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Bifunctional Reactivity of Amidoximes Observed upon Nucleophilic Addition to Metal-Activated Nitriles

Dmitrii S. Bolotin,[†] Marina Ya. Demakova,[†] Alexander S. Novikov,[†] Margarita S. Avdontceva,[‡] Maxim L. Kuznetsov,[§] Nadezhda A. Bokach,[†] and Vadim Yu. Kukushkin*[,†,∥]

[†]Institute of Chemistry, Saint Petersburg State University, Universitetsky Pr. 26, 198504 Stary Petergof, Russian Federation

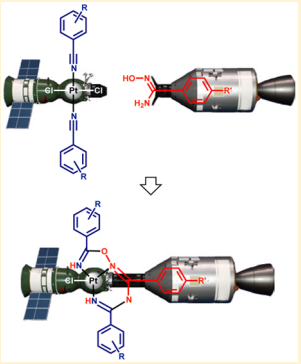
[‡]Institute of Earth Sciences, Saint Petersburg State University, University Emb. 7/9, 199034 Saint Petersburg, Russian Federation

[§]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisbon, Portugal

[∥]Institute of Macromolecular Compounds of Russian Academy of Sciences, V.O. Bolshoii Pr. 31, 199004 Saint Petersburg, Russian Federation

Supporting Information

ABSTRACT: Treatment of the aromatic nitrile complexes *trans*-$[PtCl_2(RC_6H_4CN)_2]$ (R = *p*-CF_3 **NC1**, H **NC2**, *o*-Cl **NC3**) with the aryl amidoximes *p*-$R'C_6H_4C(NH_2)$=NOH (R′ = Me **AO1**, H **AO2**, Br **AO3**, CF_3 **AO4**, NO_2 **AO5**) in all combinations, followed by addition of 1 equiv of AgOTf and then 5 equiv of Et_3N, leads to the chelates $[PtCl\{HN{=}C(RC_6H_4)O{-}N{=}C(C_6H_4R'\text{-}p)NC(RC_6H_4){=}NH\}]$ (**1**−**15**; 15 examples; yields 71−88% after column chromatography) derived from the platinum(II)-mediated coupling between metal-activated nitriles and amidoximes. The mechanism of this reaction was studied experimentally by trapping and identification of the reaction intermediates, and it was also investigated theoretically at the DFT level of theory. The combined experimental and theoretical results indicate that the coupling with the nitrile ligands involves both the HON and monodeprotonated NH_2 groups of the amidoximes, whereas in the absence of the base, the NH_2 functionality is inactive toward the coupling. The observed reaction represents the first example of bifunctional nucleophilic behavior of amidoximes. The complexes **1**−**16** were characterized by elemental analyses (C, H, N), high-resolution ESI^+-MS, FTIR, and ^1H NMR techniques, whereas unstable **17** was characterized by $HRESI^+$-MS and FTIR. In addition, **8**·$C_4H_8O_2$, **12**, and **16**·$CHCl_3$ were studied by single-crystal X-ray diffraction.



INTRODUCTION

Amidoximes, in contrast to conventional ket- and aldoximes (for reviews on oxime reactivities involving metal species see ref 1), possess two functional sites, i.e., the oxime HON and amide H_2N groups, which makes $RC(NH_2)$=NOH species versatile building blocks for the synthesis of various heterocycles.[2] In biology and medicine, amidoximes and their O-substituted derivatives exhibit a wealth of reactivity types functioning as antituberculotic, antibacterial, bacteriostatic, insecticidal, elminthicidal, antiviral, herbicidal, fungicidal, antineoplastic, antiarrythmic, antihypertensive, antihistaminic, anxiolytic-antidepressant, anti-inflammatory/antioxidant, antiaggregatory (NO donors), or plant growth regulatory agents (for reviews see ref 3). A good number of amidoximes have already been used as drugs or are currently in clinical trials. In addition to their importance in biology and medicine, polyamidoxime fibers are known in industrial chemistry as sorbents, which selectively absorb UO_2^{2+}[4] and other heavy metal cationic species.[5]

Reactivity of amidoximes is broadly investigated in metal-free organic chemistry, in particular, in reactions with various activated derivatives of carboxylic acids,[6] Vilsmeier salts,[7] and carbodiimides,[8] and also in coordination chemistry in their reactions with metal-activated nitriles[2a,9] or acylpalladates.[2d,10] All these processes proceed via nucleophilic addition of the HON moiety of amidoximes followed by intramolecular heterocyclization giving 1,2,4-oxadiazoles.

By contrast to the wealth of reactivity of the HON group, the reactivity of the amide group (or amidato group generated via deprotonation) of amidoximes is still almost unexplored, although nucleophilic addition of the amide/amidato functionality potentially constitutes an attractive way to functionalize $RC(NH_2)$=NOH species. Thus, in organic chemistry, the amide group of amidoximes was unselectively propargylated with $HC{\equiv}CCH_2Br$[11] or acylated by MeCOCl.[12] These two reactions proceed in basic media and lead to mixtures of compounds originating from electrophilic attack to both the HON and H_2N groups. In coordination chemistry, the amidato moiety of amidoximes is ligated by Sn^{IV} or Si^{IV} centers, giving novel nitrogen−element bonds.[13]

In view of our general interest in reactivity of ligands featuring a CN triple bond (for our reviews see ref 14) and organic transformations involving metal complexes (for some recent works see refs 2a, 9a, 9b, and 15), we focused our

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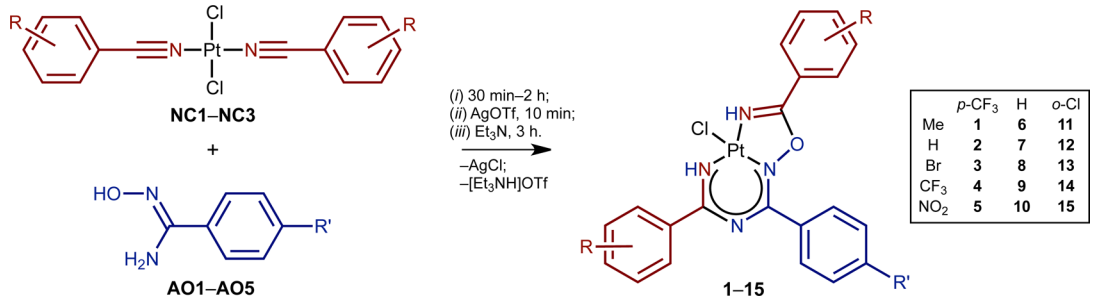
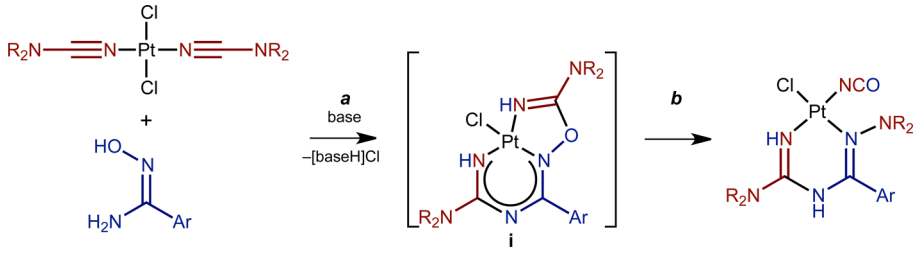
Scheme 1. Bifunctional Addition of Amidoximes



Scheme 2. Elusive Intermediate i in the Cascade Generation of Amidrazone Complexes[15a]



attention on reactions of amidoximes with nitriles. In particular, we reported amidoxime–nitrile coupling at Pt^{II},[9a,15a] Pt^{IV},[15b] and Zn^{II}[2a,9b] centers. In all instances, these reactions involve nucleophilic addition of the HON moiety of amidoximes to a metal-activated C≡N bond, whereas the H_2N moiety remains intact. The only indication that the H_2N group is also reactive was found when we studied the addition of $PhC(NH_2)$=NOH to *trans*-$[PtCl_4(NCNMe_2)_2]$ and, along with the conventional addition of the HON group, we isolated trace amounts of a byproduct that at least formally originates from amide/amidato–nitrile coupling.[15b]

In the current work, we found a system where the H_2N group of amidoximes upon deprotonation manifests its reactivity toward metal-bound nitriles, and this is the first example of *bifunctional reactivity* of amidoximes. The scenario of our work was the following. First, we found a suitable system and conditions for facile and high-yielding amide/amidato–nitrile coupling involving amidoximes and Pt^{II}-bound nitriles. Second, we trapped and identified key intermediates of this reaction. Third, we carried out a theoretical study of the mechanism of the amide/amidato–nitrile coupling and undertook the examination of the effect of substituents on the kinetics and thermodynamics of the reactions. All our experiments and theoretical calculations are disclosed in sections that follow.

RESULTS AND DISCUSSION

Bifunctional Reactivity of Amidoximes. As the starting materials for this study we addressed, on one hand, *trans*-$[PtCl_2(RC_6H_4CN)_2]$ (R = *p*-CF_3 **NC1**, H **NC2**, *o*-Cl **NC3**) and, on the other hand, the aromatic amidoximes *p*-R′$C_6H_4C(NH_2)$=NOH (R′ = Me **AO1**, H **AO2**, Br **AO3**, CF_3 **AO4**, NO_2 **AO5**) (Scheme 1).

Complexes **NC1**–**NC3** react with 1 equiv of amidoximes **AO1**–**AO5** in all possible combinations at RT for 30–120 min, whereupon 1 equiv of silver(I) triflate, AgOTf, was added to the reaction mixture. Then, after 10 min, 5 equiv of Et_3N was added to the resulting suspension, and stirring of the mixture for 3 h led to **1**–**15** (15 examples), which were isolated as pure compounds in 71–88% yields after column chromatography.

The highest yields of **1**–**15** were achieved when AgOTf was added after 30 min (for **1**–**4**), 1 h (for **5**–**9**), and 2 h (for **10**–**15**) after the addition of amidoximes. A 2-fold time reduction for this AgOTf addition results in decreasing isolated yields to ca. 30–40%, whereas the 2-fold increase leads to a drop of the yields to ca. 5%. Furthermore, addition of Et_3N to the reaction mixture after 12 h since AgOTf was added to the mixture gives **1**–**15** in ca. 10–15% yield, whereas simultaneous addition of AgOTf and Et_3N leads to 10% decreased yields of **1**–**15**. Thus, the optimal duration of this step is 3 h. The amount of Et_3N also drastically effects the yields of **1**–**15**, and maximum yields were achieved with a 5-fold excess of Et_3N.

By contrast to the reaction of the *aryl*cyanide species *trans*-$[PtCl_2(ArCN)_2]$ (**NC1**–**NC3**) with $ArC(NH_2)$=NOH (**AO1**–**AO5**) described above, the reaction between the *alkyl*cyanide complexes *trans*-$[PtCl_2(AlkCN)_2]$ (Alk = Et, $PhCH_2$) and amidoximes **AO1**–**AO5** in the temperature range from −18 to 60 °C (24 h) gives a broad spectrum of products, and no species structurally similar to **1**–**15** were detected by HRESI-MS. A mixture of various yet unidentified products was also observed when *trans*-$[PtCl_2(EtCN)_2]$ or *trans*-$[PtCl_2(PhCN)_2]$ was treated with $AlkC(NH_2)$=NOH (Me, $PhCH_2$) and $OC_4H_8NC(NH_2)$=NOH. Noticeably, degradation of the reaction mixture was also observed in the case of $RC_6H_4C(NH_2)$=NOH bearing strong donor R (R = *p*-NMe_2, *p*-OMe, *o*-OH) groups and 2- and 4-pyridylcarbamidoximes (2- and 4-$NC_5H_4C(NH_2)$=NOH). The degradation of the reaction mixtures was observed before addition of AgOTf and Et_3N, which indicates decomposition of the starting complexes or the formed amidoxime–nitrile coupling products. All these experiments indicate that the reaction is specific for *trans*-$[PtCl_2(ArCN)_2]$ and $RC_6H_4C(NH_2)$=NOH, where R is an acceptor (CF_3, NO_2) or moderate electron donor (Me, H, Br), but not a strong donor (OMe, OH, NMe_2) group. This observation can be rationalized in terms of the strong donor effect that increases the nucleophilicity of the amidoxime moiety and makes the reactions unselective.

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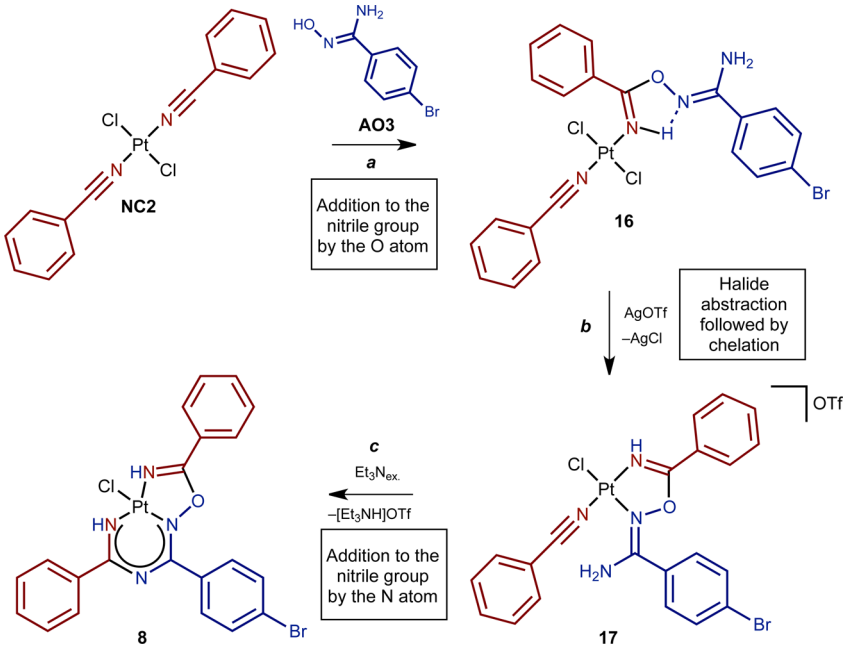
Scheme 3. Stepwise Approach to the Coupling Leading to 8



The tridentate nature of the chelated ligand gives evidence that the aromatic amidoximes serve as bifunctional nucleophiles, which couple with two nitrile ligands by both functional groups. Formation of a similar tridentate ligand was previously *postulated* in the cascade reaction (Scheme 2, *a*, intermediate **i**) that starts from *trans*-[$PtCl_2(Alk_2NCN)_2$] and aromatic amidoximes and gives metal-bound amidrazones (*b*).[15a] However, **i** was neither liberated from the reaction mixtures nor identified.

Amide/amidato−nitrile coupling was recently postulated in copper(II)-mediated amidoxime−nitrile coupling giving 1,2,4-triazoles.[16] Another relevant example that at least formally could be considered as amide/amidato−nitrile coupling was found when hydroxo nickel(II) species were treated with RCN (R = Me, Ph) and acetamide.[17] The authors[17] argue that intermediates featuring the {O═C(Me)NC(R)═NH}Ni^{II} moiety are formed in the reaction.

In our experiments, no reaction was observed for the amidoximes with dialkylcyanamides and nitriles in the absence of platinum(II), and it confirms that the studied reactions are platinum(II)-mediated. The observed coupling represents the first example of bifunctional nucleophilic behavior of amidoximes.

Plausible Mechanism of the Reaction. A stepwise approach to the studied system shed light on the mechanism of the bifunctional reactivity of amidoximes. For this study *p*-$BrC_6H_4C(NH_2)$═NOH (**AO3**) and *trans*-[$PtCl_2(PhCN)_2$] (**NC2**) were chosen as a moderately nucleophilic amidoxime and a complex bearing a moderately electrophilic nitrile ligand, correspondingly.

Reaction between **NC2** and **AO3** (30 min, RT) gives monoaddition product **16** (Scheme 3, *a*), which was isolated in 85% yield after column chromatography. This type of nucleophilic addition was previously observed, and a substantial number of such reactions were reported by us[2a,9a,b,15a,b,18] and by other groups[19] for various oximes[18a,f−i] and amidoximes.[9a,15b] Addition of 1 equiv of AgOTf to **16** results in halide abstraction accompanied by chelation of the Pt^{II} center by the oxime N atom, giving **17** (*b*). Intermediate **17** was not isolated as a pure compound due to its similar solubility with byproducts in the most common organic solvents; decomposition of **17** on silica gel prevented its chromatographic separation. However, **17** was characterized by HRESI-MS (MeOH solution) and FTIR (KBr pellets) techniques, whereas the ^{1}H NMR study was not informative due to overlap of signals from **17** with signals of byproducts. It is worthwhile mentioning that dialkylcyanamide derivatives, similar to **17**, were previously isolated and identified.[9a,15a] Compound **17** is stable as the solid, but completely degrades in neutral and acidic (1 equiv of AcOH) $CHCl_3$ solutions for 12 h at RT, giving a broad spectrum of unidentified products. In the basic media (viz., 5 equiv of Et_3N), **17** converts into **8** within 3 h and chelate **8** was isolated in 68% yield (based on **16**) after column chromatography. Thus, a one-pot approach leads to **8** in higher isolated yield (overall yield is 88%) than in the stepwise synthesis (58% based on **NC2**).

In **17**, coordination to the Pt^{II} center by the oxime N atom most probably increases acidity[20] of the NH_2 group, which undergoes deprotonation in the presence of base, giving the amidato moiety. The HN^- group is more nucleophilic than the NH_2 group[21] and intramolecularly[22] attacks the nitrile functionality, giving **8**. Importantly, no amide−nitrile coupling was observed between uncomplexed $PhC(NH_2)$═NOMe and the platinum(II) species *trans*-[$PtCl_2(RCN)_2$] (R = NMe_2, Ph, Et) and also with the substantially more reactive platinum(IV) complexes *trans*-[$PtCl_4(RCN)_2$] (R = NMe_2, Ph) in the presence of a 5-fold excess of Et_3N at RT and at 50 °C. These experiments indicate low reactivity of the NH_2 moiety of the amidoxime in the absence of bases.

In order to understand in more detail the mechanism of the amide/amidato−nitrile coupling, the theoretical DFT study of this reaction with various substituents R^1 and R^2 in the reactants was performed (for more details see the Supporting Information). We found that the cyclization occurs via an "amidato" rather than an "amide" pathway (Scheme 1S). The rate-determining step of the coupling is the second stage

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(cyclization of monocyclic intermediate), and the estimated overall Gibbs free energy of activation varies between 14.9 and 18.5 kcal/mol depending on substituents R^1 and R^2 (Figure 68S). The electron acceptor substituents R^1 and R^2 favor the cyclization, whereas the electron donor groups disfavor this process. The results of theoretical calculations are in good agreement with the experimental observations.

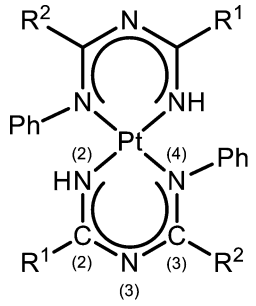
Analytical and Spectroscopy Data. Complexes **1**−**16** give satisfactory C, H, and N elemental analyses for the proposed formulas, and these species were also characterized by HRESI$^+$-MS, FTIR, and ^{1}H NMR techniques, and additionally by a single-crystal X-ray diffraction for three species (**8**·$C_4H_8O_2$, **12**, **16**·$CHCl_3$); unstable **17** was characterized by HRESI$^+$-MS and FTIR.

The positive mode high-resolution ESI mass spectra of **1**−**15** (see Supporting Information) exhibit a set of peaks corresponding to the quasi-molecular ions $[M + H]^+$, whereas the spectrum of **16** displays a set of fragmentation species $[M - Cl]^+$ and $[M - Cl - H + Na]^+$ and quasi-molecular ions $[M + H]^+$ and $[M + Na]^+$. The HRESI spectrum of **17** displays only a set of peaks from the molecular ion.

The IR spectra of **1**−**17** (see Supporting Information) exhibit two (**1**−**15**) or three (**16**, **17**) weak-medium- to medium-intensity bands at 3447−3163 cm^{-1}, which can be attributed to the N−H stretches. The spectra of **1**−**15** feature one medium-intensity absorption C═N band in the range 1633−1614 cm^{-1}. The spectra of **16** and **17** display one (**16**) or two (**17**) very strong C═N absorption bands at 1653−1624 cm^{-1}. The IR spectra of compounds with the NO_2 group (**5**, **10**, and **15**) exhibit two strong bands at 1525−1517 and 1350−1325 cm^{-1}, which can be attributed to asymmetrical and symmetrical stretches of NO_2, respectively.

Compounds **1**−**15** are poorly soluble in the most common organic solvents, except $(CD_3)_2SO$, in which they fully decompose within ca. 6 h. However, these species were isolated in their starting forms from $(CD_3)_2SO$ solutions after 10 min after dissolution by addition of excess Et_2O, and this little experiment confirms that the spectra were recorded namely for **1**−**15**, rather than for solvolysis-derived species. Thus, the ^{1}H NMR spectra of **1**−**15** (see Supporting Information) were recorded in $(CD_3)_2SO$ immediately after dissolution of the complexes. A characteristic feature of the ^{1}H NMR spectra is the availability of two low-field broad singlets at 12.59−12.12 and 10.46−9.40 ppm, which can be attributed to the N*H* resonances. The spectrum of **16** features two broad singlets at 8.81 and 7.44 ppm related to the N*H* and NH_2 resonances, correspondingly. The low-field shift of the N*H* protons of the chelate ligands relative to the open-chain species is typical for *O*-iminium amidoximes, and it was observed previously.[9a]

X-ray Structure Determinations. Molecular structures of **8**·$C_4H_8O_2$, **12**, and **16**·$CHCl_3$ indicate that all coordination polyhedra exhibit typical square-planar geometries (Figures 2 and 3). All bond angles around Pt^{II} centers are close to 90°, except N(2)−Pt(1)−N(4) in **8**·$C_4H_8O_2$ and **12**, which equal to 79.77(9)° and 80.60°, respectively. The Pt−Cl distances (2.296(1)−2.3094(7) Å) are characteristic of Pt^{II}−Cl bonds.[23] The Pt(1)−N(1) and Pt(1)−N(2) bond lengths (1.964(2)−2.007(4) Å) exhibit values characteristic for the Pt^{II}−N single bond,[23] whereas the Pt(1)−N(4) distances are shorter (1.923(2) and 1.924(4) Å for **8**·$C_4H_8O_2$ and **12**, respectively) than normal Pt−N_{oxime} bonds (1.992(3)−2.033(6) Å for related bidentate complexes[9a]), probably due to the strain in the bicyclic part of molecules. The short Pt−N_{oxime} distance was previously observed for a structurally similar Pt^{IV} complex (1.959(5) Å).[15b]



I $R^1 = R^2 = Ph$
J $R^1 = Et$; $R^2 = NHPh$

Figure 1. Platinum(II) 1,3,5-triazapentadiene complexes **I** and **J**.

In **8** and **12**, all angles in the {N(2)C(2)N(3)C(3)N(4)}Pt^{II} rings are close to 120° (122.1(4)−130.5(3)°), except the N(2)−Pt(1)−N(4) angles, which are equal to 90.11(9)° and 89.2(2)°, respectively. The π-systems of the aromatic rings partly overlap with the other part of the π-system of the tridentate ligands with torsion angles ranging from 31.3(4)° to 74.4(7)°.

In the organic ligands of **8**, **12**, and **16**, the N(1)−C(1), O(1)−C(1), and O(1)−N(4) distances (1.278(7)−1.289(13), 1.349(11)−1.353(5), and 1.444(3)−1.451(10) Å, respectively) exhibit values typical for the N−C double bond [1.281−1.316 Å][24] and the O−C [1.293−1.407 Å][24] and O−N [1.439(4)−1.477(5) Å][2a,9a] single bonds, correspondingly. In **16**, the N(4)−C(3) and N(3)−C(3) bond lengths (1.316(12) and 1.330(13) Å, respectively) indicate delocalization in the N(4)−C(3)−N(3) π-system, whereas the N(2)−C(2) distance (1.138(12) Å) is the normal triple CN bond.[24] The iminoacylated oxime ligand is in the *E* form, which is stabilized via the intramolecular hydrogen bonding between the imino H atom and the uncomplexed oxime N atom [N···N 2.580 Å; N−H···N 112.10°]. In **8** and **12**, the N(2)−C(2) and N(4)−C(3) bond lengths are in the range 1.309(5)−1.324(3) Å; the N(3)−C(2) and N(3)−C(3) distances fall in the interval between 1.339(3) and 1.359(6) Å, and this indicates partial delocalization in the π-system of the chelate.[24] The electron density delocalization in the {NCNCN}Pt^{II} system of **8** and **12** is confirmed by the analysis of the Wiberg bond indices (Table 1), which exhibit well-comparable values for all the N(4)C(3), C(3)N(3), N(3)C(2), and C(2)−N(2) bonds. A similar delocalization was also found in (1,3,5-triazapentadiene)Pt^{II} species **I** and **J** (Figure 1) synthesized previously by some of us.[25]

Final Remarks. The results of this work could be considered from at least three perspectives. First, we observed the generation of the *N*,*N*,*N*-tridentate ligand that is formed via novel Pt^{II}-mediated coupling between two nitrile moieties and one amidoxime. In this reaction, amidoxime acts as a bifunctional *HON*,*HN*-nucleophile, and it is the first example of directed and efficient coupling with the amide/amidato group of amidoximes ever observed in coordination chemistry. The only related example of the NH_2 nucleophilicity of amidoximes is the platinum(II)-mediated one-pot reaction between cyanamide ligands and amidoximes, giving, after a number of consecutive steps (Scheme 2), amidrazone species.[15a] However, in that work the amide/amidato−

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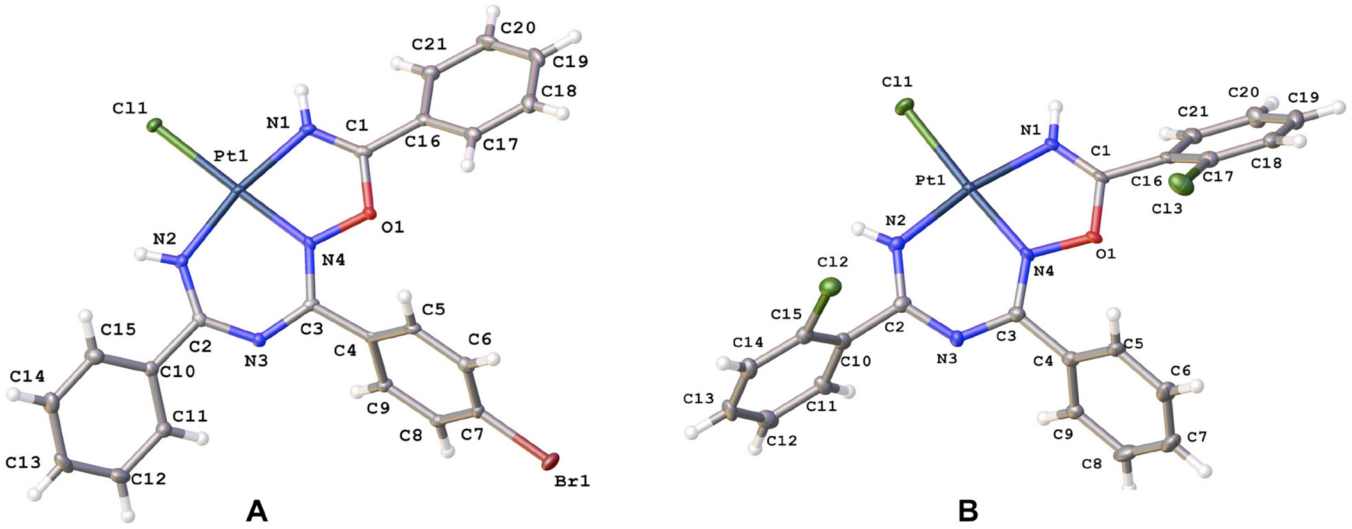

Figure 2. Molecular structures of **8**·$C_4H_8O_2$ (A) and **12** (B) with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. In A, the solvent was omitted for clarity.

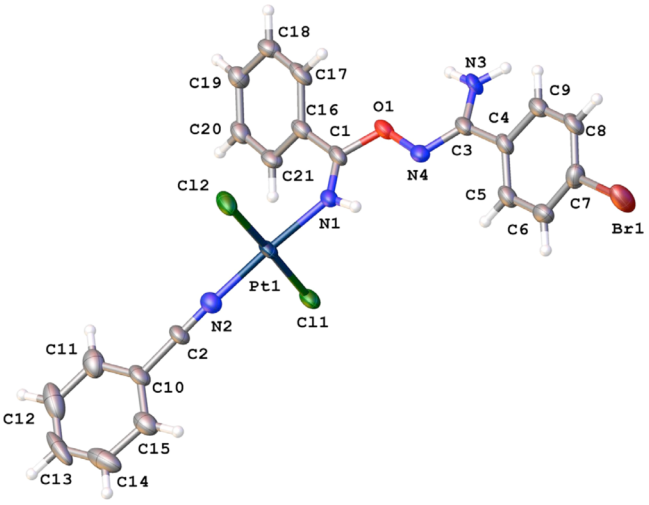

Figure 3. Molecular structure of **16**·$CHCl_3$ with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. The solvent was omitted for clarity.

Table 1. Calculated Wiberg Bond Indices for Selected Bonds in 8, 12, I, and J

bond	8	12	I	J
N(4)−C(3)	1.37	1.37	1.41	1.32
C(3)−N(3)	1.36	1.34	1.37	1.31
N(3)−C(2)	1.28	1.30	1.28	1.31
C(2)−N(2)	1.47	1.48	1.48	1.49

cyanamide coupling was only *postulated* as one of the key steps of the cascade reaction, but not confirmed experimentally.

Second, we found that for successful coupling the NH_2 group of amidoximes requires additional activation by deprotonation, giving the amidato group, which reacts with the metal-activated nitrile functionality. This deprotonation is substantially facilitated as a result of coordination by the oxime N atom. Based upon theoretical calculations the amidato coupling mechanism leading to **1**−**15** was suggested, and it includes the deprotonation of the amide moiety and intermolecular nucleophilic addition of the amidato group to the coordinated nitrile functionality (the rate-determining step), followed by proton migration (for details, see the Supporting Information).

Third, we synthesized novel *N,N,N*-tridentate systems featuring the NCNCN skeleton (Figure 4, B) that is related

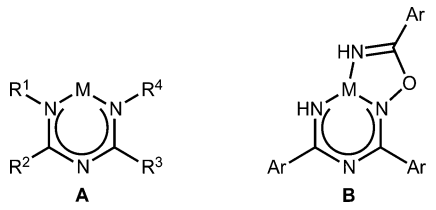

Figure 4. Known 1,3,5-triazapentadiene ligands (A) and complexes (B) obtained in this work.

to 1,3,5-triazapentadienes (A). These triazapentadienes are the subject of significant attention (for a review see ref 26; for recent works see ref 27) for the past decade due to their luminescence properties[25,27f,28] and catalytic activity.[27c,d,29]

We hope that our results open up an avenue to other coupling reactions between compounds bearing an amide/amidato group (e.g., carboxamides or amidines) and unsaturated substrates featuring triple bonds (e.g., isocyanides,[14a] dialkylcyanamides,[14d] alkynes,[30] or phosphaalkynes[31]) at various metal centers, and works in this direction are under way in our group.

EXPERIMENTAL SECTION

Materials and Instrumentation. Solvents were obtained from commercial sources and used as received. The amidoximes were synthesized according to the literature methods.[32] For chromatography, Merck silica gel 60 (70−230 mesh) was used. Melting points were measured on a Stuart SMP30 apparatus at a heating rate of 2 °C/min in capillaries and are not corrected. Microanalyses (C, H, N) were carried out on a Euro EA3028-HT analyzer. Electrospray ionization mass spectra were obtained on a Bruker maXis spectrometer equipped with an electrospray ionization (ESI) source. The instrument was operated both in positive and in negative ion modes using a m/z range of 50−3000. The capillary voltage of the ion source was set at −4500 V (ESI^+-MS), and the capillary exit at ±70−150 V. The nebulizer gas flow was 0.4 bar, and the drying gas flow 4.0 L/min. For ESI, studied complexes were dissolved in MeOH. In the isotopic pattern, the most

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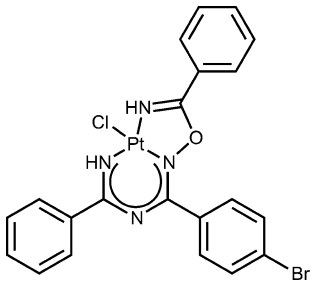
intense peak is reported. Infrared spectra (4000−400 cm^{-1}) were recorded on a Shimadzu IRPrestige-21 instrument in KBr pellets. ^1H NMR spectra were measured on a Bruker Avance 400 spectrometer in $(CD_3)_2SO$ at ambient temperature; residual solvent signals were used as the internal standard.

X-ray Structure Determinations. Suitable crystals of complexes were studied using an Agilent Technologies Excalibur Eos (**8**·$C_4H_8O_2$) and Agilent Technologies Supernova Atlas diffractometers (**12** and **16**·$CHCl_3$). All experiments were performed at 100 K. Structures have been solved by the direct methods and refined by means of the SHELXL-97[33] program incorporated in the OLEX2 program package[34] using least squares minimization. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the "riding" model approximation, with $U_{iso}(H)$ set to $1.5U_{eq}(C)$ and C−H = 0.96 Å for CH_3 groups, with $U_{iso}(H)$ set to $1.2U_{eq}(C)$ and C−H = 0.97 Å for CH_2 groups, $U_{iso}(H)$ set to $1.2U_{eq}(C)$ and C−H = 0.93 Å for the CH groups, and $U_{iso}(H)$ set to $1.2U_{eq}(N)$ and N−H = 0.86 Å for the NH groups. Empirical absorption correction was applied in the CrysAlisPro[35] program complex using spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm. Crystallographic data for these samples have been deposed at Cambridge Crystallographic Data Centre (CCDC 1038469−1038471).

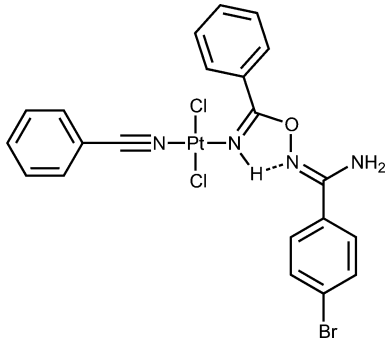
Synthetic Work. *Reaction of **NC1**−**NC3** with **AO1**−**AO5** Giving **1**−**15**.* A solution of *p*-R′$C_6H_4C(NH_2)$=NOH (80 μmol) in chloroform (2 mL; for **AO1**−**AO3**) or in a chloroform−nitromethane mixture (1:1, v/v; 2 mL; for **AO4** and **AO5**) was added to a stirred (500 rpm) solution of any one of **NC1**−**NC3** (80 μmol) in chloroform (2 mL). The solution was kept for 2 h (for **10**−**15**), 1 h (for **5**−**9**), or 30 min (for **1**−**4**) at RT, whereupon a solution of AgOTf (20.6 mg; 80 μmol) in nitromethane (2 mL) was added to the mixture. The stirred solution was kept at RT in the dark for 10 min, and then a solution of triethylamine (55 μL; 400 μmol) in chloroform (1 mL) was added to the mixture, which was stirred at RT in the dark for 3 h and transferred to a 10 mL round-bottomed flask, and the solvent was evaporated *in vacuo* at RT. Chloroform (5 mL) was added to the obtained residue, and the mixture was dispersed under ultrasound treatment. The suspension was transferred into a column filled with silica gel and eluted (eluent: chloroform to chloroform−acetone (40:1, v/v)), and the first fraction was collected. The solvent was evaporated *in vacuo* at RT to give in each case a yellow precipitate of **1**−**15**. All the reactions were conducted in air.



8. Yield: 88% (45.7 mg). Mp: 157−163 °C (dec). Anal. Calcd for $C_{21}H_{16}N_4BrClOPt$: C, 38.75; H, 2.48; N, 8.61. Found: C, 38.61; H, 2.60; N, 8.49. HRESI$^+$-MS (*m*/*z*): 650.9907 ([M + H]$^+$, calcd 650.9896). IR (KBr, selected bonds, cm^{-1}): 3369(m), 3269(m-s) ν(N−H); 1618(m) ν(C=N). TLC (eluent chloroform−acetone = 40:1, v/v) R_f = 0.63. ^1H NMR (δ): 12.16 (s, br, 1H, N*H*), 9.52 (s, br, 1H, N*H*), 8.10−8.03 (2d, 4H, C*H*), 8.00 (d, 2H, C*H*), 7.81 (d, 2H, C*H*), 7.70 (t, 1H, C*H*), 7.60−7.52 (2t, 3H, C*H*), 7.46 (t, 2H, C*H*). Crystals of **8**·$C_4H_8O_2$ suitable for X-ray diffraction were obtained by a slow evaporation of a dioxane solution at RT in air.

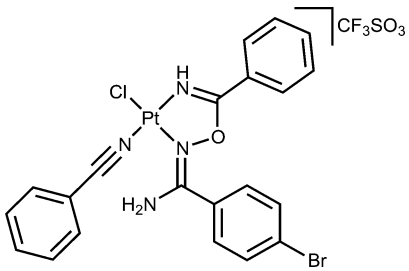
Yellow solutions (in $CHCl_3$, $MeNO_2$, Me_2CO, or MeOH) of **1**−**15** are stable in acidic (5-fold excess HCl), neutral, and basic (5-fold excess Et_3N) media at RT for at least 7 d, and they are also stable in the acidic and neutral media at 100 °C for at least 12 h. However, these species fully degrade in the basic media at 100 °C for 12 h. For characterization of **1**−**7** and **9**−**15** see the Supporting Information.

*Nucleophilic Addition of **AO3** to **NC2** Giving **16**.* A solution of *p*-$BrC_6H_4C(NH_2)$=NOH (17.2 mg; 80 μmol) in chloroform (2 mL) was added to a stirred solution of *trans*-$[PtCl_2(PhCN)_2]$ (37.7 mg; 80 μmol) in $CHCl_3$ (1 mL). The homogeneous reaction mixture was kept for 30 min at RT, whereupon it was transferred into a column filled with silica gel and eluted with chloroform to chloroform−acetone (40:1, v/v); the first fraction was collected. The solvent was evaporated *in vacuo* at RT to give **16** as a yellow precipitate. All the reactions were conducted in air.



16. Yield: 85% (46.7 mg). Mp: 131 °C (dec). Anal. Calcd for $C_{21}H_{17}N_4BrCl_2OPt$: C, 36.70; H, 2.49; N, 8.15. Found: C, 37.05; H, 2.60; N, 7.96. HRESI$^+$-MS (*m*/*z*): 650.9913 ([M − Cl]$^+$, calcd 650.9896), 672.9699 ([M − Cl − H + Na]$^+$, calcd 672.9716), 686.9645 ([M + H]$^+$, calcd 686.9659), 708.9464 ([M + Na]$^+$, calcd 708.9477). IR (KBr, selected bonds, cm^{-1}): 3389(w-m), 3312(m), 3231(w-m) ν(N−H); 1624(vs) ν(C=N). TLC (eluent chloroform−acetone = 40:1, v/v) R_f = 0.45. ^1H NMR (δ): 8.81 (s, br, 1H, N*H*), 8.78 (d, 2H, *o*-C*H*), 7.96 (d, 2H, *o*-C*H*), 7.92 (d, 2H, *o*-C*H*), 7.85 (t, 1H, *p*-C*H*), 7.77−7.62 (m, 7H, C*H*), 7.44 (s, br, 2H, NH_2). Crystals of **16**·$CHCl_3$ suitable for X-ray diffraction were obtained by a slow evaporation of a chloroform solution at RT in air.

*Halide Abstraction in **16** Followed by Chelation Giving **17**.* A solution of AgOTf (17.5 mg; 68 μmol) in nitromethane (2 mL) was added to a stirred (500 rpm) solution of **16** (46.7 mg; 68 μmol) in chloroform (2 mL), and the stirred reaction mixture was kept for 30 min at RT in the dark. After that, the solvent was evaporated *in vacuo* at RT, a precipitate that formed was treated with chloroform (4 mL), and the mixture was suspended by ultrasound treatment. The suspension was filtered through a paper filter to give a yellow solution, which was evaporated *in vacuo*, giving a brown oily residue, which was crystallized under tetrachloromethane (2 mL) by ultrasound treatment at RT to give a pale yellow powder of crude **17** (52.2 mg). All the reactions were conducted in air.



17. HRESI$^+$-MS (*m*/*z*): 650.9932 ([M − Cl]$^+$, calcd 650.9896). IR (KBr, selected bonds, cm^{-1}): 3447(w-m), 3342(m), 3192(m) ν(N−H); 1653(sh) $\nu(C{=}N)_{oxime}$; 1626(vs) $\nu(C{=}N)_{imine}$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and table of crystal data; HRESI$^+$-MS, IR, and ^1H NMR spectra of **1**−**16** and HRESI$^+$-MS and IR spectra of **17**; characterization of complexes **1**−**7** and **9**−**15**; computational details; theoretical

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considerations of the amide/amidato−nitrile coupling mechanisms and the influence of substituents; tables with calculated total energies, enthalpies, Gibbs free energies, entropies, activation, and reaction energies; Cartesian atomic coordinates of the calculated equilibrium structures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kukushkin@VK2100.spb.edu.

Notes

The authors declare no competing financial interest.

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