8678 *Inorg. Chem.* **2009**, *48*, 8678–8688
DOI: 10.1021/ic900263e

Inorganic Chemistry
Article

Different Routes for Amination of Platinum(II)-Bound Cyanoguanidine†

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Received February 12, 2009

The consecutive addition of $AgSO_3CF_3$ (1 or 2 equiv) and cyanoguanidine (1 or 2 equiv, respectively) to the platinum(II) precursor $[PtI_2(tmeda)]$ leads to the *cis*-$[PtI(tmeda)\{\underline{N}CN{=}C(NH_2)_2\}](SO_3CF_3)$ (**1**·(SO_3CF_3)) or *cis*-$[Pt(tmeda)\{\underline{N}CN{=}C(NH_2)_2\}_2](SO_3CF_3)_2$ (**2**·$(SO_3CF_3)_2$) complexes. The reaction between **1**·(SO_3CF_3) or **2**·$(SO_3CF_3)_2$ and the excess of R_2NH (R = H, $R_2 = C_5H_{10}$) in EtOH gives the triazapentadiene compounds *cis*-$[Pt(tmeda)\{\underline{N}HC(NR_2)NC(NH_2)\underline{N}H\}](SO_3CF_3)$ (**3**·(SO_3CF_3) and **4**·(SO_3CF_3), correspondingly). Protonation of these species results in *cis*-$[Pt(tmeda)\{\underline{N}HC(NR_2)NHC(NH_2)\underline{N}H\}](SO_3CF_3)_2$ ([**3**·H]$(SO_3CF_3)_2$ and [**4**·H]$(SO_3CF_3)_2$, respectively). The interaction of solid **2**·$(SO_3CF_3)_2$ and the gaseous RNH_2 (R=H, Me) leads to *cis*-$[Pt(tmeda)\{\underline{N}HC(NHR)NHC(NH_2)NH\}_2](SO_3CF_3)_2$ (**5**·$(SO_3CF_3)_2$ and **6**·$(SO_3CF_3)_2$, respectively). Treatment of an acetone solution of **2**·$(SO_3CF_3)_2$ with an aqueous NH_3 or the reaction of **5**·$(SO_3CF_3)_2$ with Me_2CO produces the triazine complex *cis*-$\{Pt(tmeda)\{\underline{N}H{=}CNHC(Me)_2\}NHC(NH)_2N\}_2(SO_3CF_3)_2$ (**7**·$(SO_3CF_3)_2$). The reaction of **5**·$(SO_3CF_3)_2$ with Me_2CO also leads to **7**·$(SO_3CF_3)_2$. All new complexes were characterized by elemental analyses (C, H, N), electrospray ionization mass spectrometry, IR, and ^1H and ^{13}C NMR spectroscopies. The structures of **1**·(SO_3CF_3), **2**·$(SO_3CF_3)_2$, **3**·(SO_3CF_3), [**4**·H]$(SO_3CF_3)_2$, **5**·$(SO_3CF_3)_2$, and **7**·$(SO_3CF_3)_2$ were determined by single-crystal X-ray diffraction.

Introduction

Nitrile ligands usually do not behave as strong σ donors or effective π acceptors (as confirmed by their Pickett and Lever parameters[1]), and this imparts on them a lability character. Accordingly, their complexes have been widely applied as convenient starting materials in substitution reactions.[2,3] However, in spite of their rather poor coordinating properties, RCN species can be strongly activated by metalation, which often results in an enhancement of the electrophilicity of the unsaturated nitrile carbon atom, thus promoting the addition of a nucleophile. These addition reactions result in a great variety of compounds with C−O, C−S, C−P, C−C, and C−N bonds. The reactions of metal-activated RCN species have been surveyed in a number of reviews,[4] including those written by two of us.[5]

Within the metal-mediated reaction systems mentioned above, the most commonly employed strategy involves the formation of a C−N bond. Our research in the field of the addition of *N*-donors to metal-activated RCN substrates refers to ammination of nitriles at Rh^{III} [6] and Pt^{II} [7] centers;

† This work is dedicated to Yurii Nikolaevich Bubnov, Full Member of the Russian Academy of Sciences, on the occasion of his 75th birthday.

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 Published on Web 08/18/2009

coupling of RCN ligands with pyrazoles,[8] imines,[9] or heteroimines;[10] and reactions with bifunctional nucleophiles bearing at least one *N*-donor site.[11] We also identified the metal-mediated nitrile−amine coupling as a key intermediate step in the formation of amidines,[12] 1,3,5-triazapentadiene(ato) complexes,[13] and phthalocyanines.[14]

The abundance of accounts on reactions of conventional alkyl- or arylnitriles at different metal centers contrasts strikingly with the insignificant number of reports on reactivity patterns of other nitrile species, in particular, cyanoguanidine $NCN{=}C(NH_2)_2$. This species is an important precursor for the synthesis of polymers, pesticides, and pharmaceuticals.[15] Special attention should be drawn to the fact that this ligand and its derivatives are of biological importance (as a nitrogenase substrate[16] and histamine H_2-receptor antagonists[5]) and this gives a strong motivation for studies on metal-binding and reactivity properties of $NCN{=}C(NH_2)_2$. Thus far, the reported nucleophilic additions to the metal-activated CN triple bond of cyanoguanidine included only Cu^{II}-,[17,18] Ni^{II}-,[17] and Zn^{II}-mediated[19] aminations of $NCNC(NH_2)_2$ and the additions of alcohols to $NCN{=}C(NH_2)_2$ in Cu^{II}-,[20] Zn^{II}-,[21] and Pt^{II}-assisted[22] processes.

In this work, we describe various routes for the amination of Pt^{II}-bound cyanoguanidine that provide, depending on amine and reaction conditions, an easy entry to monodentate or chelated (1,3,5-triazapentadiene)Pt^{II} species. Furthermore, we found that, in acetone, the monodentate 1,3,5-triazapentadiene (or, in another terminology, biguanidine) ligands generate unusual (triazine)Pt^{II} complexes, and all of these results are described in this article.

Results

Synthesis of (Cyanoguanidine)Pt^{II} Complexes. In contrast to complexes bearing the conventional alkyl- and arylnitrile ligands, metal compounds with cyanoguanidine are substantially less explored, although species having metal-bound $NCN{=}C(NH_2)_2$ are known for Ni^{II},[23] Cu^{I},[24] Cu^{II},[25,26] Zn^{II},[27] Ag^{I},[28] Cd^{II},[29] Re^{I},[30] Hg^{II},[31] Tb^{III},[32] and Pt^{II} [22,33] metal centers. All reported synthetic approaches to the cyanoguanidine metal compounds involve substitution reactions performed either in water or in organic solvents, depending on solubilities of the reactants and final complexes. As far as the platinum complexes with cyanoguanidine are concerned, the number of their representatives is very small and restricted only to $[PtL\{\underline{N}CN{=}C(NH_2)_2\}(PPh_3)_2](BF_4)_n$ (L = CF_3, Cl, n = 1; L = $\underline{N}CN{=}C(NH_2)_2$, n = 2) species.[22,33]

For this study, we addressed new Pt^{II} compounds bearing cyanoguanidine, that is, *cis*-[PtI(tmeda)$\{\underline{N}CN{=}C(NH_2)_2\}$]$(SO_3CF_3)$ (**1**·(SO_3CF_3)) and *cis*-[Pt(tmeda)-$\{\underline{N}CN{=}C(NH_2)_2\}_2$]$(SO_3CF_3)_2$ (**2**·$(SO_3CF_3)_2$) insofar as (*i*) they are easily accessible starting from the [PtI_2-(tmeda)][9] (tmeda = *N*,*N*,*N*′,*N*′-tetramethyl-ethane-1,2-diamine) precursor and (*ii*) the lipophilic bidentate tmeda ligand, which is strongly bound to the Pt^{II} center, provides reasonable solubility of **1**·(SO_3CF_3) and **2**·$(SO_3CF_3)_2$ in organic solvents, gives a convenient "internal standard" for ^{1}H NMR integration, and also prevents difficulties associated with *cis*−*trans* isomerization of the starting materials and final products.

Complexes **1**·(SO_3CF_3) and **2**·$(SO_3CF_3)_2$ were prepared from [PtI_2(tmeda)] by abstracting one (Scheme 1, route A) or two iodides (route B) with $AgSO_3CF_3$ (1 or 2 equivs) in nitromethane at 90 °C followed by the addition of 1 or 2 equivs, respectively, of cyanoguanidine. Complex **2**·$(SO_3CF_3)_2$ was also generated by the consecutive addition of $AgSO_3CF_3$ (1 equiv) and cyanoguanidine (1 equiv) to **1**·(SO_3CF_3) in $MeNO_2$ at 90 °C (route C).

Compounds **1**·(SO_3CF_3) and **2**·$(SO_3CF_3)_2$ were isolated in good (ca. 80%) yields as yellow solids and were characterized by elemental analyses (C, H, N), electrospray ionization mass spectrometry (ESI-MS), IR, ^{1}H

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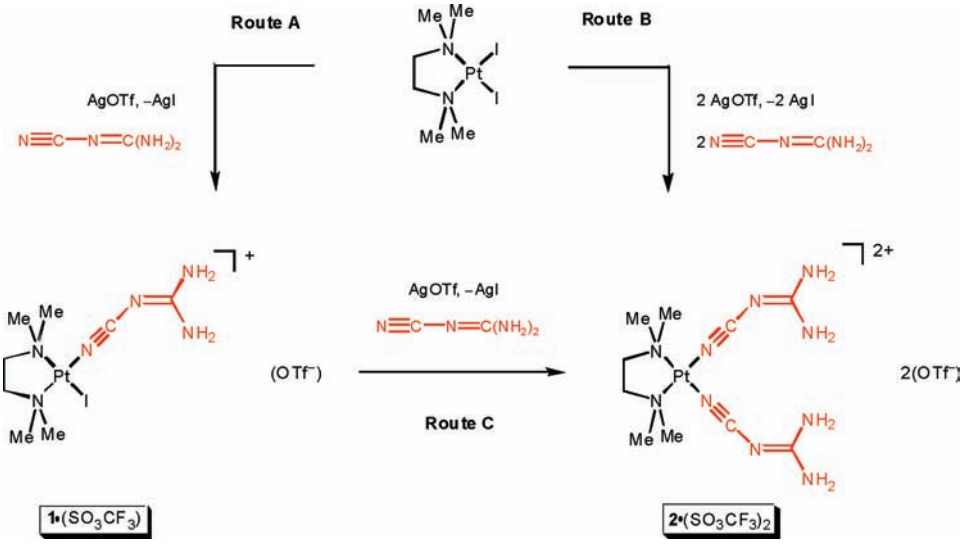
Scheme 1. Synthesis of Cyanoguanidine Complexes $\mathbf{1}\cdot(SO_3CF_3)$ and $\mathbf{2}\cdot(SO_3CF_3)_2$



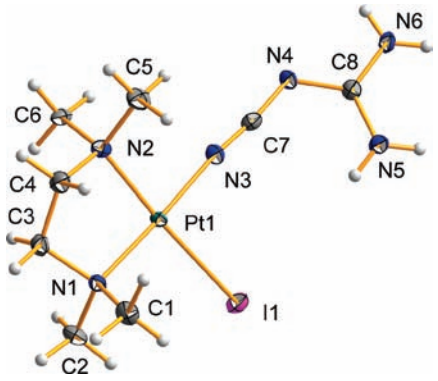


Figure 1. View of $\mathbf{1}^+$ with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

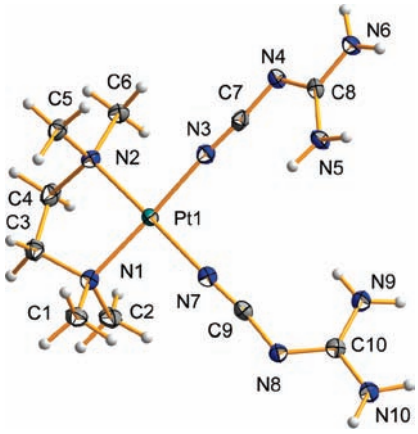


Figure 2. View of $\mathbf{2}^{2+}$ with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

and ^{13}C NMR spectroscopies, and X-ray diffraction (Figures 1 and 2; Tables 1−3). In both complexes, bond lengths of the coordinated CN groups fall within the interval 1.144−1.162 Å, which is close to the common range for the CN triple bonds in free (1.171−1.179 Å)[34,35] and complexed (from 1.102 Å for Cu^I [36] to 1.172 Å for Re^I [29]) cyanoguanidine and also in other (nitrile)Pt^{II} complexes (1.113−1.163 Å).[37] In the cyanoguanidine ligands, all other bond lengths and angles agree well with those reported for the free cyanoguanidine.[34,35] The angles C−N−C at the imine nitrogen and N−C−N at the guanidine carbon in the cyanoguanidine moieties are close to 120°, thus indicating sp^2 character of the C and N atoms. The Pt−N−C−N arrangement in both compounds deviates from the linearity by 12−17°.

In the IR spectra, $\mathbf{1}\cdot(SO_3CF_3)$ and $\mathbf{2}\cdot(SO_3CF_3)_2$ exhibit two strong ν(N≡C) bands (at 2262 and 2205 and at 2279 and 2214 cm^{-1}, respectively) due to symmetric and asymmetric stretches, while the ν(N≡C) peaks for the free cyanoguanidine were detected at 2185 and 2140 cm^{-1}. The increase of the ν(N≡C) frequency of cyanoguanidine upon its coordination gives an indication that the Pt^{II} center makes the nitrile group potentially more susceptible toward nucleophilic attack as compared to the uncomplexed form.[4,5] Broad and intensive bands in the range 2942−2920 cm^{-1} were assigned to ν(N−H) and other strong bands at 1650−1630 cm^{-1} to δ(N−H) and ν(N=C). Furthermore, intensive stretches due to ν(C−H) were observed at 3460−3442 cm^{-1}, whereas ν(SO) and ν(C−F) from $CF_3SO_3^-$ were found at 1257 cm^{-1} and 1030 cm^{-1}, respectively. In the ^1H NMR spectra of $\mathbf{1}\cdot(SO_3CF_3)$ and $\mathbf{2}\cdot(SO_3CF_3)_2$ in DMSO-d_6, the broad NH_2 resonances from the cyanoguanidine were found at ca. 7.24 ppm, and they exhibit expected integration with the tmeda protons. In the ^{13}C NMR spectra, a singlet was observed at 162.6 ppm for $\mathbf{1}\cdot(SO_3CF_3)$ and 163.0 ppm for $\mathbf{2}\cdot(SO_3CF_3)_2$, and it corresponds to the imine carbon of cyanoguanidine. Resonances of the tmeda carbons were found in the range between 64.8 and 52.2 ppm.

Amination of Ligated Cyanoguanidines Accomplishing Chelated 1,3,5-Triazapentadienes. We observed that the

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Table 1. Crystal Data

	$1\cdot(SO_3CF_3)$	$2\cdot(SO_3CF_3)_2$	$3\cdot(SO_3CF_3)$	$[4\cdot H](SO_3CF_3)_2$	$5\cdot(SO_3CF_3)_2$	$7\cdot(SO_3CF_3)_2$
empirical formula	$C_{11}H_{24}Cl_2F_3IN_6O_3PtS$	$C_{12}H_{24}F_6N_{10}O_6PtS_2$	$C_9H_{22}F_3N_7O_3PtS$	$C_{15}H_{33}F_6N_7O_7PtS_2$	$C_{12}H_{30}F_6N_{12}O_7PtS_2$	$C_{24}H_{50}F_6N_{12}O_8PtS_2$
fw	770.31	777.62	560.49	796.69	829.71	1007.97
temp (K)	100(2)	120(2)	100(2)	120(2)	100(2)	120(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$Pbca$	$C2/c$
a (Å)	8.5269(2)	8.9656(2)	11.2813(3)	16.1325(3)	17.9807(2)	27.3322(6)
b (Å)	21.033(2)	15.4406(4)	14.7872(4)	9.0097(1)	9.33440(10)	9.07160(10)
c (Å)	12.9561(10)	18.0497(5)	21.1274(3)	18.5102(4)	33.4060(4)	16.2278(3)
β (deg)	99.957(3)	99.622(2)	95.591(2)	90.230(1)	90	102.273(1)
V (Å^3)	2288.6(3)	2463.54(11)	3507.68(14)	2690.42(8)	5606.83(11)	3931.67(12)
Z	4	4	8	4	8	4
ρ_{calcd} (Mg/m^3)	2.236	2.097	2.123	1.967	1.966	1.703
μ(Mo Kα) (mm^{-1})	7.853	5.962	8.174	5.461	5.250	3.762
no. reflns	42686	47873	76027	48094	69479	41793
unique reflns	5178	5602	8056	6147	6414	4514
R_{int}	0.0499	0.0503	0.0795	0.0368	0.0675	0.0597
R1[a] ($I \geq 2\sigma$)	0.0240	0.0266	0.0317	0.0232	0.0395	0.0250
wR2[b] ($I \geq 2\sigma$)	0.0463	0.0533	0.0530	0.0478	0.0851	0.0453

[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. Selected Bond Lengths (Å) for $1\cdot(SO_3CF_3)$–$7\cdot(SO_3CF_3)_2$

	$1\cdot(SO_3CF_3)$	$2\cdot(SO_3CF_3)_2$	$3\cdot(SO_3CF_3)$ (A)	$3\cdot(SO_3CF_3)$ (B)	$[4\cdot H](SO_3CF_3)_2$	$5\cdot(SO_3CF_3)_2$	$7\cdot(SO_3CF_3)_2$
Pt(1)–N(1)	2.058(3)	2.043(3)	2.089(4)	2.082(4)	2.076(3)	2.074(5)	2.081(2)
Pt(1)–N(2)	2.079(3)	2.042(3)	2.075(4)	2.089(4)	2.074(3)	2.075(5)	2.008(2)
Pt(1)–N(3)	1.971(3)	1.990(3)	1.982(4)	1.984(4)	1.995(3)	2.021(4)	
Pt(1)–N(6)					1.996(3)		
Pt(1)–N(7)		1.993(3)	1.984(4)	1.976(4)			
Pt(1)–N(8)						2.013(5)	
Pt(1)–I(1)	2.5996(3)						
N(1)–C(3)					1.499(4)		
N(2)–C(4)					1.497(4)		1.310(3)
N(3)–C(4)							1.372(3)
N(3)–C(5)							1.334(3)
N(3)–C(7)	1.149(5)	1.157(5)				1.315(7)	
N(4)–C(5)							1.341(3)
N(4)–C(7)	1.300(5)	1.306(5)			1.347(4)	1.345(7)	
N(4)–C(8)	1.346(5)	1.353(4)					
N(5)–C(5)							1.335(3)
N(5)–C(6)							1.467(4)
N(5)–C(7)					1.376(4)	1.365(7)	
N(5)–C(8)	1.332(5)	1.336(5)			1.375(4)	1.312(7)	
N(6)–C(4)							1.356(3)
N(6)–C(6)							1.463(4)
N(6)–C(8)	1.317(5)	1.323(5)			1.298(4)	1.342(7)	
N(7)–C(8)					1.357(4)	1.347(7)	
N(7)–C(9)		1.152(5)					
N(8)–C(9)		1.299(5)				1.305(7)	
N(8)–C(10)		1.341(5)					
N(9)–C(9)						1.349(7)	
N(9)–C(10)		1.331(5)					
N(10)–C(9)						1.374(7)	
N(10)–C(10)		1.325(5)				1.315(8)	
N(11)–C(10)						1.348(8)	
N(12)–C(10)						1.340(8)	

reaction between $1\cdot(SO_3CF_3)$ or $2\cdot(SO_3CF_3)_2$, dissolved in EtOH, with an aqueous solution of NH_3 at 60 °C or with an excess of piperidine (also at 60 °C) proceeds for ca. 30 min and leads to azametallacyclic compounds $3\cdot(SO_3CF_3)$ and $4\cdot(SO_3CF_3)$, respectively (Scheme 2, routes D and E). In contrast, $2\cdot(SO_3CF_3)_2$ reacts with 1 equiv of piperidine, producing $[4\cdot H](SO_3CF_3)_2$ (route F). Compounds $3\cdot(SO_3CF_3)$ and $4\cdot(SO_3CF_3)$ can be converted to their protonated forms $[3\cdot H](SO_3CF_3)_2$ and $[4\cdot H](SO_3CF_3)_2$ by treatment with CF_3SO_3H (route G). One should notice that the amination reactions efficiently proceed in an ethanol medium, and molecules of the alcohol are not involved in the addition to the nitrile group because amines are, in general, better nucleophiles toward RCN than ROH species. The latter is collaterally illustrated by the two-step Pinner synthesis.[38]

Compounds $3\cdot(SO_3CF_3)$, $4\cdot(SO_3CF_3)$, $[3\cdot H](SO_3CF_3)_2$, and $[4\cdot H](SO_3CF_3)_2$ were isolated in 60–65% yields as yellow solids, and they were characterized by elemental analyses (C, H, N), ESI-MS, IR, ^{1}H and ^{13}C NMR

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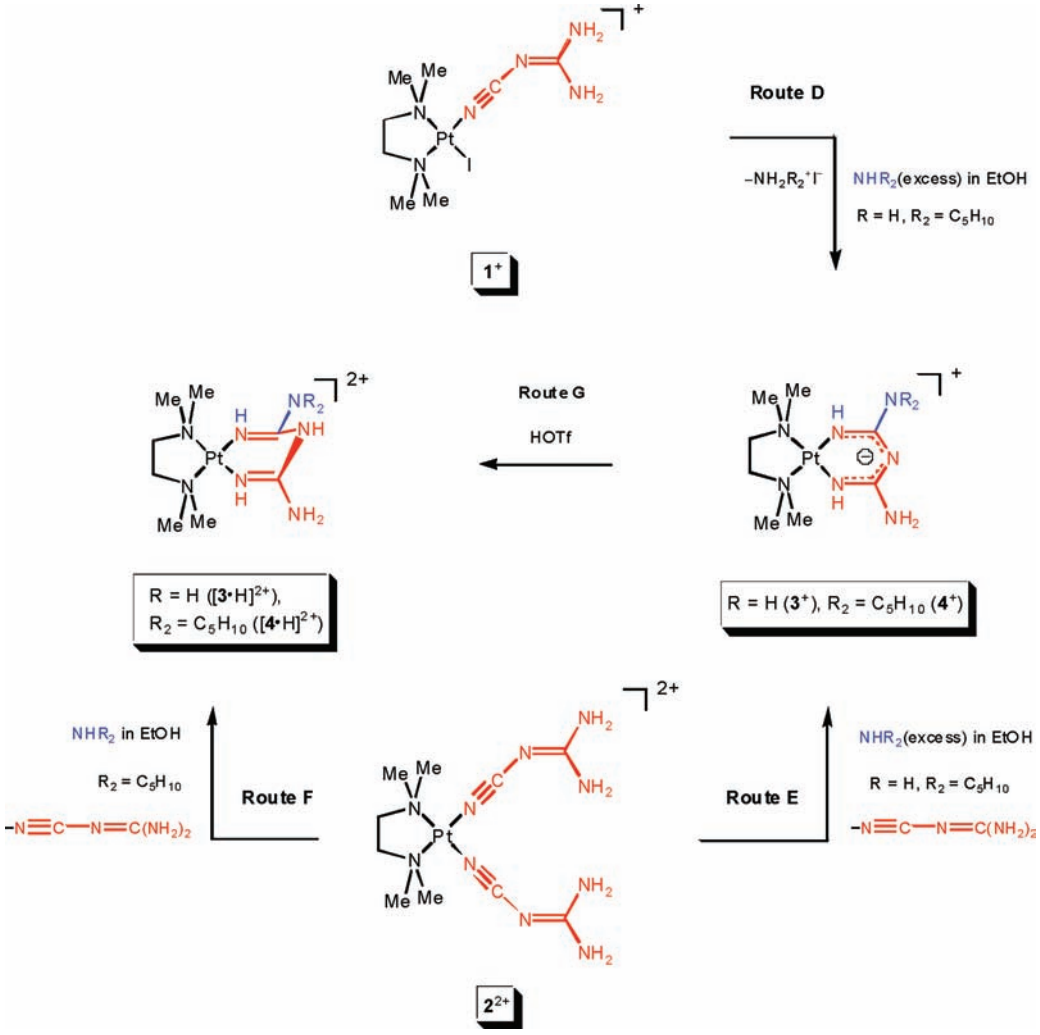
Table 3. Selected Bond Angles (deg) for $1\cdot(SO_3CF_3)$–$7\cdot(SO_3CF_3)_2$

	$1\cdot(SO_3CF_3)$	$2\cdot(SO_3CF_3)_2$	$3\cdot(SO_3CF_3)$ (A)	$3\cdot(SO_3CF_3)$ (B)	$[4\cdot H](SO_3CF_3)_2$	$5\cdot(SO_3CF_3)_2$	$7\cdot(SO_3CF_3)_2$
N(1)–Pt(1)–N(2)	85.92(11)	85.82(12)	84.83(16)	85.22(16)	85.60(10)	85.5(2)	92.65(9)
N(1)–Pt(1)–N(7)							
N(3)–Pt(1)–N(6)					87.57(11)		
N(3)–Pt(1)–N(7)		89.83(12)	88.09(17)	87.82(17)			
N(3)–Pt(1)–N(8)						88.8(2)	
N(3)–Pt(1)–I(1)	86.28(9)						
Pt(1)–N(1)–C(3)							106.3(2)
Pt(1)–N(2)–C(4)							131.1(2)
Pt(1)–N(3)–C(7)	173.2(3)						
C(7)–N(4)–C(8)	119.0(3)	117.5(3)			127.0(3)		
C(7)–N(5)–C(8)							
N(3)–C(7)–N(4)						118.2(5)	
N(3)–C(7)–N(5)					122.7(3)	127.9(5)	
N(4)–C(7)–N(5)						113.6(5)	
N(5)–C(8)–N(6)						126.8(5)	
N(6)–C(8)–N(5)	120.1(3)				122.2(3)		
N(6)–C(8)–N(7)						115.5(5)	
N(10)–C(10)–N(11)						126.1(6)	
N(12)–C(10)–N(11)						116.3(6)	
C(9)–N(8)–C(10)		120.3(3)					

Scheme 2. Amination of Cyanoguanidine at the Pt^{II} Centers



spectroscopies, and X-ray diffraction for $3\cdot(SO_3CF_3)$ and $[4\cdot H](SO_3CF_3)_2$ (Figures 3 and 4; Tables 1–3).

In $3\cdot(SO_3CF_3)$ and $[4\cdot H](SO_3CF_3)_2$, the Pt^{II} centers exhibit square planar geometries, and the metal is bonded to the 1,3,5-triazapentadiene/ato and tmeda ligands. In $3\cdot(SO_3CF_3)$, the azachelate is planar (mean deviation from the plane is 0.009 Å), and the bond lengths N(3)–C(7), N(5)–C(7), N(5)–C(8), N(7)–C(8), and N(6)–C(8)

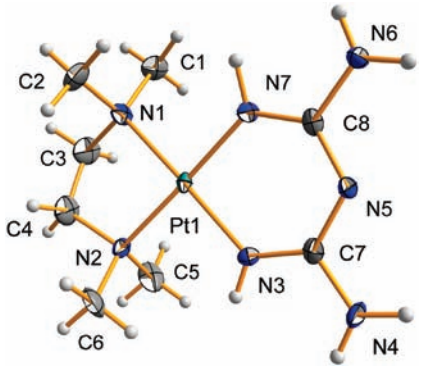


Figure 3. View of $\mathbf{3}^{+}$ with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

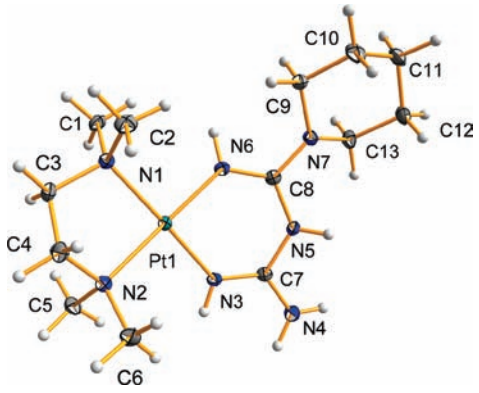


Figure 4. View of $[\mathbf{4}\cdot\mathrm{H}]^{2+}$ with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

are equal to each other within 3σ. These data lead to the conclusion that the triazadiene chelate comprises a delocalized π-electron system, and this statement agrees well with the previous data.[22] In $[\mathbf{4}\cdot\mathrm{H}](SO_3CF_3)_2$, the planarity and bond delocalization within the metallacycle is being lost due to the protonation of the N(5) atom with its mean deviation from the plane of 0.206 Å.

In the IR spectra of $\mathbf{3}\cdot(SO_3CF_3)$, $\mathbf{4}\cdot(SO_3CF_3)$, $[\mathbf{3}\cdot\mathrm{H}](SO_3CF_3)_2$, and $[\mathbf{4}\cdot\mathrm{H}](SO_3CF_3)_2$, bands from ν(N≡C) were not observed. Broad and intensive peaks in the range between 3450 and 3400 cm^{-1} were assigned to ν(N−H) and other strong bands at ca. 1680 cm^{-1} to δ(N−H) and ν(N=C). Furthermore, intensive stretching vibrations due to ν(C−H) were found at 3000−2850 cm^{-1}, while stretches corresponding to ν(SO) were at ca. 1250 cm^{-1} and to ν(C−F) at ca. 1030 cm^{-1}. In the ^{1}H NMR spectra of $[\mathbf{3}\cdot\mathrm{H}](SO_3CF_3)_2$ and $[\mathbf{4}\cdot\mathrm{H}](SO_3CF_3)_2$ in DMSO-d_6, the broad signals of the protons at the central N atoms were detected at 8.92 and 9.52 ppm. All other azametallacyclic NH protons of these four complexes were detected at 6.62−5.37, and they integrate with the tmeda protons in accord with the proposed formulas. In the ^{13}C NMR spectra, a singlet was observed at 152.1 for $\mathbf{3}\cdot(SO_3CF_3)$ and at 151.9 ppm for $[\mathbf{3}\cdot\mathrm{H}](SO_3CF_3)_2$, and in each case it corresponds to two imine carbons of biguanidinate and two signals at ca. 153.8 and 152.2 ppm for $\mathbf{4}\cdot(SO_3CF_3)$ and $[\mathbf{4}\cdot\mathrm{H}](SO_3CF_3)_2$, corresponding to two different imine carbons of biguanidine; resonances of the tmeda carbons were observed in the range 64.8−52.1 ppm.

In the metal-free organic chemistry, the amination of cyanoguanidine to achieve various biguanidine derivatives is the known reaction.[39] It usually proceeds in the presence of 1 equiv of HCl per 1 equiv of $NCNC(NH_2)_2$ and requires elevated temperatures and long reaction times (e.g., the reaction with piperidine derivatives proceeds in BuOH at 116−118 °C for 10 h followed by keeping the reaction mixture for 2 days at 20−25 °C[40]). Moreover, treatment of cyanoguanidine with $(NH_4)Cl$ results in the decyanation of $NCNC(NH_2)_2$ to furnish guanidine.[41] A comparison of the conditions applied for the amination in pure organic syntheses with those used for our Pt^{II} systems gives evidence favoring the metal-mediated nature of the amination of the ligated cyanoguanidine.

Reaction of Ligated Cyanoguanidines with the System NH_3/Acetone. Treatment of solid $\mathbf{2}\cdot(SO_3CF_3)_2$ with gaseous NH_3 or NH_2Me at 25 °C for 1 day results in the generation of $\mathbf{5}\cdot(SO_3CF_3)_2$ and $\mathbf{6}\cdot(SO_3CF_3)_2$, respectively, each containing two molecules of biguanidine (Scheme 3, route H).

These complexes represent the first examples of metal species with *monodentately* bound biguanidine, while only the bidentate *chelated* coordination mode for this ligand was previously recognized.[15] Furthermore, refluxing $\mathbf{5}\cdot(SO_3CF_3)_2$ or $\mathbf{6}\cdot(SO_3CF_3)_2$ in $MeNO_2$ or EtOH for 2 days gives no ring closure, and the starting complex remains intact. We anticipate that stabilization of the monodentate coordination mode of biguanidine can be related to the relative inertness of Pt^{II} centers and a strong $Pt-N_{imine}$ bond, and all of this inhibits the ring closure. As can be inferred from these synthetic experiments, the formation of the chelated triazapentadiene in solution proceeds via the amination of one cyanoguanidine and the following ring closure and liberation of the second cyanoguanidine (Scheme 4).

The ammination of $\mathbf{2}\cdot(SO_3CF_3)_2$ with NH_3 shows a remarkable solvent dependence. As described above, $\mathbf{2}\cdot(SO_3CF_3)_2$ interacts with an aqueous solution of NH_3 in ethanol or nitromethane, giving $\mathbf{3}\cdot(SO_3CF_3)$ (Scheme 2, route E). In contrast, the treatment of an acetone solution of $\mathbf{2}\cdot(SO_3CF_3)_2$ with an aqueous solution of NH_3 at 25 °C for 1 day affords $\mathbf{7}\cdot(SO_3CF_3)_2$, which contains two molecules of the triazine (IUPAC name:[42] 4-imino-6, 6-dimethyl-1,4,5,6-tetrahydro-[1,3,5]triazin-2-ylamine) (Scheme 3, route I). Compound $\mathbf{7}\cdot(SO_3CF_3)_2$ was also synthesized by keeping $\mathbf{5}\cdot(SO_3CF_3)_2$ in acetone at 60 °C for 1 day (Scheme 3, route J). Structurally relevant uncomplexed triazines are known, and they can be obtained by the reflux of guanidine or biguanidine in acetone solutions.[43]

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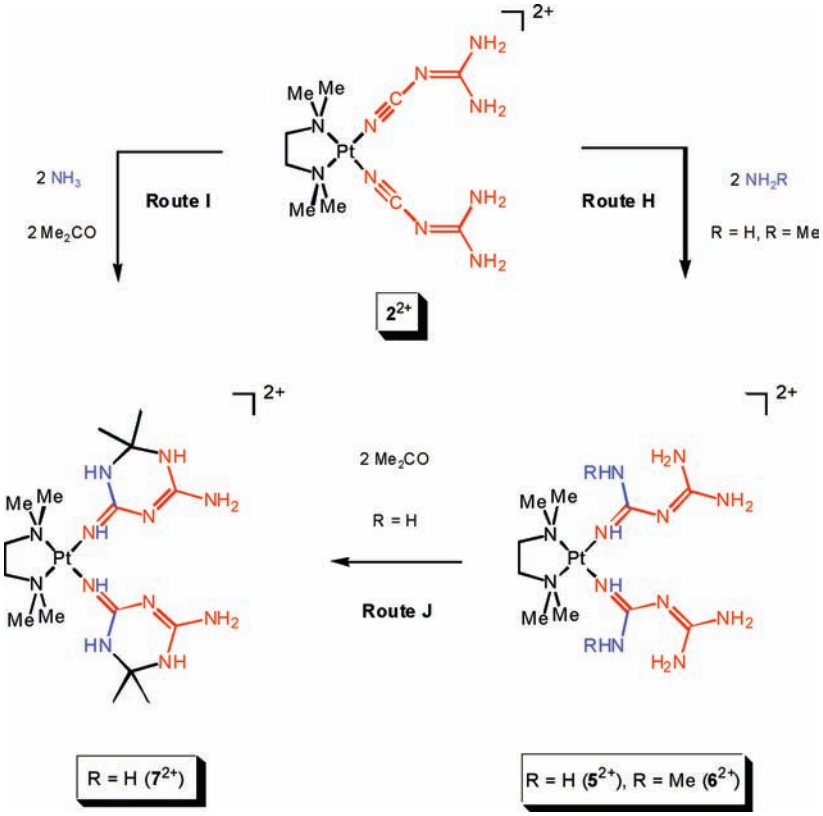
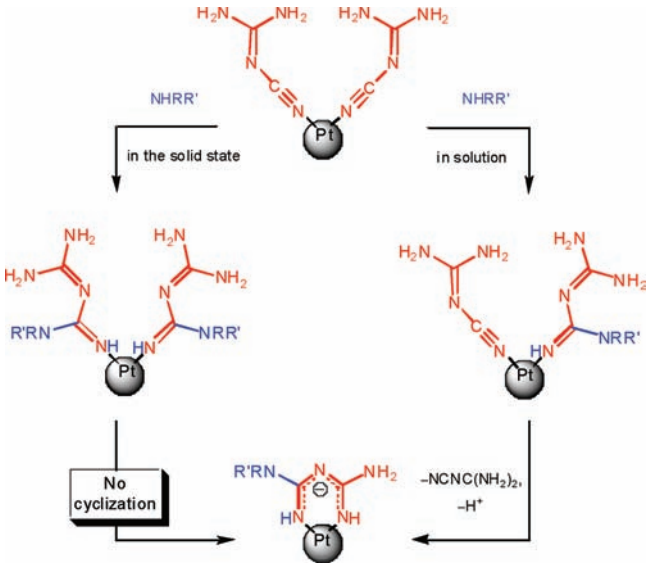
Scheme 3. Amination of the Cyanoguanidine Ligands in $2\cdot(SO_3CF_3)_2$ in the Solid State and in Acetone[a]



[a] Complex 7^{2+} is represented in the *E*,*E*-configuration that was observed in the solid state by X-ray diffraction.

Scheme 4. Amination of Cyanoguanidine in Solution and in the Solid State



The structures of $5\cdot(SO_3CF_3)_2$ and $7\cdot(SO_3CF_3)_2$ have been determined by X-ray diffraction (Figures 5 and 6; Tables 1−3). In both complexes, the tmeda N atoms and two newly formed ligands complete the slightly distorted square planar environment around metal center. In $5\cdot(SO_3CF_3)_2$, the bond lengths N(3)−C(7) and N(5)−C(8) are shorter than the other N−C distances in the biguanidine ligand, thus indicating their double character; the coordinating moieties of the biguanidine ligands are in the

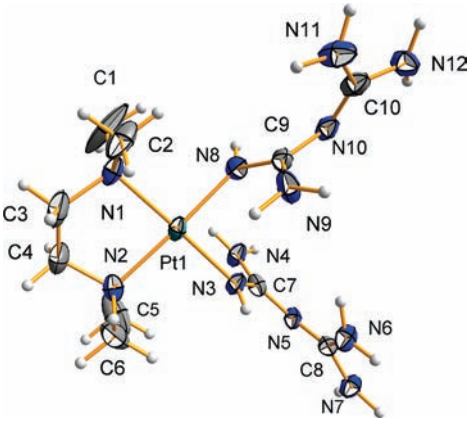


Figure 5. View of 5^{2+} with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

E configuration. In $7\cdot(SO_3CF_3)_2$, the N(2)−C(4) bond is marginally shorter than the other carbon−nitrogen bonds in the triazine molecule, suggesting the existence of the double bond between these atoms. The essentially identical bond lengths N(3)−C(5), N(5)−C(5), and N(4)−C(5) indicate extensive delocalization in this fragment of the heterocyclic ring. The N(2), C(4), N(6), N(3), C(5), N(4), and N(5) atoms are coplanar within ±0.05 Å, while the N(6)−C(6) and N(5)−C(6) bond lengths and angle N(5)−C(6)−N(6) display pure sp^3 character of the C(6) atom.

In the IR spectra of $5\cdot(SO_3CF_3)_2$, $6\cdot(SO_3CF_3)_2$, and $7\cdot(SO_3CF_3)_2$, the biguanidine and the triazine ligands

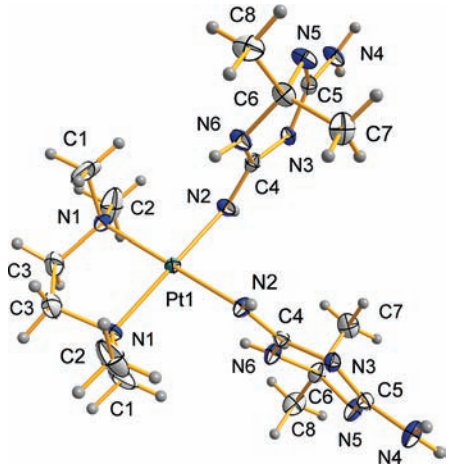


Figure 6. View of $\mathbf{7}^{2+}$ with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

exhibit strong broad bands at 3416−3228 cm^{-1}, which can be attributed to ν(N−H) vibrations, and display no bands in the region specific for the ν(N≡C) stretches. The spectra display ν(N=C) and δ(N−H) absorption bands in the range between 1691 and 1529 cm^{-1}, and these are close to those found in $\mathbf{3}\cdot(SO_3CF_3)$ and $\mathbf{4}\cdot(SO_3CF_3)$ for the bidentately coordinated biguanidine. Furthermore, strong signals assigned to ν(C−H) were observed at 2950−2900 cm^{-1}, to ν(SO) at 1263−1250 cm^{-1}, and to ν(C−F) at 1032−1030 cm^{-1}. In the ^{1}H NMR spectrum of $\mathbf{5}\cdot(SO_3CF_3)_2$ and $\mathbf{6}\cdot(SO_3CF_3)_2$, the NH resonances are displayed as broad singlets at 6.57−4.84 ppm, and they integrate with the tmeda protons in accord with the proposed formulas. In the ^{13}C NMR spectra, the carbons from the N=C−N moieties were found at 165.4−156.4 ppm for $\mathbf{5}\cdot(SO_3CF_3)_2$ and $\mathbf{6}\cdot(SO_3CF_3)_2$. Resonances of the tmeda carbons are observed in the range 65.5−51.3 ppm for three complexes. In the ^{1}H NMR spectra of $\mathbf{7}\cdot(SO_3CF_3)_2$, a few sets of signals of the NH protons were detected at 8.06−4.57 ppm.

We anticipate that the multiplication of peaks is related to the existence of the isomeric forms of $\mathbf{7}\cdot(SO_3CF_3)_2$ in solution. Indeed, the nuclear Overhauser effect spectrometry NMR spectrum of $\mathbf{7}\cdot(SO_3CF_3)_2$ in Me_2CO-d_6 favors the presence of the *E*,*Z* and *Z*,*Z* forms (Scheme 5), but no peaks due to the *E*,*E*-conformation were detected. Furthermore, a variable-temperature NMR experiment performed in the range between 20 and 50 °C indicated only some NH proton shifts (0.10−0.15 ppm), but the *E*,*E* isomer was not observed.

In contrast to the solution, the X-ray diffraction study for $\mathbf{7}\cdot(SO_3CF_3)_2$ (see above) verified the *E*,*E* form in the solid state. The DFT calculations of the isomeric forms of $\mathbf{7}^{2+}$ indicate that, in the gas phase and in both acetone and DMSO solutions, the most stable form is the *Z*,*Z* conformation followed by the *E*,*Z* and *E*,*E* conformations. However, the energy difference between all of these forms is within 1.6 kcal/mol (Table 1S, Supporting Information), consistent with experimental results about the existence of the mixture of the isomeric forms in solutions. The isolation of the *E*,*E* form in the solid phase despite its lower stability is conceivably accounted for by intermolecular interactions and packing effects (for computation details and references, see the Supporting Information).

Discussion

The results from this study could be summarized into three perspectives. First, the amination of the cyanoguanidine ligands described above represents a rare reactivity mode of these nitrile substrates. Indeed, despite a wealth of reports on additions to complexed *alkyl*- and *arylnitriles*,[5] these reactions with metal-bound *cyanoguanidine* received substantially less attention. Indeed, the known examples are restricted only to the Cu^{II}-,[17,18] Ni^{II}-,[17] and Zn^{II}-mediated[19] amination of $NCNC(NH_2)_2$ to yield *N*,*N*-biguanidine chelates and the additions of alcohols to cyanoguanidine in Cu^{II}-,[20] Zn^{II}-,[21] and Pt^{II}-mediated[22] processes.

Second, the amination constitutes a facile route to the trisnitrogen analogues of the 1,3-dicarbonyls, that is, 1,3,5-triazapentadienyl Pt complexes. These systems have become the center of attention in the recent years[44] (for our works, see refs 9 and 13), but relevant reports on exploration of these species are still uncommon, mainly because the synthetic methods thus far are poorly developed. In this context, it is worth mentioning that 1,3,5-triazapentadienyl complexes having chelated biguanidine are known for a number of transition metals (e.g., group 5, V^{IV};[45] 6, Cr^{III};[15] 7, Mn^{III}, Mn^{IV} Re^{V};[46] 8, Os^{VI};[15] 9, Co^{II}, Co^{III};[47] 10, Ni^{II}, Pd^{II};[47,48] 11, Cu^{II}, Ag^{III};[49] 12, Zn^{II} [50]), but not for platinum. All indicated complexes were prepared by the direct addition of the preprepared biguanidine to water solutions of metal precursors. However, the addition of biguanidine to an aqueous solution of $K_2[PtCl_4]$ leads to the reduction of the starting platinum(II) complex to furnish the platinum black. We have now found a useful method for the preparation of Pt^{II} biguanidine complexes derivatives via platinum-mediated amination followed by ring closure of the formed intermediate.

Third, the observed addition of NH_3 (ammination) proceeds differently depending on applied conditions. In solution, the reaction gives biguanidine, which undergoes ring closure with concomitant displacement of the neighboring unreacted cyanoguanidine. However, in the solid state, two $NCNC(NH_2)_2$ ligands are subjected to ammination, and the formed biguanidines remain monodentately coordinated to the metal center. Moreover, the ammination also depends on

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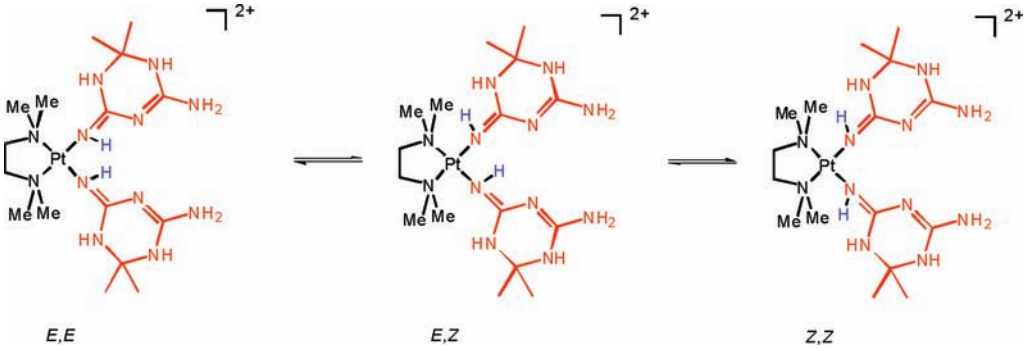
Scheme 5. Three Possible Isomeric Forms for 7^{2+}



the employed solvent. The reaction yields the complexed biguanidine in chloroform or nitromethane but furnishes the metal-bound triazines when the process is performed in acetone. The triazines represent a class of compounds with a great variety of biological properties (e.g., they are extensively used as herbicides[51]), but the coordination chemistry of these species is almost unexplored. We anticipate that the ammination/condensation observed in this work should shed light on metal-catalyzed conversions (e.g., reactions catalyzed by Al^{III},[52] Fe^{III},[53] Cu^{II},[54] Cu^{I},[53] Zn^{II},[55] Sn^{II},[56] and Er^{III}[57]) of $NCNC(NH_2)_2$ employed in organic chemistry for syntheses of various pharmacologically important triazines.

Experimental Section

Materials and Instrumentation. Cyanoguanidine (Merck), *N*,*N*,*N*′,*N*′-tetramethyl-ethane-1,2-diamine (Aldrich), silver trifluoromethanesulfonate (Fluka), and solvents were obtained from commercial sources and used as received. The complex [PtI_2(tmeda)] was prepared in accord with the published method.[9]

Elemental analyses were obtained on a 185B Carbon Hydrogen Nitrogen Analyzer Hewlett-Packard instrument. Electrospray ionization mass spectrometry time of flight mass spectra were measured on a MX-5310 mass spectrometer. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a Shimadzu FTIR 8400S instrument in KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker-DPX 300 spectrometer at ambient temperature. In **1**·(SO_3CF_3), **2**·H(SO_3CF_3)$_2$, **3**·(SO_3CF_3), **4**·(SO_3CF_3), [**3**·H](SO_3CF_3)$_2$, [**4**·H](SO_3CF_3)$_2$, **5**·(SO_3CF_3)$_2$, **6**·(SO_3CF_3)$_2$, and **7**·(SO_3CF_3)$_2$, the carbons of the CN and CF_3 groups were not detected even at high acquisition time.

X-Ray Crystal Structure Determinations. The crystals were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100−120 K. The X-ray diffraction data were collected by means of a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The *Denzo-Scalepack*[58] or *EvalCCD*[59] program package was used for cell refinements and data reductions. The structures were solved by direct methods using *SIR97*[60] or *SIR2004*[61] with the *WinGX*[62] graphical user interface. A semiempirical absorption correction (*SADABS*,[63] *SORTAV*,[64] or *XPREP* in *SHELXTL*[65]) was applied to all data. Structural refinements were carried out using *SHELXL-97*.[66]

The asymmetric unit of **3**·(SO_3CF_3) contained two independent Pt molecules. One of the carbon atoms (C4B/C4C) and hydrogens on C3B and C6B in **3**·(SO_3CF_3) were disordered over two sites with occupancies of 0.69/0.31. The disordered carbons (C4B/C4C) were refined with equal anisotropic displacement parameters. The carbon, fluorine, and oxygen atoms on one of the CF_3SO_3 ions in **5**·(SO_3CF_3)$_2$ were disordered over two sites with occupancies of 0.57/0.43. The C−F and S−O distances were restrained to be approximately equal. Also, the disordered oxygen atoms were refined with equal anisotropic displacement parameters. The carbon atoms C3 and C4 in **5**·(SO_3CF_3) were restrained to have similar U_{ij} components within a standard deviation of 0.01.

The NH, NH_2, and H_2O hydrogen atoms were located using the difference Fourier map but were constrained to ride on their parent atom, with U_{iso} = 1.5. Other hydrogens were positioned geometrically and constrained to ride on their parent atoms, with C−H = 0.95−0.99 Å and U_{iso} = 1.2−1.5 U_{eq} (parent atom). The crystallographic details are summarized in Table 1, and selected bond lengths and angles are in Tables 2 and 3.

Synthetic Work. 1·(SO_3CF_3). $AgSO_3CF_3$ (66 mg, 0.26 mmol) was added to a suspension of [PtI_2(tmeda)] (145 mg, 0.26 mmol) in nitromethane (3 mL), and the reaction mixture was heated at 90 °C for 30 min on stirring, whereupon the solid NCN=$C(NH_2)_2$ (22 mg, 0.26 mmol) was added. The reaction mixture was stirred at 90 °C for 1 h. The yellow solution of the formed *cis*-[PtI(tmeda){NCN=$C(NH_2)_2$}](SO_3CF_3) was separated by centrifugation from the solid AgI, and the solvent was evaporated in the air at 40 °C for ca. 3 days. The yellow oily residue released was stirred with Et_2O (2 mL) at 20−25 °C until the yellow solid was formed. The latter was filtered off and washed with Et_2O (three 0.5 mL portions) and dried in the air at 20−25 °C. Yield: 135 mg, 78%.

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Anal. Calcd for $C_9H_{20}N_6F_3IPtSO_3$: C, 16.10; H, 3.00; N, 12.51. Found: C, 16.08; H, 2.96; N, 12.60%. ESI$^+$-MS, *m*/*z*: 522 $[M - CF_3SO_3]^+$, 395 $[M - I - CF_3SO_3]^+$. IR (KBr, selected bonds, cm^{-1}): ν(N−H) 3423 (s, br), ν(C−H) 2920 (m, br), ν(N≡C) 2262 (s), 2205 (s), ν(N=C) 1636 (s, br), ν(SO) 1258 (s, br), ν(C−F) 1029 (s). ^{1}H NMR (DMSO-d_6, δ): 7.28 (s, br, 4*H*, NCN=C$(NH_2)_2$), 3.03 (s, 4*H*, N−CH_2), 2.96 (s, 12*H*, N−CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 162.6 ($(NH_2)_2C$=N), 63.5 (CH_2−N), 52.3 (CH_3−N). Slow evaporation of a saturated solution of **1**·(SO_3CF_3) in dichloroethane at 55 °C gave bright yellow needles suitable for X-ray study.

2·$(SO_3CF_3)_2$**.** $AgSO_3CF_3$ (91 mg, 0.35 mmol) was added to a suspension of $[PtI_2(tmeda)]$ (100 mg, 0.18 mmol) in nitromethane (5 mL) at 20−25 °C, and the reaction mixture was heated at 90 °C for 1 h upon stirring, whereupon the solid NCN=C$(NH_2)_2$ (30 mg, 0.35 mmol) was added. The reaction mixture was stirred at 90 °C for 3 h. The yellow solution of the formed *cis*-[Pt(tmeda){NCN=C$(NH_2)_2$}$_2$]$(SO_3CF_3)_2$ was separated by centrifugation from the solid AgI, and the solvent was evaporated in the air at 90 °C. The yellow oily residue formed was stirred with Et_2O (2 mL) at 20−25 °C until the colorless solid was formed. The latter was filtered off and washed with EtOH (0.5 mL) and Et_2O (0.5 mL) and dried in the air at 20−25 °C. The addition of cyanoguanidine (1 equiv) and $AgSO_3CF_3$ (1 equiv) to **1**·(SO_3CF_3) at 90 °C also gives **2**·$(SO_3CF_3)_2$. Yield: 114 mg, 82%.

Anal. Calcd for $C_{12}H_{24}N_{10}F_6PtS_2O_6$: C, 18.54; H, 3.11; N, 18.01. Found: C, 18.93; H, 3.35; N, 18.11%. ESI$^+$-MS, *m*/*z*: 628 $[M - CF_3SO_3]^+$, 544 $[M - NC{-}NC(NH_2)_2 - CF_3SO_3]^+$. IR (KBr, selected bonds, cm^{-1}): ν(N−H) 3352 (s, br), 3229 (s, br), ν(C−H) 2942 (m, br), ν(N≡C) 2279 (s), 2214 (s), ν(N=C) 1650 (s, br), 1570 (s, br), ν(SO) 1257 (s, br), ν(C−F) 1030 (s). ^{1}H NMR (DMSO-d_6, δ): 7.20 (s, br, 8*H*, NCN=C$(NH_2)_2$), 3.17 (s, 4*H*, N−CH_2), 3.11 (s, 12*H*, N−CH_3). $^{13}C\{^1H\}$ NMR (MeOH-d_4, δ): 163.0 ($(NH_2)_2C$=N), 64.8 (CH_2−N), 52.5 (CH_3−N). Evaporation of an acetone−toluene solution (3:1, v/v) at 50 °C gave colorless needles suitable for X-ray study.

3·(SO_3CF_3)**.** NH_3 (25% water solution, 100 mkL) was added to a solution of **1**·(SO_3CF_3) or **2**·$(SO_3CF_3)_2$ (0.08 mmol) in ethanol (1.5 mL) at 60 °C, and the system was left to stand for 1 day, whereupon it was evaporated in the air at 90 °C (for **1**·(SO_3CF_3)) or filtered off from cyanoguanidine and then evaporated in the air at 90 °C (for **2**·$(SO_3CF_3)_2$). The yellow oily residue formed was stirred with Et_2O (three 0.5 mL portions) at 20−25 °C until the yellow solid formed. The latter was filtered off, washed with Et_2O (0.5 mL), and dried in the air at 20−25 °C. Yields were ca. 60% in both cases.

Anal. Calcd for $C_9H_{22}N_7F_3PtSO_3 \cdot 2H_2O$: C, 18.11; H, 4.39; N, 16.44. Found: C, 17.56; H, 3.95; N, 15.87%. ESI$^+$-MS, *m*/*z*: 560 $[M]^+$, 411 $[M - CF_3SO_3]^+$. IR (KBr, selected bonds, cm^{-1}): ν(N−H) 3408 (s, br), ν(C−H) 2982 (s, br), 2916 (m, br), ν(N=C) 1680 (s, br), ν(SO) 1252 (s), ν(C−F) 1033 (s). ^{1}H NMR (DMSO-d_6, δ): 6.69 (s, br, 2*H*), 6.63 (s, br, 2*H*), 6.57 (s, br, 2*H*)(NH=C and NH_2), 2.96 (s, 4*H*, N−CH_2), 2.79 (s, 12*H*, N−CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 152.1 (two C from biguanidinate), 64.3 (CH_2−N), 52.5 (CH_3−N). Slow evaporation of an ethanol solution at 60 °C gave colorless prisms suitable for X-ray study.

4·(SO_3CF_3)**.** Piperidine (100 mL, 1.06 mmol) was added to a yellow solution of *cis*-[PtI(tmeda){NCN=C$(NH_2)_2$}](SO_3CF_3) (56 mg, 0.09 mmol) in ethanol (2 mL) at 60 °C, and the system was left to stand for 1 day, whereupon it was evaporated in the air at 80 °C. The yellow oily residue formed was stirred with Et_2O (3 mL) at 20−25 °C until the yellow solid formed. The latter was filtered off, washed with Et_2O (0.5 mL), and dried in the air at 20−25 °C. Yield: 26 mg, 51%.

Anal. Calcd for $C_{14}H_{30}N_7F_3PtSO_3 \cdot 2H_2O$: C, 25.29; H, 5.15; N, 14.75. Found: C, 24.89 H, 4.96; N, 14.57%. ESI$^+$-MS, *m*/*z*: 628 $[M]^+$. IR (KBr, selected bonds, cm^{-1}): ν(N−H) 3423 (s, br), ν(C−H) 2936 (m, br), 2854 (m, br), ν(N=C) 1675 (s, br), ν(SO) 1248 (s), ν(C−F) 1030 (s). ^{1}H NMR (DMSO-d_6, δ): 5.88 (s, br, 1*H*) 5.77 (s, br, 2*H*), 5.04 (s, br, 1*H*)(NH=C and NH_2), 3.01−2.96 (m, 4*H*, 2 α-CH_2 from piperidyl), 2.85 (s, 4*H*, N−CH_2), 2.82 (s, 12*H*, N−CH_3), 1.64−1.48 (m, 6*H*, 3 β- and γ-CH_2 from piperidyl). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 156.7, 154.9 (two C from biguanidinate), 64.4, (CH_2−N), 52.5 (CH_3−N), 47.6, 44.6 (two CH_2 from piperidyl), 26.2, 23.1, 22.4 (three CH_2 from piperidyl).

[3·H]$(SO_3CF_3)_2$. Compound **3**·(SO_3CF_3) (34 mg, 0.06 mmol) was dissolved in Me_2CO (1.5 mL) and treated with HSO_3CF_3 (10.5 mg, 0.07 mmol) at 25 °C, and the system was left to stand for 1 h, whereupon the solvent was evaporated in the air at 70 °C. The yellow oily residue formed was stirred with Et_2O (2 mL) at 20−25 °C until the colorless solid was formed. The latter was filtered off and washed with Et_2O (0.5 mL) and dried in the air at 20−25 °C. Yield: 36 mg, 85%.

Anal. Calcd for $C_{10}H_{23}N_7F_6PtS_2O_6 \cdot H_2O$: C, 16.48; H, 3.45; N, 13.45. Found: C, 16.71; H, 3.95; N, 13.08%. ESI$^+$-MS, *m*/*z*: 562 $[M - CF_3SO_3]^+$. IR (KBr, selected bonds, cm^{-1}): ν(N−H) 3412 (s, br), ν(C−H) 2972 (s, br), 2916 (m, br), ν(N=C) 1672 (s, br), ν(SO) 1249 (s), ν(C−F) 1031 (s). ^{1}H NMR (DMSO-d_6, δ): 8.31 (s, br, 1*H*, −NH−), 6.54 (s, br, 2*H*), 6.29 (s, br, 2*H*), 6.21 (s, br, 2*H*)(2NH=C, $2NH_2$), 2.94 (s, 4*H*, N−CH_2), 2.77 (s, 12*H*, N−CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 151.9 (two C from biguanidine), 64.8 (CH_2−N), 52.7 (CH_3−N).

[4·H]$(SO_3CF_3)_2$. Piperidine (16 mkL, 0.17 mmol) was added to a yellow solution of *cis*-[Pt(tmeda){NCN=C$(NH_2)_2$}$_2$]-$(SO_3CF_3)_2$ (112 mg, 0.14 mmol) in ethanol (3 mL) at 60 °C, and the system was left to stand for 1 day, whereupon it was filtered off from the unreacted cyanoguanidine and the filtrate evaporated in the air at 80 °C. The yellow oily residue formed was stirred with Et_2O (2 mL) at 20−25 °C until the yellow solid formed. The latter was filtered off, washed with Et_2O (0.5 mL), and dried in the air at 20−25 °C. Yield: 72 mg, 69%.

Anal. Calcd for $C_{15}H_{31}N_7F_6PtS_2O_6 \cdot 1\frac{1}{2}H_2O$: C, 22.35; H, 4.25; N, 12.17. Found: C, 22.59; H, 4.46; N, 11.96%. ESI$^+$-MS, *m*/*z*: 629 $[M - CF_3SO_3]^+$. IR (KBr, selected bonds, cm^{-1}): ν(N−H) 3421 (s, br), ν(C−H) 2939 (m, br), 2856 (m, br), ν(N=C) 1676 (s, br), ν(SO) 1248 (s), ν(C−F) 1029 (s). ^{1}H NMR (DMSO-d_6, δ): 8.35 (s, br, 1*H*, −NH−), 5.81 (s, br), 5.69 (s, br), 4.98 (s, br)(4*H*, 2NH=C, NH_2), 2.91−2.87 (m, 4*H*, $2CH_2$ from piperidyl), 2.84 (s, 4*H*, N−CH_2), 2.76 (s, 12*H*, N−CH_3), 1.67−1.51 (m, 6*H*, $3CH_2$ from piperidyl). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 158.0, 155.6 (two C from biguanidine), 64.8 (CH_2−N), 53.0 (CH_3−N), 47.8, 44.7 (two CH_2 from piperidyl), 26.3, 23.7, 22.6 (three CH_2 from piperidyl). Slow evaporation of an ethanol solution at 60 °C gave colorless prisms suitable for X-ray study.

5·$(SO_3CF_3)_2$**.** The powder of *cis*-[Pt(tmeda){NCN=C-$(NH_2)_2$}$_2$]$(SO_3CF_3)_2$ (257 mg, 0.33 mmol) was kept in a desiccator under aqueous NH_3 (25%) for 1 day at room temperature. The yellow oily residue formed was stirred with Et_2O (2 mL) at 20−25 °C until the yellow solid formed. The latter was filtered off and washed with Et_2O (0.5 mL) and dried in the air at 20−25 °C. Yield: 251 mg, 94%.

Anal. Calcd for $C_{12}H_{30}N_{12}F_6PtS_2O_6 \cdot 2\frac{1}{2}H_2O$: C, 16.82; H, 4.11; N, 19.62. Found: C, 17.13; H, 3.50; N, 19.63%. ESI$^+$-MS, *m*/*z*: 812 $[M + H]^+$, 811 $[M]^+$, 662 $[M - CF_3SO_3]^+$, 561 $[M - NHC(NH_2)NHC(NH_2)NH - CF_3SO_3]^+$. IR (KBr, selected bonds, cm^{-1}): ν(N−H) 3413 (s, br), 3228 (s, br), ν(C−H) 2942 (m, br), ν(N=C) 1616 (s, br), 1563 (s, br), ν(SO) 1254 (s, br), ν(C−F) 1031 (s). ^{1}H NMR (DMSO-d_6, δ): 6.57 (s, br, 1*H*), 6.50 (s, br, 1*H*), 5.99 and 5.80 (s, br, 8*H*), 5.05 (s, br, 4*H*) NH=C and NH_2), 2.80 (s, 4*H*, N−CH_2), 2.71 (s, 12*H*, N−CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 165.2, 156.4 (C from biguanidines), 64.1 (CH_2−N), 51.5 (CH_3−N). The addition of Et_2O (1 mL) at room temperature to an ethanol solution (1 mL) of **5**·$(SO_3CF_3)_2$ gave pale yellow prisms suitable for X-ray study.

6·(SO_3CF_3)$_2$. The powder of *cis*-[Pt(tmeda){NCN=C(NH_2)$_2$}$_2$]-[SO_3CF_3]$_2$ (60 mg, 0.08 mmol) was kept in a desiccator under aqueous $MeNH_2$ for 1 day at room temperature. The yellow solid formed was washed with Et_2O (2 mL) at 20−25 °C and dried in the air at 20−25 °C. Yield: 58 mg, 86%.

Anal. Calcd for $C_{14}H_{34}N_{12}F_6PtS_2O_6$: C, 20.02; H, 4.08; N, 20.01. Found: C, 19.94; H, 3.84; N, 19.99%. ESI$^+$-MS, *m*/*z*: 840 $[M + H]^+$, 690 $[M - CF_3SO_3]^+$. IR (KBr, selected bonds, cm^{-1}): ν(N−H) 3413 (s, br), 3236 (s, br), ν(C−H) 29837 (m, br), ν(N=C) 1616 (s, br), 1596 (s, br), ν(SO) 1263 (s, br), ν(C−F) 1032 (s). ^{1}H NMR (DMSO-d_6, δ): 6.57 (s, br, 2*H*), 5.88 (s, br, 8*H*), 4.84 (s, br, 2*H*) (NH=C, NH_2 and N*H*Me), 2.78 (s, 4*H*, N−CH_2), 2.70 (s, 12*H*, N−CH_3), 2.64 (s, 6*H*, N−CH_3 from biguanidines). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 165.4, 156.6, (C from biguanidines), 64.2 (N−CH_2), 51.6 (N−CH_3 from tmeda), 29.3 (N−CH_3 from biguanidines).

7·(SO_3CF_3)$_2$. A yellow solution of *cis*-[Pt(tmeda){NCN=C-(NH_2)$_2$}$_2$](SO_3CF_3)$_2$ (103 mg, 0.13 mmol) in acetone (5 mL) was kept in a desiccator under aqueous NH_3 (25%) for 1 day at room temperature without stirring, and then the reaction mixture was evaporated in the air at 20−25 °C. The yellow oily residue formed was stirred with Et_2O (2 mL) at 20−25 °C until the yellow solid formed. The latter was filtered off and washed with Et_2O (0.5 mL) and dried in the air at 20−25 °C. Yield: 90 mg, 78%.

Anal. Calcd for $C_{18}H_{38}N_{12}F_6PtS_2O_6 \cdot 2\frac{1}{2}H_2O$: C, 23.07; H, 4.62; N, 17.94. Found: C, 22.70; H, 4.05; N, 17.84%. ESI$^+$-MS, *m*/*z*: 892 $[M + H]^+$, 742 $[M - CF_3SO_3]^+$. IR (KBr, selected bonds, cm^{-1}): ν(N−H) 3416 (s, br), ν(C−H) 2942 (m, br), 2835 (m), ν(N=C) 1691 (s, br), 1529 (s, br), ν(SO) 1250 (s, br), ν(C−F) 1030 (s). ^{1}H NMR (acetone-d_6, δ) (two isomers, *ZZ* and *EZ*): 7.99 (s, br), 7.68 (s, br), 7.53 (s, br), 7.24 (s, br), 7.54 (s, br), 6.24 (s, br), 6.21 (s, br), 5.74 (s, br), 5.13 (s, br), 4.96 (s, br), 4.39 (s, br)(10*H*, NH's), 2.83 (s), 2.79 (s, 4*H*, N−CH_2), 2.69 and 2.67 (two s, 12*H*, N−CH_3), 1.40 (s, 6*H*, Me's), 1.31 (s, 6*H*, Me's). ^{13}C{^{1}H} NMR (acetone-d_6, δ) (two isomers, *ZZ* and *EZ*): 160.7, 160.4, 157.7, 156.5. 156.3 (C from the triazine rings), 64.8 (N−CH_2), 51.8 (N−CH_3), 29.7, 29.5 (Me's from the triazine rings). Evaporation of an acetone−toluene solution (2:1, v/v) at 50 °C gave colorless prisms suitable for X-ray study.

Acknowledgment. This work was supported by the Russian Fund for Basic Research (grants 08-03-12027-ofi, 08-03-00631, and 09-03-00065) and RAS Presidium Program coordinated by acad. Nikolay T. Kuznetsov (grant 8P). Drs. Maxim L. Kuznetsov and Stanislav I. Selivanov are thanked for their kind assistance and valuable discussions.

Supporting Information Available: Computational details of the DFT calculations of various isomeric forms of 7^{2+}, total energies, enthalpies, Gibbs free energies (Hartree), and relative Gibbs free energies of various isomeric forms of 7^{2+} in the gas phase, in acetone, and in DMSO solutions (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.