]$^+$, 219 [NH═C(Ph)N═C(NMe$_2$)$_2$ + H]$^+$. TLC: R_f = 0.67 (eluent MeOH:CHCl$_3$ = 1:10). IR (KBr, selected bands) cm^{-1}: 3489 (m-w), 3323 (m-w), ν(N−H); 2937 (m-w), 2868 (w), ν(C−H from Ph and N*Me*$_2$); 1533 (s), ν(C═N and/or C═C from Ph); 1471 (m), 1421 (m-s), 1408 (m-s), 1390 (m-s), δ(C−H from N*Me*$_2$); 702 (m), δ(C−H from Ph). ^{1}H NMR (CDCl$_3$), δ: 7.65−7.61 (m, 4H), 7.40−7.28 (m, 6H) (Ph's), 6.30 (s, br, 2H, N*H*, {*Z*}-*ZZ*), 3.14 (s, {*Z*}-*ZZ*), 3.09 (s, {*Z*}-*EZ*), 2.91 (s, {*E*}-*EZ*), 2.73 (s, {*E*}-*EE*) (24H, N*Me*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 170.8, 163.7 (*C*═N), 130.6, 128.9, 127.4 (Ph's), 40.8, 40.3 (N*Me*$_2$). Complex **2** crystallizes from a CH$_2$Cl$_2$:hexane (1:1, v/v) mixture as *trans*-[PtCl$_2${*N*H═C(Ph)N═C(NMe$_2$)$_2$}$_2$] (**2**) and from a CHCl$_3$:hexane (1:1, v/v) mixture as the monohydrate *trans*-[PtCl$_2${*N*H═C(Ph)N═C(NMe$_2$)$_2$}$_2$]·H$_2$O·0.5CHCl$_3$ (**2b**), and structures of both **2** and **2b** were determined by X-ray crystallography.

Reaction of *cis*-[PtCl$_2$(RCN)$_2$] and TMG. HN═C(NMe$_2$)$_2$ (30 μL; 0.24 mmol) was added to a yellow suspension of *cis*-[PtCl$_2$(MeCN)$_2$] (0.12 mmol) in MeCN (1 mL) or a yellow solution of *cis*-[PtCl$_2$(EtCN)$_2$] (0.12 mmol) in EtCN (1 mL). In the case of *cis*-[PtCl$_2$(MeCN)$_2$], a pale-yellow precipitate starts to form immediately. In both cases, bright yellow solutions were evaporated to dryness. The solid residues formed were washed with two 2-mL portions of acetone (R = Me) or two 1.5-mL portions of a mixture acetone:hexane = 1:2 (R = Et) and one 1.5-mL portion of Et$_2$O (R = Me, Et) and dried in air at 20−25 °C. The washing waters were kept in air for slow evaporation to two-thirds of the initial volume. Released pale-yellow precipitates were separated by decantation and washed with two 0.5-mL portions of Et$_2$O (R = Me) or one 0.5-mL portion of acetone:hexane = 1:2 mixture and one 0.5-mL portion of Et$_2$O (R = Et) and dried in air at 20−25 °C. The separated compound dried in air at 20−25 °C and was combined with the first fraction. Yields are 50 mg (72% (R = Me)) and 43 mg (60% (R = Et)).

***cis*-[PtCl$_2${NH═C(Me)N═C(NMe$_2$)$_2$}$_2$] (3).** Anal. Calcd for $C_{14}H_{32}N_8Cl_2Pt$: C, 29.06; H, 5.53; N, 19.37. Found: C, 28.99; H, 5.57; N, 19.28. FAB$^+$-MS, *m/z*: 601 [M + Na]$^+$, 578 [M]$^+$, 543 [M − Cl]$^+$, 506 [M − 2Cl]$^+$, 157 [NH═C(Me)N═C(NMe$_2$)$_2$ + H]$^+$. TLC: R_f = 0.54 (eluent MeOH:CHCl$_3$ = 1:5). IR (KBr, selected bands) cm^{-1}: 3467 (br, m-w), 3257 (m-s), ν(N−H); 2925 (m), 2893 (m), 2797 (m-w), ν(C−H from Me and N*Me*$_2$); 1544 (s), ν(C═N); 1484 (s), 1423 (s), 1390 (s), δ(C−H from Me and N*Me*$_2$). ^{1}H NMR (CDCl$_3$), δ: 6.88 (s, br, {*E*}-*EE*), 6.48 (s, br, {*E*}-*EZ*), 6.16 (s, br, {*Z*}-*EZ* and {Z}-*ZZ*) (2H, N*H*), 3.07 (s), 3.02 (s), 2.87 (s), 2.84 (s) (24H, N*Me*$_2$), 2.56 (s, {*E*}-*EE*), 2.27 (s, {*E*}-*EZ*), 2.13 (s, {*Z*}-*EZ*), 2.11 (s, {*Z*}-*ZZ*) (*Me*). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 173.1, 172.2, 171.5, 163.0, 162.9 (*C*═N), 40.6, 40.5, 40.2 (N*Me*$_2$), 28.0, 27.2, 25.5, 24.0 (*Me*). Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a hexane: chloroform (1:1, v/v) solution of **3**.

***cis*-[PtCl$_2${NH═C(Et)N═C(NMe$_2$)$_2$}$_2$] (4).** Anal. Calcd for $C_{16}H_{36}N_8Cl_2Pt$: C, 31.68; H, 5.94; N, 18.48. Found: C, 31.35; H, 5.93; N, 18.37. FAB$^+$-MS, *m/z*: 629 [M + Na]$^+$, 606 [M]$^+$, 534 [M − HCl − Cl]$^+$, 171 [NH═C(Et)N═C(NMe$_2$)$_2$ + H]$^+$. TLC: R_f = 0.50 (eluent MeOH:CHCl$_3$ = 1:10). IR (KBr, selected bands) cm^{-1}: 3510 (br, m), 3267 (m-s), ν(N−H); 2934 (m), 2872 (m), ν(C−H from Me and N*Me*$_2$); 1544 (s), ν(C═N); 1472 (m-s), 1422 (m-s), 1397 (m-s), 1389 (s), δ(C−H from Et and N*Me*$_2$). ^{1}H NMR (CDCl$_3$), δ: 6.54 (s, br, {*E*}-*EE*), 6.32 (s, br, {*Z*}-*EZ*), 6.17 (s, br, {*E*}-*EZ*), 5.90 (s, br, {*Z*}-*ZZ*) (2H, N*H*), 3.07 (s), 3.03 (s), 2.91 (s) and 2.84 (s) (24H, N*Me*$_2$), 2.97−2.91 (m, 7.26 Hz, {*E*}-*EE*), 2.74 (q, 7.26 Hz, {*E*}-*EZ*), 2.40 (q, 7.26 Hz, {*Z*}-*EZ*), 2.32 (q, 7.26 Hz, {*Z*}-*ZZ*) (4H, C*H*$_2$ from Et), 1.27 (t, 7.26 Hz, {*E*}-*EE*), 1.19−1.09 (m, {*E*}-*EZ*, {*Z*}-*EZ*, {*Z*}-*ZZ*) (6H, C*H*$_3$ from Et). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 177.9, 175.5, 163.2, 163.0 (*C*═N), 40.6, 40.3 (N*Me*$_2$), 34.6 (*C*H$_2$ from Et), 12.2 (*C*H$_3$ from Et). Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a hexane: chloroform (1:1, v/v) solution of **4**.

Liberation of the Diazadiene from *trans*-[PtCl$_2${NH═C(R)-N═C(NMe$_2$)$_2$}$_2$]. 1,2-Bis-(diphenylphosphino)ethane (dppe; 0.2 mmol) was added to a solution of complex (**1**−**3**) (0.1 mmol) in CDCl$_3$ (1 mL) at 20−25 °C, and the mixture was left to stand for 20, 30, and 240 min (for **1**, **2**, and **3**, respectively) until a colorless precipitate of the known [Pt(dppe)$_2$](Cl)$_2$[6,8,9,14] (^{31}P{^{1}H} NMR in CDCl$_3$: 48.4 ppm, J_{Pt-P} 2348.5 Hz; lit.[68] 45.7 ppm, J_{Pt-P} 2360.5 Hz) was released. The latter complex was filtered off, and NH═C(R)N═C(NMe$_2$)$_2$, liberated quantitatively, was characterized in the filtrate by NMR and ESI-MS methods.

HN═C(Me)N═C(NMe$_2$)$_2$ (5). MS (ESI$^+$) *m/z*: 157 [M + H]$^+$. ^{1}H NMR (CDCl$_3$), δ: 2.81 (s, 12H, N*Me*$_2$), 2.03 (s, 3H, *Me*). ^{13}C-{^{1}H} NMR (CDCl$_3$), δ: 172.1, 162.1 (*C*═N), 40.0 (N*Me*$_2$), 25.9 (*Me*).

HN═C(Et)N═C(NMe$_2$)$_2$ (6). MS (ESI$^+$) *m/z*: 171 [M + H]$^+$. ^{1}H NMR (CDCl$_3$), δ: 2.80 (s, 12H, N*Me*$_2$), 2.29 (q, 7.27 Hz, 2H, C*H*$_2$), 1.15 (t, 7.27 Hz, 3H, C*H*$_3$) (*Et*). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 176.0, 162.4 (*C*═N), 40.0 (N*Me*$_2$), 32.0 (*C*H$_2$), 11.8 (*C*H$_3$) (*Et*).

HN═C(Ph)N═C(NMe$_2$)$_2$ (7). MS (ESI$^+$) *m/z*: 219 [M + H]$^+$. ^{1}H NMR (CDCl$_3$), δ: 7.35 (d, 3H), 7.29 (d, 2H) (Ph's), 2.79 (s, 12H, N*Me*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 170.4, 162.9 (*C*═N), 139.4 (C_{ipso}), 130.0, 128.4, 127.9 (Ph's), 40.0 (N*Me*$_2$).

Reaction of Diazadienes 5−7 with 1,3-Di-*p*-tolylcarbodiimide. Dppe (40 mg, 0.10 mmol) was added to a solution of **1**−**3** (0.05 mmol) in CDCl$_3$ (1 mL), and the reaction mixture was left to stand at 20−25 °C for 20, 30, and 240 min (for **1**, **2**, and **3**, respectively), whereupon the colorless precipitate of [Pt(dppe)$_2$](Cl)$_2$ was removed by filtration and the filtrate was added to the suspension of 1,3-di-*p*-tolylcarbodiimide (23 mg, 0.10 mmol) in CDCl$_3$ (1 mL), and the new reaction mixture was stirred for 20 h at 20−25 °C. The pale-yellow (R = Me, Et) or bright-yellow (R = Ph) suspension formed was evaporated to dryness. The solid residue thus obtained was crystallized under a layer of EtOH (0.75 mL) to form pale-yellow (R = Me, Et) or bright-yellow (R = Ph) precipitate, which was filtered off after 2.5 h and washed with one 0.5-mL portion of EtOH. Yields are 16 mg (47% (R = Me; **8**)), 17 mg (50% (R = Et; **9**)), and 21 mg (53% (R = Ph; **10**)).

(6*E*)-*N*,*N*,4-Trimethyl-1-(4-methylphenyl)-6-[(4-methylphenyl)-imino]-1,6-dihydro-1,3,5-triazin-2-amine (8). MS (ESI$^+$) *m/z*: 334 [M + H]$^+$. ^{1}H NMR (CDCl$_3$), δ: 7.32 (d, 8 Hz, 2H), 7.22 (d, 8 Hz, 2H), 7.02 (d, 8 Hz, 2H), 6.88 (d, 8 Hz, 2H) (*p*-CH$_3$*Ph*), 3.08 (s, 1H), 2.74 (s, 5H) (N*Me*$_2$), 2.38 (s, 3H), 2.27 (s, 3H) (*p*-C*H*$_3$Ph), 2.21 (s, 3H, *Me*). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 171.4, 160.7, 150.6 (*C*═N), 146.6, 138.1, 137.8, 131.4 (C_{ipso}), 129.7, 129.2, 123.3 (*p*-CH$_3$*Ph*), 41.2, 40.4 (N*Me*$_2$), 26.4 (*Me*), 21.6, 21.3 (*p*-*C*H$_3$Ph).

(6*E*)-4-Ethyl-*N*,*N*-dimethyl-1-(4-methylphenyl)-6-[(4-methylphenyl)imino]-1,6-dihydro-1,3,5-triazin-2-amine (9). MS (ESI$^+$) *m/z*: 348 [M + H]$^+$. ^{1}H NMR (CDCl$_3$), δ: 7.33 (d, 8 Hz, 2H), 7.22 (d, 8 Hz, 2H), 7.01 (d, 8 Hz, 2H), 6.94 (d, 8 Hz, 2H) (*p*-

(68) Anderson, G. K.; Davies, J. A.; Schoeck, D. J. *Inorg. Chim. Acta* **1983**, *76*, L251.

Table 1. Crystallographic Data for **1**, **2**, **2b**, **3**, **4**, **9**, **10**, and **11**

	1	**2**	**2b**	**3**	**4**	**9**	**10**	**11**
empirical formula	$C_{16}H_{36}Cl_2N_8Pt$	$C_{24}H_{36}Cl_2N_8Pt$	$C_{49}H_{77}Cl_7N_{16}O_2Pt_2$	$C_{15}H_{33}Cl_5N_8Pt$	$C_{17}H_{37}Cl_5N_8Pt$	$C_{21}H_{25}N_5$	$C_{25}H_{25}N_5$	$C_5H_{14}ClN_3$
fw	606.52	702.60	1560.60	697.83	725.89	347.46	395.50	151.64
temp. (K)	120(2)	120(2)	120(2)	105(2)	120(2)	120(2)	120(2)	120(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073 Å
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	6.5007(2)	10.4573(8)	10.1658(8)	17.5830(8)	19.0947(11)	10.2649(4)	6.05060(10)	6.9690(2)
b (Å)	9.3467(4)	11.2403(12)	11.2026(8)	12.5070(7)	12.4624(8)	15.1605(7)	16.3902(4)	13.1080(4)
c (Å)	18.9815(6)	12.2694(8)	15.1162(10)	12.3850(4)	12.5981(6)	12.3997(4)	21.2859(5)	9.2807(3)
α (deg)	90	90	75.797(5)	90	90	90	90	90
β (deg)	98.563(2)	112.070(7)	85.330(7)	113.346(2)	107.268(4)	104.013(3)	93.6880(10)	104.757(2)
γ (deg)	90	90	65.379(6)	90	90	90	90	90
V (Å^3)	1140.46(7)	1336.5(2)	1516.7(2)	2500.6(2)	2862.8(3)	1872.23(13)	2106.56(8)	819.82(4)
Z	2	2	1	4	4	4	4	4
ρ_{calcd} (mg/m^3)	1.766	1.746	1.709	1.854	1.684	1.233	1.247	1.229
μ(Mo Kα) (mm^{-1})	6.404	5.479	4.967	6.165	5.389	0.076	0.076	0.392
no. reflns	9105	17 165	28 628	25 331	21 418	17 497	50 887	14 254
no. unique reflns	2618	3050	6936	2868	3299	4066	4851	1867
R_{Int}	0.0376	0.0569	0.0558	0.0521	0.0634	0.0452	0.0651	0.0433
R1[a] ($I \geq 2\sigma$)	0.0201	0.0253	0.0334	0.0292	0.0303	0.0453	0.0439	0.0286
wR2[b] ($I \geq 2\sigma$)	0.0403	0.0515	0.0688	0.0521	0.0580	0.1036	0.1007	0.0697

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

Table 2. Bond Distances (Å) and Angles (deg) for **1**, **2**, **3** and **4**

1		**2**		**3**		**4**	
Pt(1)−N(1)	2.015(2)	Pt(1)−N(1)	2.009(3)	Pt(1)−N(1)	1.995(3)	Pt(1)−N(1)	2.001(3)
Pt(1)−Cl(1)	2.3050(7)	Pt(1)−Cl(1)	2.2999(9)	Pt(1)−Cl(1)	2.3102(11)	Pt(1)−Cl(1)	2.3187(9)
N(1)−C(1)	1.296(3)	N(1)−C(1)	1.305(4)	N(1)−C(1)	1.300(5)	N(1)−C(1)	1.300(5)
C(1)−C(2)	1.503(3)	N(2)−C(1)	1.346(4)	C(1)−C(2)	1.500(7)	C(1)−C(2)	1.518(5)
C(2)−C(3)	1.528(4)	N(2)−C(8)	1.324(4)	N(2)−C(1)	1.332(7)	C(2)−C(3)	1.503(6)
N(2)−C(1)	1.357(3)	N(3)−C(8)	1.346(4)	N(2)−C(3)	1.308(7)	N(2)−C(1)	1.334(5)
N(2)−C(4)	1.326(3)	N(3)−C(9)	1.453(5)	N(3)−C(3)	1.361(7)	N(2)−C(4)	1.317(5)
N(3)−C(4)	1.361(3)	N(3)−C(10)	1.464(5)	N(3)−C(4)	1.451(7)	N(3)−C(4)	1.352(5)
N(3)−C(5)	1.458(4)	N(4)−C(8)	1.355(4)	N(3)−C(5)	1.450(7)	N(3)−C(5)	1.443(5)
N(3)−C(6)	1.467(3)	N(4)−C(11)	1.476(4)	N(4)−C(3)	1.350(7)	N(3)−C(6)	1.456(5)
N(4)−C(4)	1.358(3)	N(4)−C(12)	1.441(4)	N(4)−C(6)	1.447(8)	N(4)−C(4)	1.347(5)
N(4)−C(7)	1.457(3)			N(4)−C(7)	1.453(8)	N(4)−C(7)	1.452(5)
N(4)−C(8)	1.463(3)					N(4)−C(8)	1.458(5)
N(1)−Pt(1)−N(1A)	180.00(12)	N(1)−Pt(1)−N(1A)	179.998(1)	N(1)−Pt(1)−N(1)	97.03(19)	N(1)−Pt(1)−N(1A)	94.94(18)
N(1)−Pt(1)−Cl(1A)	91.07(7)	N(1)−Pt(1)−Cl(1A)	92.92(9)	N(1)−Pt(1)−Cl(1)	176.53(10)	N(1)−Pt(1)−Cl(1)	177.27(10)
Cl(1)−Pt(1)−Cl(1A)	180.0	Cl(1)−Pt(1)−Cl(1A)	179.999(1)	N(1)−Pt(1)−Cl(1)	86.37(10)	N(1)−Pt(1)−Cl(1A)	87.19(9)
C(1)−N(1)−Pt(1)	130.76(17)	C(1)−N(1)−Pt(1)	135.3(2)	Cl(1)−Pt(1)−Cl(1)	90.24(6)	Cl(1)−Pt(1)−Cl(1A)	90.73(5)
N(1)−C(1)−C(2)	119.7(2)	N(1)−C(1)−C(2)	119.3(3)	C(1)−N(1)−Pt(1)	133.1(4)	C(1)−N(1)−Pt(1)	131.7(3)
N(1)−C(1)−N(2)	124.9(2)	N(1)−C(1)−N(2)	125.7(3)	N(1)−C(1)−C(2)	119.0(5)	N(1)−C(1)−C(2)	118.5(3)
N(2)−C(1)−C(2)	115.2(2)	N(2)−C(1)−C(2)	114.9(3)	N(1)−C(1)−N(2)	126.6(5)	N(1)−C(1)−N(2)	127.4(4)
C(4)−N(2)−C(1)	123.7(2)	C(8)−N(2)−C(1)	125.9(3)	N(2)−C(1)−C(2)	114.2(4)	N(2)−C(1)−C(2)	113.8(3)
N(2)−C(4)−N(3)	118.2(2)	N(2)−C(8)−N(3)	118.5(3)	C(3)−N(2)−C(1)	126.4(4)	C(4)−N(2)−C(1)	126.8(3)
C(4)−N(3)−C(5)	118.7(2)	C(8)−N(3)−C(9)	119.2(3)	N(2)−C(3)−N(3)	124.5(5)	N(2)−C(4)−N(3)	124.0(4)
C(4)−N(3)−C(6)	122.4(2)	C(8)−N(3)−C(10)	122.1(3)	C(3)−N(3)−C(4)	119.9(5)	C(4)−N(3)−C(5)	120.6(3)
C(5)−N(3)−C(6)	114.7(2)	C(9)−N(3)−C(10)	114.5(3)	C(3)−N(3)−C(5)	122.3(4)	C(4)−N(3)−C(6)	122.1(4)
N(2)−C(4)−N(4)	124.8(2)	N(2)−C(8)−N(4)	123.4(3)	C(5)−N(3)−C(4)	115.4(5)	C(5)−N(3)−C(6)	115.1(3)
C(4)−N(4)−C(7)	123.3(2)	C(8)−N(4)−C(11)	122.3(3)	N(2)−C(3)−N(4)	119.0(6)	N(2)−C(4)−N(4)	117.8(4)
C(4)−N(4)−C(8)	121.5(2)	C(8)−N(4)−C(12)	121.1(3)	C(3)−N(4)−C(6)	123.0(6)	C(4)−N(4)−C(7)	119.2(3)
C(7)−N(4)−C(8)	114.5(2)	C(12)−N(4)−C(11)	114.1(3)	C(3)−N(4)−C(7)	118.0(6)	C(4)−N(4)−C(8)	123.5(4)
N(4)−C(4)−N(3)	116.9(2)	N(3)−C(8)−N(4)	117.6(3)	C(6)−N(4)−C(7)	115.7(6)	C(7)−N(4)−C(8)	113.9(3)
				N(4)−C(3)−N(3)	116.1(6)	N(4)−C(4)−N(3)	117.6(3)

CH_3*Ph*), 3.10 (s, 1H), 2.75 (s, 5H) (N*Me*$_2$), 2.46 (q, 7.27 Hz, 2H, C*H*$_2$ from Et), 2.39 (s, 3H), 2.27 (s, 3H) (*p*-C*H*$_3$Ph), 1.22 (t, 7.27 Hz, 3H, C*H*$_3$ from Et). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 175.1, 160.9, 150.9 (*C*═N), 146.4, 138.0, 137.8, 131.4 (C_{ipso}), 129.7, 129.2, 129.1, 123.7 (*p*-CH_3*Ph*), 41.3, 40.4 (N*Me*$_2$), 32.5 (*C*H$_2$ from Et), 21.6, 21.3 (*p*-*C*H$_3$Ph), 11.6 (*C*H$_3$ from Et). Crystals suitable for X-ray single-crystal diffraction study were obtained by slow evaporation of a toluene:chloroform (1:1, v/v) solution of **9**.

(6*E*)-*N*,*N*-Dimethyl-1-(4-methylphenyl)-6-[(4-methylphenyl)-imino]-4-phenyl-1,6-dihydro-1,3,5-triazin-2-amine (10). MS (ESI$^+$) *m*/*z*: 396 [M + H]$^+$. ^{1}H NMR ($CDCl_3$), δ: 8.33 (d, 2H), 7.49−7.39 (m, 5H), 7.26 (t, 2H), 7.08 (s, 4H) (*p*-CH_3*Ph*), 3.18 (s, 1H), 2.87 (s, 5H) (N*Me*$_2$), 2.41 (s, 3H), 2.33 (s, 3H) (*p*-C*H*$_3$Ph). ^{13}C-{^{1}H} NMR ($CDCl_3$), δ: 165.3, 161.4, 151.2 (*C*═N), 146.6, 138.2, 137.8, 137.3, 131.4 (C_{ipso}), 131.8, 129.8, 129.4, 129.3, 129.0, 128.4, 124.0 (*p*-CH_3*Ph*), 41.5, 40.5 (N*Me*$_2$), 21.6, 21.3 (*p*-*C*H$_3$Ph). Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a toluene:chloroform (1:1, v/v) solution of **10**.

For comparison of X-ray data we prepared crystals of TMG·HCl (**11**) and determined its X-ray structure.

X-ray Structure Determinations. Crystals were immersed in cryo-oil, mounted in a nylon loop, and measured at a temperature

Table 3. Bond Distances (Å) and Angles (deg) for **9** and **10**

bonds and angles	**9**	**10**
N(1)−C(1)	1.312(2)	1.3154(18)
N(2)−C(1)	1.349(2)	1.3471(18)
N(2)−C(8)	1.330(2)	1.3329(18)
N(4)−C(8)	1.345(2)	1.3403(18)
N(4)−C(9)	1.465(2)	1.4664(19)
N(4)−C(10)	1.465(2)	1.4665(17)
N(3)−C(8)	1.378(2)	1.3777(18)
N(3)−C(11)	1.450(2)	1.4443(17)
N(3)−C(18)	1.429(2)	1.4332(17)
N(5)−C(18)	1.290(2)	1.2811(18)
N(5)−C(19)	1.409(2)	1.4148(18)
N(1)−C(18)	1.370(2)	1.3714(17)
N(1)−C(1)−N(2)	127.52(15)	127.44(12)
C(8)−N(2)−C(1)	116.09(14)	116.48(12)
N(2)−C(8)−N(4)	117.97(14)	117.43(12)
C(8)−N(4)−C(9)	118.20(15)	117.79(12)
C(9)−N(4)−C(10)	114.30(13)	114.22(11)
C(8)−N(4)−C(10)	125.31(14)	126.03(12)
N(4)−C(8)−N(3)	120.55(15)	121.44(12)
N(2)−C(8)−N(3)	121.46(14)	121.12(12)
C(8)−N(3)−C(11)	122.36(13)	123.22(11)
C(18)−N(3)−C(11)	117.14(12)	117.66(11)
C(8)−N(3)−C(18)	118.88(13)	118.49(11)
N(5)−C(18)−N(3)	115.40(14)	116.21(12)
C(18)−N(5)−C(19)	122.29(14)	120.41(12)
N(5)−C(18)−N(1)	126.60(14)	125.79(13)
N(1)−C(18)−N(3)	117.99(13)	118.00(12)
C(1)−N(1)−C(18)	117.29(13).	117.11(12).

of 105−120 K. X-ray diffraction data was collected by means of a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The DENZO/SCALEPACK[69] or EvalCCD[70] program packages were used for cell refinements and data reductions. All of the structures were solved by direct methods using SHELXS-97,[71] SIR-97,[72] SIR2002,[73] or SIR2004.[74] An empirical absorption correction was applied to all of the data (XPREP in SHELXTL[75] or SADABS;[76] T_{max}/T_{min} were 0.2226/0.3371, 0.4048/0.7199, 0.4048/0.7199, 0.2950/0.7818, 0.4672/0.7273, 0.9870/0.9894, 0.9763/0.9921, and 0.9222/0.9414, respectively, for **1**, **2**, **2b**, **3**, **4**, **9**, **10**, and **11**). Structural refinements were carried out using SHELXL-97[77] with WinGX[78] graphical user interface. Complex **2** was crystallized without and with solvent of crystallization in two different space groups $P2_1/c$ (**2**) and $P\bar{1}$ (**2b**). The NH, NH_2, and H_2O hydrogens were located from the difference Fourier map and either refined isotropically (**2**) or constrained to ride on their parent atoms. Other hydrogens were positioned geometrically and constrained to ride on their parent atoms. The asymmetric unit of **2b** contains two independent halves of the Pt complexes. In all Pt structures, Pt atoms are coordinated by two Cl atoms and two N atoms in a slightly distorted square planar geometry. The $CHCl_3$ solvent molecule in **2b** is disordered over two positions with two shared Cl atoms and equal occupation parameters of 0.5. Also, in **3** the hydrogen and chlorine atoms of the $CHCl_3$ solvent are disordered over two positions with equal occupation parameters of 0.5. In **4**, the $CHCl_3$ solvent molecule was refined over two positions with equal occupancy of 0.5. The crystallographic details are summarized in Table 1. The selected bond lengths and angles are given in the figure captions and Tables 2 and 3.

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Supporting Information Available: Figures S1 and S3 with thermal ellipsoid views of **2b** and **11**, respectively, Figures S2, S4, and S5 with hydrogen-bonding schemes for **2b**, **3**, and **4**, Tables S1−S3 with hydrogen bonds for **2b**, **3**, and **4**, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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