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Article

Nitrile–Amidine Coupling at Pt(IV) and Pt(II) Centers. An Easy Entry to Imidoylamidine Complexes

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Treatment of *trans*-[PtCl₄(RCN)₂] (R = Me, Et, Ph, NEt₂) with 2 equiv of the amidine PhC(=NH)NHPh in a suspension of MeCN (R = Me), CHCl₃ (R = Et, Ph), or in CHCl₃ solution (R = NEt₂) results in the formation of the imidoylamidine complexes *trans*-[PtCl₄{*N*H=C(R)N=C(Ph)NHPh}₂] (**1**–**4**) isolated in good yields (66–84%). The reaction of soluble complexes **3** and **4** with 2 equiv of Ph₃P=CHCO₂Me in CH₂Cl₂ (40 °C, 5 h) leads to dehydrochlorination resulting in a chelate ring closure to furnish the platinum(IV) chelates [PtCl₂{*N*H=C(R)NC(Ph)=*N*Ph}₂] (R = Ph, **5**; R = NEt₂, **6**), accordingly, and the phosphonium salt [Ph₃PCH₂CO₂Me]Cl. Treatment of **5** with 3 equiv of Ph₃P=CHCO₂-Me at 50 °C for 5 d resulted in only a 30% conversion to the corresponding Pt(II) complex [Pt{*N*H=C(NEt₂)NC-(Ph)=*N*Ph}₂] (**15**). The reduction can be achieved within several minutes, when Ph₂PCH₂CH₂PPh₂ in CDCl₃ is used. When the platinum(II) complex *trans*-[PtCl₂(RCN)₂] is reacted with 2 equiv of the amidine, the imidoylamidinato complexes [PtCl(RCN){*N*H=C(R)NC(Ph)=*N*HPh}] (**8**–**11**) and [PhC(=NH)NHPh]·HCl (**7**) are formed. The reaction of *trans*-[PtCl₂(RCN)₂] with 4 equiv of the amidine under a prolonged reaction time or treatment of [PtCl(RCN)-{*N*H=C(R)NC(Ph)=*N*HPh}] (**8**–**11**) with 2 more equiv of the amidine yields the complex bearing two chelate rings [Pt{*N*H=C(R)NC(Ph)=*N*HPh}₂] (**12**–**15**). The treatment of *cis*-[PtCl₂(RCN)₂] (R = Me, Et) with the amidine gives ca. 50–60% yield of [PtCl₂{*N*H=C(R)NHC(Ph)=*N*HPh}] (**16** and **17**). All of the platinum compounds were characterized by elemental analyses; FAB mass spectrometry; IR spectroscopy; ¹H, ¹³C{¹H}, and ¹⁹⁵Pt NMR spectroscopies, and four of them (**4**, **6**, **8**, and **15**) were also characterized by X-ray crystallography. The coupling of the Pt-bound nitriles and the amidine is metal-mediated insofar as RCN and PhC(=NH)NHPh do not react in the absence of the metal centers in conditions more drastic than those of the observed reactions. The nitrile–amidine coupling reported in this work constitutes a route to the synthesis of imidoylamidine complexes, some of them exhibiting luminescent properties.

Introduction

The wealth of ligand reactivity patterns exhibited by metal-bound RC≡N species and their useful applications (e.g., the usage of nitriles as versatile synthons for the preparation of new compounds via C–O, C–N, C–C, C–P, and C–S bond making *and* the metal-catalyzed hydrolytic transformation of RCN species to amides of industrial and pharmacological significance) have triggered a large amount of studies

focused, in particular, on nucleophilic additions to ligands in (RCN)[M] complexes, and this topic has been the subject of comprehensive reviews and books,[1] including recent surveys by some of us.[2–5] The analysis of experimental material collected to date[1–5] shows that the largest fraction of works in this area is devoted to the creation of the C–N bond by the addition of ammonia and amines, hydrazines, and hydroxylamines as well as by the coupling of some nitrogen heterocycles with ligated RCN species;[2] for recent examples, see ref 6.

Despite the great number of examples of the metal-mediated RCN–*amine* integration, only a few reports deal with nitrile–*imine* (or *heteroimine*) coupling. Thus, all

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studies known to date include platinum-mediated nitrile−imine coupling with the imines HN=ER′R″ (E = C, R′ = R″ = Ph;[7] E = S, R′/R″ = aryls;[8,9] E = C, R′/R″ = Alkyl/OAlkyl[10]) to give products of the type HN=C(R)−N=ER′R″2, which are difficult to obtain by conventional organic synthesis. Our current interest in the addition of imines to complexed nitriles has recently been sparked by the discovery of two unusual reactions mediated jointly by a Ni(II) center and a ketoxime (e.g., Me2C=NOH; Scheme 1), that is, the formation of imidoylamidines[11] (top) and phthalocyanines[12] (bottom). The triaza fragment of the two molecules shown in bold could be, at least formally, considered as derived from nitrile−amidine coupling, which, however, was not observed.

Hence, we now have to extend our investigations of reactions of metal-activated nitriles, in general,[2−5] and of nitrile−imine coupling, in particular,[7,9,10] to studies of the coupling between complexed nitriles and amidines. For this work, we addressed, on one hand, the kinetically inert (relative to other nitrile metal compounds) (nitrile)Pt(II and

Scheme 1
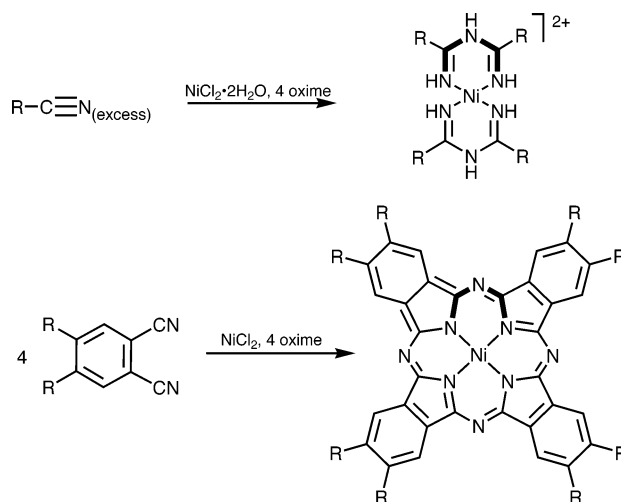
IV) complexes [PtCl$_n$(RCN)$_2$] (n = 2, 4), which proved to be superior models for investigations of the additions to nitriles, and, on the other hand, the easily accessible[13] and soluble solid amidine HN=C(Ph)NHPh, which can be handled as a stable free base. Our interest in studying the addition of the latter to the former was three-fold: (i) to observe nitrile coupling with a nucleophile of a novel type, that is, amidine; (ii) to verify the effect of the oxidation state of the Pt center on the addition of amidines to coordinated nitriles; and (iii) to develop an understanding of the mechanism for the formation of imidoylamidines and phthalocyanines at a Ni(II) center.

Results and Discussion

Nitrile−Amidine Coupling at a Pt(IV) Center. Treatment of the platinum(IV) complexes *trans*-[PtCl$_4$(RCN)$_2$] (R = Me, Et, Ph, NEt$_2$) with 2 equiv of the amidine PhC(=NH)-NHPh (Scheme 2) in a suspension of MeCN (R = Me), CHCl$_3$ (R = Et, Ph), or in a CHCl$_3$ solution (R = NEt$_2$) in the temperature range from 25 to 40 °C for 1−7 h (reaction time depends mostly on solubility of the starting material) results in the formation of the imidoylamidine complexes *trans*-[PtCl$_4${NH=C(R)N=C(Ph)NHPh}$_2$] (**1−4**) isolated in good yields (66−84%). The reaction failed only in the case of [PtCl$_4$(PhCH$_2$CN)$_2$], where the formation of a broad mixture of products, which were not separated, was observed.

Complexes **1−4** gave satisfactory C, H, and N elemental analyses and the expected molecular ion/fragmentation patterns (typically [M − nCl]$^+$, n = 1−4) in FAB$^+$ mass spectra. These four compounds were also characterized by IR and ^{1}H, ^{13}C{^{1}H}, and ^{195}Pt NMR spectroscopies and (complex **4**; see below) by X-ray crystallography.

In the IR spectra, **1−4** exhibit one strong band in the range from 1645 to 1656 cm^{-1}, which corresponds to ν(N=C) stretching vibrations of the monodentately coordinated imidoylamidine species, and another band of ν(N=C) appears on the interval between 1531 and 1537 cm^{-1} and overlaps with ν(C=C) vibrations. Because of a very low solubility, **2** was characterized only by ^{1}H NMR, whereas **1** is so poorly

(1) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299. Eglin, J. *Comments Inorg. Chem.* **2002**, *23*, 23. Murahashi, S. I.; Takaya, H. *Acc. Chem. Res.* **2000**, *33*, 225. Kukushkin, Yu. N. *Russ. J. Coord. Chem.* **1998**, *24*, 173. Parkins, A. W.; *Platinum Met. Rev.* **1996**, *40*, 169. da Rocha, Z. N.; Chiericato, G., Jr.; Tfouni, E. *Adv. Chem. Ser.* **1997**, 297. Kuznetsov, M. L. *Usp. Khim.* (*Russ. Chem. Rev.*) **2002**, *71*, 307. Constable, E. C. *Metals and Ligand Reactivity. An Introduction to the Organic Chemistry of Metal Complexes*; VCH: Weinheim, Germany, 1995; p 65. Corain, B.; Basato, M.; Veronese, A. C. *J. Mol. Catal.* **1993**, *81*, 133. Chin, J. *Acc. Chem. Res.* **1991**, *24*, 145. Eloy, F.; Lenaers, R. *Chem. Rev.* **1962**, *62*, 155. Zilberman, E. N. *Reactions of Nitriles*, in Russian; Khimia: Moscow, 1972; p 166. Dayagi, S.; Degani, Y. In *The Chemistry of the Carbon−Nitrogen Double Bond*; Patai, S., Ed.; Interscience: London, 1970; p 111.
(2) Kukushkin, V. Yu.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771.
(3) Pombeiro, A. J. L.; Kukushkin, V. Yu. Reactions of Coordinated Nitriles. In *Comprehensive Coordination Chemistry*, second edition; Elsevier: New York, 2003, Chapter 1.34, Vol. 1, pp 639−660.
(4) Kukushkin, V. Yu.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **2005**, *358*, 1.
(5) Bokach, N. A.; Kukushkin, V. Yu. *Usp. Khim.* (*Russ. Chem. Rev.*) **2005**, *74*, 164.
(6) Zhang, J. P.; Zheng, S. L.; Huang, X. C.; Chen, X. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 206. Kumagai, N.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 13632. Fomina, I. G.; Sidorov, A. A.; Aleksandrov, G. G.; Mikhailova, T. B.; Pakhmutova, E. V.; Novotortsev, V. M.; Ikorskii, V. N.; Eremenko, I. L. *Russ. Chem. Bull.* **2004**, *53*, 1477. Makarycheva-Mikhailova, A. V.; Kukushkin, V. Yu.; Nazarov, A. A.; Garnovskii, D. A.; Pombeiro, A. J. L.; Haukka, M.; Keppler, B. K.; Galanski, M. *Inorg. Chem.* **2003**, *42*, 2805. Kollipara, M. R.; Sarkhel, P.; Chakraborty, S.; Lalrempuia, R. *J. Coord. Chem.* **2003**, *56*, 1085. Belluco, U.; Benetollo, F.; Bertani, R.; Bombieri, G.; Michelin, R. A.; Mozzon, M.; Tonon, O.; Pombeiro, A. J. L.; Guedes da Silva, F. C. *Inorg. Chim. Acta* **2002**, *334*, 437. Makarycheva-Mikhailova, A. V.; Tronova, E. A.; Kukushkin, V. Yu. *Russ. Chem. Bull.* **2005**, in press.
(7) Garnovskii, D. A.; Kukushkin, V. Yu.; Haukka, M.; Wagner, G.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2001**, 560.
(8) Kelly, P. F.; Slawin, A. M. Z. *Chem. Commun.* **1999**, 1081. Kelly, P. F.; Slawin, A. M. Z. *Eur. J. Inorg. Chem.* **2001**, 263.
(9) Makarycheva-Mikhailova, A. V.; Bokach, N. A.; Kukushkin, V. Yu.; Kelly, P. F.; Gilby, L. M.; Kuznetsov, M. L.; Holmes, K. E.; Haukka, M.; Parr, J.; Stonehouse, J. M.; Elsegood, M. R. J.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 301. Makarycheva-Mikhailova, A. V.; Selivanov, S. I.; Bokach, N. A.; Kukushkin, V. Yu.; Kelly, P. F.; Pombeiro, A. J. L. *Russ. Chem. Bull.* **2004**, 1618.
(10) Bokach, N. A.; Kukushkin, V. Yu.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 3602.
(11) Kopylovich, M. N.; Pombeiro, A. J. L.; Fischer, A.; Kloo, L.; Kukushkin, V. Yu. *Inorg. Chem.* **2003**, *42*, 7239.
(12) Kopylovich, M. N.; Kukushkin, V. Yu.; Haukka, M.; Luzyanin, K. V.; Pombeiro, A. J. L. *J. Am. Chem. Soc.* **2004**, *126*, 15040.
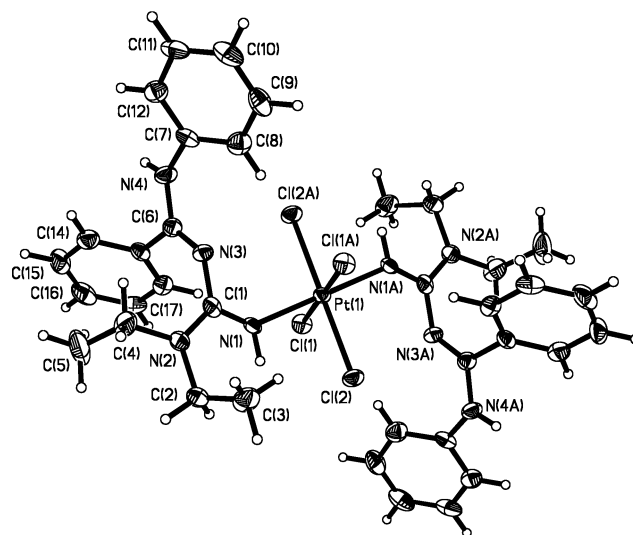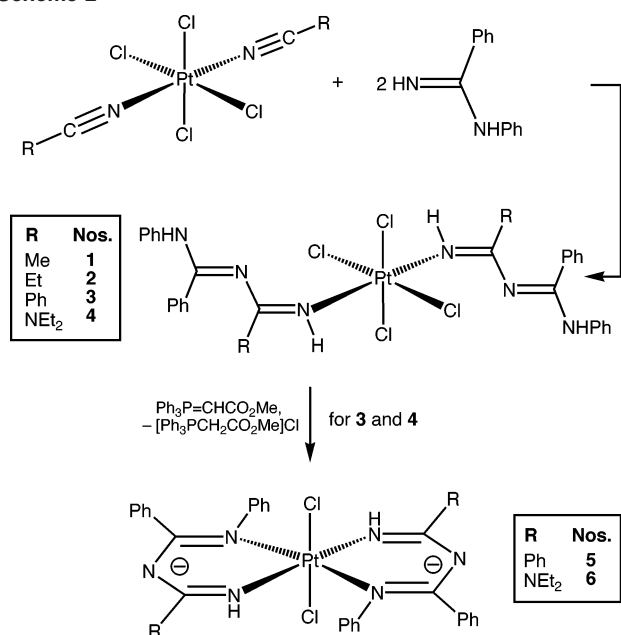(13) Cooper, F.; Partridg, M. *Org. Synth.* **1958**, *36*, 62.

Scheme 2

Figure 1. Thermal ellipsoid view of complex **4** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.036(4), Pt(1)−Cl(2) 2.3095(11), Pt(1)−Cl(1) 2.3249(11), N(1)−C(1) 1.301(6), N(1)−Pt(1)−N(1A) 180, N(1)−Pt(1)−Cl(1) 89.15(11), N(1)−Pt(1)−Cl(2) 82.58(12), Pt(1)−N(1)−C(1) 134.1(3).

soluble that it was not characterized even by the latter method. Complexes **3** and **4**, which are sufficiently soluble in the common deuterated solvents, were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{195}Pt NMR spectroscopies. In the ^{195}Pt spectra, both **3** and **4** exhibit two signals, which are probably due to their existence in two configurations; these signals are unlikely due to cis and trans isomers because (i) **3** and **4** were derived from the isomerically pure *trans*-[PtCl$_4$-(RCN)$_2$] and subsequent trans-to-cis isomerization is unlikely for octahedral Pt(IV) complexes[14] and (ii) both **3** and **4** display only one spot each on thin layer chromatography (TLC), whereas the geometric isomers of Pt complexes are usually strongly different in R_f values. All signals from the imidoylamidine ligand in the ^{1}H NMR spectrum of **4** are broad because of exchange processes in the coordinated NH=C(NEt$_2$)N=C(Ph)NHPh species such as, for example, dynamic $E-Z$ isomerization observed recently, by some of us, in other Pt(IV)-bound diazadiene species.[9]

In the solid state, complex **4** has two imidoylamidine ligands in the mutually trans position and both are in Z configuration (Figure 1).

In the (*Z*)-NH=C(NEt$_2$)−N=C(Ph)−NHPh fragment, the N=C bond lengths [N(1)−C(1) and N(3)−C(6), 1.301(6) and 1.298(6) Å, respectively] correspond, within 3σ, to the typical double N=C bonds [1.279(8) Å in C$_{Ar}$−C=N−C[15]], whereas the N(3)−C(1) [1.365(6) Å], N(4)−C(6) [1.331(6) Å], and N(2)−C(1) [1.357(6) Å] distances belong to the typical single N−C bonds [e.g., Nsp^2−Csp^2 in amides 1.346(11) Å[15]]. All of these observations demonstrate the absence of electron delocalization in the imine ligand. A similar phenomenon has been observed in the guanidine complexes [PtI$_2${NH=C(NEt$_2$)$_2$}(NHEt$_2$)],[16] [PdCl$_2${NPh=C-

(NHPh)$_2$}],[17] and [Co(NH$_3$)$_5${NH=C(NH$_2$)NMe$_2$}]$^{2+}$,[18] where the guanidine ligands have distinct single and double CN bonds with no electron delocalization.

Dehydrochlorination of 3 and 4. In coordination chemistry, the carbonyl-stabilized phosphorus ylides Ph$_3$P=CHCO$_2$R display two principal reactivity modes; that is, they act as C-donor ligands toward metal centers[19] and as nucleophiles in the addition to metal-activated organonitriles[20] and alkenes.[21] Rather recently, we discovered an efficient method for the generation of (imine)Pt(II) compounds that involves *reduction* (i.e., a third reactivity pattern of the ylides in coordination chemistry) of the corresponding readily available Pt(IV)-based imines by Ph$_3$P=CHCO$_2$R in nonaqueous media.[22] We attempted to apply the latter technique to the reduction of **3** and **4** (low solubility of **1** and **2** precluded our endeavors) and treated these complexes with 2 equiv of Ph$_3$P=CHCO$_2$Me in CH$_2$Cl$_2$ (40 °C, 5 h). In contrast to our expectations, instead of the reduction, we observed the *dehydrochlorination* of **3** and **4**, resulting in chelate ring closure (Scheme 2) to furnish **5** and **6**, respectively, and the phosphonium salt [Ph$_3$PCH$_2$CO$_2$Me]-

(14) Kukushkin, V. Yu. *Zh. Neorg. Khim.* **1988**, *33*, 1905; *Russ. J. Inorg. Chem.* **1988**, *33*, 1085.

(15) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(16) Fehlhammer, W. P.; Metzner, R.; Sperber, W. *Chem. Ber.* **1994**, *127*, 829.

(17) Mincheva, N.; Todorov, T.; Angelova, O.; Bailey, P. J.; Miteva, M. *J. Coord. Chem.* **2000**, *60*, 169.

(18) Fairlie, D. P.; Jackson, W. G.; Skelton, B. W.; Wen, H.; White, A. H.; Wickramasinghe, W. A.; Woon, T. C.; Taube, H. *Inorg. Chem.* **1997**, *36*, 1020.

(19) Bokach, N. A.; Selivanov, S. I.; Kukushkin, V. Yu.; Vicente, J.; Haukka, M.; Pombeiro, A. J. L. *Organometallics* **2002**, *21*, 3744.

(20) Vicente, J.; Chicote, M. T.; Beswick, M. A.; Ramirez de Arellano, M. C. *Inorg. Chem.* **1996**, *35*, 6592. Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *Inorg. Chem.* **1995**, *34*, 5441. Vicente, J.; Chicote, M. T.; Fernández-Baeza, J.; Lahoz, F. *Inorg. Chem.* **1991**, *30*, 3617.

(21) Vicente, J.; Chicote, M. T.; MacBeath, C.; Fernández-Baeza, J.; Bautista, D. *Organometallics*, **1999**, *18*, 2677.

(22) Wagner, G.; Pakhomova, T. B.; Bokach, N. A.; Fraústo da Silva, J. J. R.; Vicente, J.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chem.* **2001**, *40*, 1683.
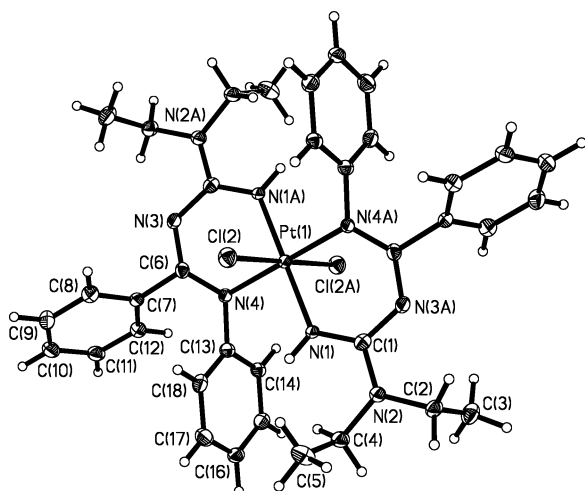
Figure 2. Thermal ellipsoid view of complex **6** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.018(2), Pt(1)−N(4) 2.054(3), Pt(1)−Cl(2) 2.3313(8), N(1)−Pt(1)−N(4) 92.95(10), N(1)−Pt(1)−Cl(2) 87.53(8), N(4)−Pt(1)−Cl(2) 87.44(7).

Cl. Treatment of **6** with 3 equiv of Ph_3P=$CHCO_2Me$ at 50 °C for 5 d resulted in only 30% conversion to the corresponding Pt(II) complex [Pt{*N*H=C(NEt$_2$)NC(Ph)=*N*Ph}$_2$] (**15**). The reduction can be achieved within several minutes, when $Ph_2PCH_2CH_2PPh_2$ (dppe) in $CDCl_3$ is used. However, in the latter case, (imidolyamidinato)Pt^{II} complex **15** is contaminated with the solid [Pt(dppe)$_2$]Cl$_2$.

In the IR spectra of **5** and **6**, in contrast to those of **3** and **4** (where strong bands at 1656 and 1645 cm^{-1}, correspondingly, from ν(N=C) in the *monodentately* bound imidoylamidine were observed), there is a strong band at 1550 (**5**) and 1556 cm^{-1} (**6**); its appearance is typical for the *bidentate*-bound imidoylamidines in the platinum(II) complexes (see below). Complex **5** was not analyzed by NMR spectroscopy because of its poor solubility in the most common deuterated solvents. In the ^{1}H and ^{13}C{^{1}H} NMR spectra of **6**, all signals from the organic ligand are well-resolved, reflecting the absence of the proton exchange or a rotation in the ligand, which is observed for the coordinated imidoylamidine species in complex **4**. Compound **6** exhibits one signal in the ^{195}Pt NMR spectrum at 103 ppm, in the region characteristic for some other *trans*-[PtCl$_4$(imine)$_2$] complexes.[23]

The X-ray structure was obtained for **6** (Figure 2). The bond lengths, N(1)−C(1) [1.318(4) Å], N(2)−C(1) [1.358(4) Å], N(3)−C(1) [1.357(4) Å], N(3)−C(6) [1.316(4) Å], and N(3)−C(6) [1.335(4) Å], in the *metallacycle* are similar within 3σ with those found in complex **4** for the *monodentately* coordinated ligand. Similar to **4**, bond delocalization was not observed in the NCNCN fragment. The metallacycles are distorted square planes: torsion angles are Pt(1)−N(1)−

C(1)−N(3)#1, 8.4(4); Pt(1)−N(4)−C(6)−N(3), 18.6(4); and C(1)#1−N(3)−C(6)−N(4), 7.1(5); the maximum deviation of the N(1) atom from the plane Pt(1)N(1)C(1)N(3)C(6)N(4) is 0.196(3) Å [N(1), −0.145(3) Å; N(3), −0.159(3) Å], and the root mean square of the deviations from the plane is 0.203(3) Å.

Hence, in the reaction with **3** and **4**, the phosphorus ylide Ph_3P=$CHCO_2Me$ abstracts HCl, acting as a base, and this reactivity mode is the fourth one observed in coordination chemistry for the carbonyl-stabilized phosphorus ylides.

Nitrile−Amidine Coupling at a Pt(II) Center. The route of the reaction between the platinum(II) complexes [PtCl$_2$-(RCN)$_2$] and the amidine PhC(=NH)NHPh depends on the cis/trans configuration of the starting metal complex (Scheme 3, A[24]), the molar ratio of the reactants, and the reaction time. In this section, we will consider first the nitrile−amidine coupling at *trans*-[PtCl$_2$(RCN)$_2$] (R = Et, Ph, CH$_2$Ph, NEt$_2$; the acetonitrile complex was not employed because of its very poor solubility), whereupon the coupling with the nitriles in *cis*-[PtCl$_2$(RCN)$_2$] (R = Me, Et) will be described.

When *trans*-[PtCl$_2$(RCN)$_2$] was reacted with 2 equiv of the amidine (Scheme 3, B), two products were isolated from the reaction mixture. The first one corresponds to the addition of one amidine to the nitrile C atom of *trans*-[PtCl$_2$(RCN)$_2$] and the ring closure of the imidoylamidinato ligand formed in the metal-mediated reaction, that is, [PtCl(RCN)-{*N*H=C(R)NC(Ph)=*N*Ph}] (**8**−**11**); another product released from the reaction mixture is the hydrochloride [PhC(=NH)-NHPh]·HCl (**7**; characterized by FAB$^+$ MS and X-ray crystallography, see Experimental Section and the Supporting Information). When *trans*-[PtCl$_2$(RCN)$_2$] reacts with 4 equiv of the amidine under a prolonged reaction time (Scheme 3, C) or [PtCl(RCN){*N*H=C(R)NC(Ph)=*N*Ph}] (**8**−**11**) is treated with 2 more equiv of the amidine (Scheme 3, D), the complex bearing two chelate rings [Pt{*N*H=C(R)NC-(Ph)=*N*Ph}$_2$] (**12**−**15**) is formed. We discovered that the latter group of complexes represents a new class of efficient Pt-based luminophores showing pH-dependent phosphorescence previously not recognized by others.[25] These results include the photophysical properties of [Pt{*N*H=C(R)NC-(Ph)=*N*Ph}$_2$].[26]

When *cis*-[PtCl$_2$(RCN)$_2$] (R = Me, Et; ca. 80:20% cis/trans mixtures) reacts with the amidine, the latter couples with one RCN moiety with the substitution of the other RCN for the other end of the bidentate imidoylamidine (Scheme 3, E). The reaction proceeds at 40 °C for 1 h to give ca. 50−60% yield of [PtCl$_2${*N*H=C(R)NHC(Ph)=*N*Ph}] (**16** and **17**).

In a related work, Baker and colleagues treated benzamidine hydrochloride, PhC(=NH)NH$_2$·HCl, with two equiv of

(23) Kukushkin, V. Yu.; Pakhomova, T. B.; Kukushkin, Yu. N.; Herrmann, R.; Wagner, G.; Pombeiro, A. J. L. *Inorg. Chem.* **1998**, *37*, 6511. Kukushkin, V. Yu.; Pakhomova, T. B.; Bokach, N. A.; Wagner, G.; Kuznetsov, M. L.; Galanski, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2000**, *39*, 216. Luzyanin, K. V.; Kukushkin, V. Yu.; Kuznetsov, M. L.; Garnovskii, D. A.; Haukka, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2002**, *41*, 2981. Makarycheva-Mikhailova, A. V.; Haukka, M.; Bokach, N. A.; Garnovskii, D. A.; Galanski, M.; Keppler, B. K.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *New J. Chem.* **2002**, *26*, 1085.

(24) Svensson, P.; Lövqvist, K.; Kukushkin, V. Yu.; Oskarsson, Å. *Acta Chem. Scand.* **1995**, *49*, 72. Kukushkin, V. Yu.; Oskarsson, Å.; Elding, L. I. *Zh. Obsch. Khim.* **1994**, *64*, 881; *Russ. J. Gen. Chem.* **1994**, *64*, 793. Kukushkin, V. Yu.; Oskarsson, Å.; Elding, L. I. *Inorg. Synth.* **1997**, *31*, 279. Kukushkin, V. Yu.; Tkachuk, V. M. *Z. Anorg. Allg. Chem.* **1992**, *613*, 123.

(25) Baker, J.; Kilner, M.; Mahmoud, M. M.; Wallwork, S. C. *J. Chem. Soc., Dalton Trans.* **1989**, 837.

(26) Sarova, G. H.; Bokach, N. A.; Berberan Santos, M. N.; Kukushkin, V. Yu.; Pombeiro, A. J. L. **2005**, manuscript in preparation.

Scheme 3

| R	Nos.
Me	16
Et	17

E

−EtCN

A | Δ

B

−(amidine)·HCl (7)

R	Nos.
Et	8
CH₂Ph	9
Ph	10
NEt₂	11

C   4 HN=C(Ph)NHPh
−2 (amidine)·HCl (7)

2 HN   D

−(amidine)·HCl (7)

R	Nos.
Et	12
CH₂Ph	13
Ph	14
NEt₂	15
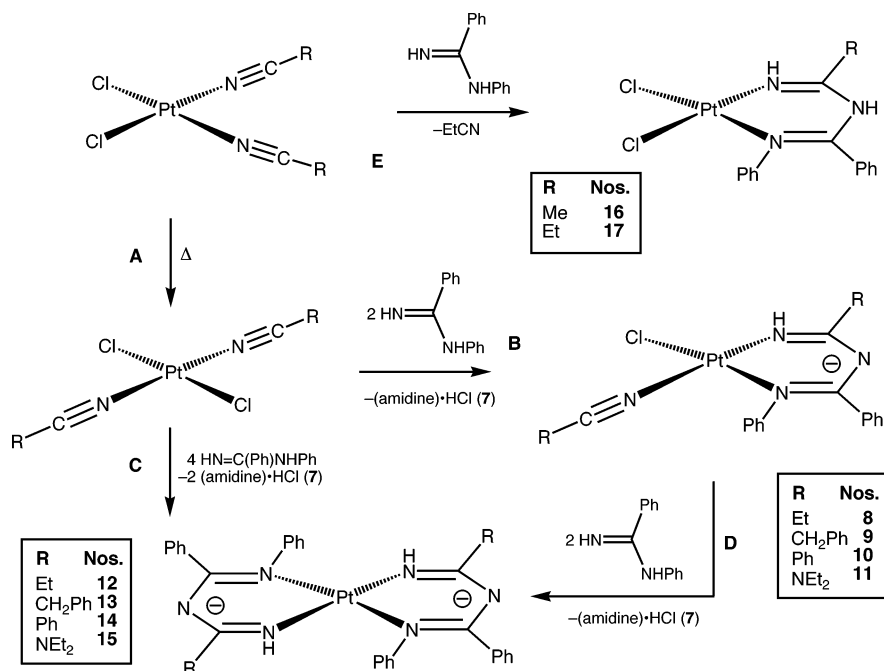
Li(Bu-n) in diethyl ether, with a further reaction of Li-[(NH)₂CPh], obtained in situ, with the platinum(II) complex [PtCl₂(PhCN)₂].[25] Nucleophilic addition of (NH)₂CPh⁻ to the ligated benzonitrile gave the azametallacycle, depicted in Scheme 4.

Scheme 4

[PtCl₂(N≡CPh)₂] + 2   Ph   −2Cl⁻
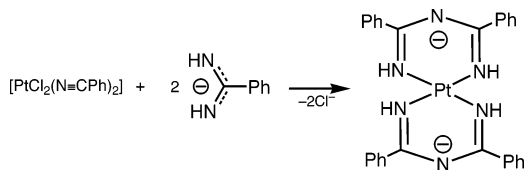
The X-ray crystal structure was determined, but the poor quality of crystals and, consequently, high estimated standard deviations precluded any solid conclusions on bond delocalization within the metallacycle. Hence, the structure of the product in Scheme 4 is given in accord with our observations. Our experiments, in contrast to those of the previous work,[25] show that additional activation of amidines toward the coupling, by deprotonation, is not necessary and amidines are sufficiently nucleophilic in these reactions.

Characterization of (Imidoylamidine)Pt(II) Complexes. All complexes give satisfactory elemental analyses for the proposed formulation. In FAB⁺ MS, the complexes [PtCl(RCN){NH=C(R)NC(Ph)=NPh}] give fragmentation patterns characteristic for platinum chlorides with the following ions: [M − Cl]⁺, [M − RCN]⁺, [M − RCN − Cl]⁺ (8−11), and [M]⁺ or [M + H]⁺ for [Pt{NH=C(R)NC(Ph)=NPh}₂] (12−15). There are two types of imidoylamidine complexes that were prepared from *trans*-[PtCl₂(RCN)₂] (R = Et, Ph, CH₂Ph, NEt₂), which are [PtCl(RCN){NH=C(R)NC-(Ph)=NPh}] (8−11) and [Pt{NH=C(R)NC(Ph)=NPh}₂] (12−15). These compounds do not have intense bands at ca. 1650 cm⁻¹, but they exhibit a strong band at 1540−1561

cm⁻¹, which could be attributed to ν(C=N); ν(C=C) (from Ar) might contribute to the overall intensity. The ν(C≡N) vibrations were detected for complexes **10** and **11**. In the ¹H NMR spectra, complexes **8−15** exhibit one signal for the NH group, at 5.56−7.34 ppm for **8−11** and 3.84−6.38 ppm for **12−15**. In the ¹³C{¹H} spectra of [PtCl(RCN)-{NH=C(R)NC(Ph)=NPh}] (**8−10**), the signal from the R*C*N (R = Et, Ph, PhCH₂) moiety appears at 109.65−118.08 ppm. ¹³C signals of the C=N group vary in the range 158.66−187.03 ppm for the NH=C and 145.86−151.82 ppm for the NPh=C fragments. Complexes **8−15** exhibit one signal in the ¹⁹⁵Pt NMR spectra in the range from −2145 to −2296 ppm; this range agrees well with ¹⁹⁵Pt NMR parameters for other (imino)Pt(II) complexes.[22,23]

In the IR spectra, complexes [PtCl₂{NH=C(R)NHC-(Ph)=NPh}] (R = Me, **16** and R = Et, **17**) exhibit strong bands at 1685 and 1688 cm⁻¹, respectively, from ν(C=N) and, in the ¹H NMR spectra, two signals from the two different N*H* hydrogens (10.07 and 7.39 for **16**; 11.33 and 9.98 for **17**).

The structures of **8** and **15** were determined by X-ray single-crystal diffraction (Figures 3 and 4), and it was observed that both have square planar geometry. Atoms of the metallacycles lie in one plane with a maximum deviation of 0.045(2) Å for N(2), 0.028(1) Å for Pt(1), and 0.028(2) Å for C(7) in Pt(1)N(2)C(4)N(3)C(7)N(4), and the root mean square of the deviations for this ring is 0.039(2) Å in **8**. The N=C bond lengths [N(2)C(4), 1.305(3) and N(4)C(7), 1.323(3) Å for **8**] and the N−C bond lengths [N(3)C(4), 1.338(4) and N(3)C(7), 1.342(3) Å for **8**] in the metallacycle have values typical for bonds in Ni(II) imidoylamidine(ato) complexes.[11,27] Complex **15** has another, based on bond

(27) Kryatov, S. V.; Nazarenko, A. Y.; Smith, M. B.; Rybak-Akimova, E. V. *Chem. Commun.* **2001**, 1174. Norrestam, R. *Acta Crystallogr., Sect. C* **1984**, *40*, 955.
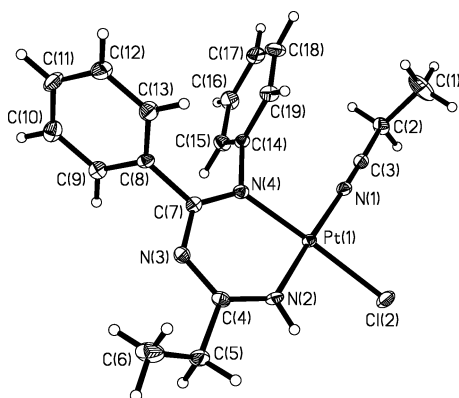
Figure 3. Thermal ellipsoid view of complex **8** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 1.987(2), Pt(1)−N(2) 1.945(2), Pt(1)−N(4) 1.998(2), Pt(1)−Cl(2) 2.3015(6), N(1)−C(3) 1.126(3), N(1)−Pt(1)−N(2) 177.35(8), N(2)−Pt(1)−N(4) 88.98(9), N(1)−Pt(1)−N(4) 93.40(9), N(1)−Pt(1)−Cl(2) 88.92(6), Pt(1)−N(1)−C(3) 177.0(2).
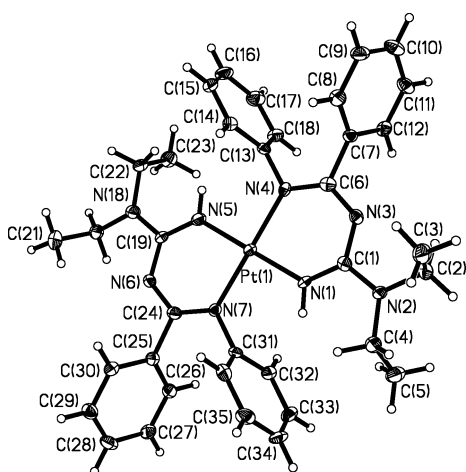

Figure 4. Thermal ellipsoid view of complex **15** with atomic numbering scheme. The asymmetric unit contains a complete molecule and two halves (labeled B and C). Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.000(3), Pt(1)−N(4) 2.023(3), Pt(1)−N(5) 2.003(3), Pt(1)−N(7) 2.032(3), Pt(1B)−N(1B) 2.005(3), Pt(1B)−N(4B) 2.040(3), Pt(1C)−N(1C) 2.000(3), Pt(1C)−N(4C) 2.028(3), N(1)−Pt(1)−N(4) 87.33(12), N(5)−Pt(1)−N(7) 87.54(12), N(1B)−Pt(1B)−N(4B) 87.42(13), N(1C)−Pt(1C)−N(4C) 87.68(13).

lengths, distribution of double and single CN bonds in the metallacycle [N(1)C(1), 1.318(4) Å; C(1)N(3), 1.357(4) Å; N(3)C(6), 1.316(4) Å; and C(6)N(4), 1.335(4) Å], which can be related to the influence of the NEt$_2$ group, but all values still remain typical, within 3σ, for such types of imidoylamidine(ato) metallacycles. Atoms of the metallacycles lie in one plane, with a maximum deviation of 0.016(4) Å for N(1) and 0.013(4) Å for N(4) in Pt(1)N(1)C(1)N(3)C(6)N(4), and the root mean square of the deviations for this ring is 0.019(3) Å in **15**.

Final Remarks. Heating of the free nitriles (in particular, PhCN as the most reactive toward the nucleophilic addition among chosen for this study) and the amidine PhC(=NH)-NHPh gave no reaction for at least 1 d, whereas the coordinated nitriles react rapidly under milder conditions. These observations provide explicit evidence for the metal-mediated character of the coupling. Moreover, it is clear that Pt(IV) provides a better activation toward the coupling than

the Pt(II) center does, and Pt(II) shows a stepwise pattern for the reaction. Thus, for the Pt(II) complexes, the reaction between [PtCl$_2$(RCN)$_2$] and PhC(=NH)NHPh leads to the addition of amidine to the coordinated nitrile followed by the coordination of the newly formed imidoylamidine via the NHPh end to the Pt(II) center with a ring closure accompanied by the leaving behind of one of the ligands (Cl$^-$ or RCN).

Hence, the nitrile−amidine coupling reported herein constitutes a route to the synthesis of imidoylamidine complexes,[11,27] some of them, as we have also found,[26] exhibiting useful luminescent properties. In addition, results from this study support the hypothesis that nitrile−amidine coupling could be one of the plausible steps in the recently discovered Ni(II)/oxime-mediated conversion of nitriles to imidoylamidines[11] and phthalonitriles.[12]

Experimental Section

Materials and Instrumentation. Solvents were obtained from commercial sources and used as received. PhC(=NH)NHPh,[13] [PtCl$_2$(RCN)$_2$], and [PtCl$_4$(RCN)$_2$] (R = Me, Et, Ph, CH$_2$Ph, NEt$_2$) were prepared in accord with the published method.[28] Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrixes of the samples with 8 keV (ca. 1.28 × 10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (400−4000 cm^{-1}) were recorded on a Nicolet magna 750 FT/IR instrument using KBr pellets. TLC were performed on Merck 60 F$_{254}$ SiO$_2$ plates. ^{1}H, ^{13}C{^{1}H}, and ^{195}Pt NMR spectra were measured on Bruker-DPX 300 and Varian UNITY 300 spectrometers at ambient temperature. ^{195}Pt chemical shifts (measured on a Varian UNITY 300 spectrometer) are given relative to Na$_2$[PtCl$_6$] (by using K$_2$[PtCl$_4$], $\delta = -1630$, as a standard), and the half-height line width is given in parentheses.

Nitrile−Amidine Coupling at a Pt(IV) Center. A solution of the amidine HN=C(Ph)NHPh (97 mg, 0.49 mmol) in CH$_2$Cl$_2$ (2 mL) was added dropwise while stirring at room temperature to a suspension of [PtCl$_4$(RCN)$_2$] (R = Me, Et, Ph, NEt$_2$) (0.24 mmol) in CH$_2$Cl$_2$ (3 mL). For R = Me, the reaction mixture was stirred at room temperature overnight until completeness of the reaction, and for the other cases (R = Et, Ph, NEt$_2$), the reaction mixture was left to stand at 40 °C for 1, 7, and 3 h, respectively. For R = Me, Et, and Ph, poorly soluble product was filtered off, washed with Et$_2$O (three 5-mL portions), and dried in the air, whereas for R = NEt$_2$, the reaction mixture was evaporated and the yellow oily residue released was crystallized under a layer of Et$_2$O and dried on air at 20−25 °C. Yields are 66−84%.

[PtCl$_4${*N*H=C(Me)N=C(Ph)NHPh}$_2$] (1).** Anal. Calcd for C$_{30}$H$_{30}$N$_6$Cl$_4$Pt·2H$_2$O: C, 42.52; H, 4.04; N, 9.92. Found: C, 42.50; H, 3.65; N, 10.21%. FAB$^+$ MS, *m/z*: 812 [M − H]$^+$, 788 [M − Cl]$^+$, 740 [M − 2HCl]$^+$, 705 [M − 2HCl − Cl]$^+$. mp = 178 °C. TLC: R_f = 0.37 (eluent: CH$_2$Cl$_2$). IR (KBr, selected bands, cm^{-1}): 3404 (w), ν(O−H); 3299 (m), 3265 (w), ν(N−H); 1655 (s), ν(C=N); 1535 (s), ν(C=N and C=C from Ar); 773 (w), 693 (m), δ(C−H). The compound is insoluble in all common deuterated solvents, and this precluded NMR measurements.

[PtCl$_4${*N*H=C(Et)N=C(Ph)NHPh}$_2$] (2).** Anal. Calcd for C$_{32}$H$_{34}$N$_6$Cl$_4$Pt·H$_2$O: C, 44.82; H, 4.23; N, 9.80. Found: C, 44.97;

(28) Luzyanin, K. V.; Haukka, M.; Bokach, N. A.; Kuznetsov, M. L.; Kukushkin, V. Yu.; Pombeiro, A. J. L. *Dalton Trans.* **2002**, 1882. Bokach, N. A.; Pakhomova, T. B.; Kukushkin, V. Yu.; Haukka, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 7560.

H, 4.05; N, 9.70%. FAB$^+$ MS, m/z: 732 [M − 3HCl]$^+$, 696 [M − 3HCl − Cl]$^+$. mp = 184 °C (dec). TLC: R_f = 0.35 (eluent CH$_2$Cl$_2$). IR (KBr, selected bands, cm^{-1}): 3429 (w), ν(O−H); 3320 (m), 3273 (w), ν(N−H); 1656 (s), ν(C=N); 1531 (s), ν(C=N and C=C from Ar); 773 (w), 693 (m), δ(C−H). ^{1}H NMR (CD$_2$Cl$_2$, δ): 12.83 (s, br, 1H, NH), 7.56 (s, br, 1H, NH), 6.8−7.4 (m, 10H, 2 Ph), 3.22 (q, 7.4 Hz, 2H, CH$_2$), 1.38 (t, 7.4 Hz, 3H, CH$_3$).

[PtCl$_4$\{NH=C(Ph)N=C(Ph)NHPh\}$_2$] (3). Anal. Calcd for C$_{40}$H$_{34}$N$_6$Cl$_4$Pt: C, 52.14; H, 4.03; N, 8.57. Found: C, 51.95; H, 3.74; N, 8.84%. FAB$^+$ MS, m/z: 935 [M]$^+$, 900 [M − Cl]$^+$, 862 [M − 2HCl]$^+$, 830 [M − 3Cl]$^+$, 793 [M − 3HCl − Cl]$^+$. mp = 155 °C (dec). TLC: R_f = 0.56 (eluent CH$_2$Cl$_2$). IR (KBr, selected bands, cm^{-1}): 3429 (w), ν(O−H); 3320 (m), 3273 (w), ν(N−H); 1656 (s), ν(C=N); 1531 (s), ν(C=N and C=C from Ar); 773 (w), 693 (m), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 9.89 and 9.64 (2 s, br, 1H, NH), 7.91 (t, 2H, Ph), 7.4−7.0 (m, 11H, Ph), 6.92 (t, 2H, Ph), 6.44 (s, br, 1H, NH). ^{13}C\{^{1}H\} NMR (CDCl$_3$, δ): 168.49 (br, C=N); 147.92 and 146.88 (2 s, N−C=N); 135.24, 132.60, 132.32, 132.10, 131.46, 131.22, 129.53, 129.00, 128.67, 128.58, 128.15, 128.07, 127.57, 127.24, 124.71, 121.44, 120.92 (carbons in Ph's). ^{195}Pt NMR (CDCl$_3$, δ): −139.74 (299.1 Hz) (60%), −192.46 (375.4 Hz) (40%).

[PtCl$_4$\{NH=C(NEt$_2$)NHC(Ph)=NPh\}$_2$] (4). Anal. Calcd for C$_{32}$H$_{44}$N$_8$Cl$_4$Pt·H$_2$O: C, 45.82; H, 4.91; N, 11.87. Found: C, 45.90; H, 5.12; N, 11.64%. FAB$^+$ MS, m/z: 926 [M]$^+$, 891 [M − Cl]$^+$, 853 [M − 2HCl]$^+$, 819 [M − 3Cl]$^+$, 782 [M − 2Cl − 2HCl]$^+$. mp = 162 °C. TLC: R_f = 0.54 (eluent CH$_2$Cl$_2$). IR (KBr, selected bands, cm^{-1}): 3358 (m), ν(N−H); 1645 (ms), ν(C=N); 1596 (m), 1537 (s), ν(C=N and C=C from Ar); 759 (m), 697 (m), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.7−7.2 (m, 10H, 2 Ph), 5.30 (s, br, 1H, NH), 3.37 (s, br, 4H, CH$_2$), 1.10 (s, br, 3H, CH$_3$). ^{13}C\{^{1}H\} NMR (CDCl$_3$, δ): 130.39, 129.28, 128.62, 128.20, 123.88, 122.01 (Ph); 43.80 and 13.13 (Et). ^{195}Pt NMR (CDCl$_3$, δ): 193.05 (323.4 Hz) (50%), 86.92 (50%) (290.1 Hz).

Dehydrohalogenation of 3 and 4 with the ylide Ph$_3$P=CH-CO$_2$Me. Complex **3** or **4** (0.032 mmol) and Ph$_3$P=CHCO$_2$Me (11 mg, 0.033 mmol) were dissolved (**4**) or suspended (**3**) in CH$_2$Cl$_2$ (1 mL) and left to stand for 5 h at 40 °C. Completeness of the reaction was monitored by TLC. After 5 h, product **6** was separated by column chromatography on silicagel (Aldrich, 70−230 mesh, 70 Å) in the first fraction by using CH$_2$Cl$_2$ as an eluent. Product **5** was released and separated as a yellow powder after 12 h. Yields are ca. 50%.

[PtCl$_2$\{NH=C(Ph)NC(Ph)=NPh\}$_2$] (5). Anal. Calcd for C$_{40}$H$_{32}$N$_6$Cl$_2$Pt·0.5CH$_2$Cl$_2$: C, 53.74; H, 3.67; N, 9.28. Found: C, 53.97; H, 3.50; N, 9.17%. FAB$^+$ MS, m/z: 862 [M]$^+$, 828 [M − Cl + H]$^+$, 792 [M − 2Cl]$^+$. mp = 280 °C (dec). TLC: R_f = 0.67 (eluent CH$_2$Cl$_2$/acetone = 1:1). IR (KBr, selected bands, cm^{-1}): 3343 (m), ν(N−H); 1550 (s), ν(C=N and C=C from Ar); 1417 (ms), ν(C=C from Ar); 699 (m), δ(C−H). NMR spectra were not measured because of the poor solubility of the complex.

[PtCl$_2$\{NH=C(NEt$_2$)NC(Ph)=NPh\}$_2$] (6). Anal. Calcd for C$_{36}$H$_{42}$N$_8$Cl$_2$Pt: C, 50.70; H, 4.96; N, 13.14. Found: C, 50.52; H, 5.12; N, 12.77%. FAB$^+$ MS, m/z: 853 [M − H]$^+$, 816 [M − 3H − Cl]$^+$, 781 [M − 4H − 2Cl]$^+$. mp = 217 °C (dec). TLC: R_f = 0.34 (eluent CH$_2$Cl$_2$). IR (KBr, selected bands, cm^{-1}): 3412 (m), ν(N−H); 1556 (s), ν(C=N and C=C from Ar); 1471 (ms), ν(C=C from Ar); 694 (m), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.18 (m, 10H, 2 Ph), 4.77 (sd, 26.37 Hz, 1H, NH), 3.18 and 3.05 (2 m, 4H, CH$_2$), 0.94 (t, 7.2 Hz, 3H, CH$_3$). ^{13}C\{^{1}H\}NMR (CDCl$_3$, δ): 160.08 (C=N−Pt); 147.82 and 147.32 (C=N); 140.92, 131.26, 131.14, 128.94, 128.86, 128.07, 127.99 (all br, NHPh); 128.21, 127.27,

127.17, 125.73 (CPh); 42.65 and 13.37 (Et$_2$NC=N). ^{195}Pt NMR (CDCl$_3$, δ): 103 (305 Hz).

The Nitrile−Amidine Coupling at Pt(II) Center. Reaction of *trans*-[PtCl$_2$(RCN)$_2$] and the Amidine (2 Equiv). *trans*-[PtCl$_2$(RCN)$_2$] (0.053 mmol) and PhC(=NH)NHPh (21 mg, 0.106 mmol) were dissolved in CH$_2$Cl$_2$ (0.5 mL) and left overnight at 40 °C. The released colorless crystals of the amidinium hydrochloride were removed by filtration, and the filtrate was evaporated until dryness under a vacuum at room temperature to form a pale-yellow powder of the platinum complexes, which were recrystallized from CH$_2$-Cl$_2$−Et$_2$O to give analytically pure samples. Yields of **8**−**11** after crystallization were 50−60%. The amidinium hydrochloride (**7**) was also detected in the reaction mixture.

[PhC(=NH)NHPh]·HCl (7). Colorless crystals, insoluble in CH$_2$Cl$_2$. FAB$^+$MS, m/z: 197 [M]$^+$. For X-ray structure, see Supporting Information.

[PtCl(NCEt)\{NH=C(Et)NC(Ph)NPh\}] (8). Anal. Calcd for C$_{19}$H$_{21}$N$_4$ClPt: C, 42.50; H, 3.95; N, 10.45. Found: C, 42.90; H, 3.87; N, 10.13%. FAB$^+$ MS, m/z: 536 [M]$^+$, 500 [M − Cl]$^+$, 481 [M − EtCN]$^+$, 444 [M − Cl − EtCN]$^+$. mp = 213 °C (dec). TLC: R_f = 0.38 (eluent Et$_2$O/CH$_2$Cl$_2$ = 2:3). IR (KBr, selected bands, cm^{-1}): 3341 (mw), 3282 (m), ν(N−H); 1552 (ms), ν(C=N and C=C from Ar); 1444 (s), ν(C=C from Ar); 700 (m), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.34 (s, br, 1H, NH), 7.10 (t, 2H, m-Ph), 7.07 (m, 5H, Ph), 6.96 (d, 2H, o-Ph), 6.88 (t, 1H, p-Ph−N), 2.41 (q, 7.5 Hz, 2H) and 1.25 (t, 7.5 Hz, 3H) (EtC=N), 2.14 (q, 7.5 Hz, 2H) and 0.92 (t, 7.5 Hz, 3H) (EtC≡N). ^{13}C\{^{1}H\} NMR (CDCl$_3$, δ): 162.03 (C=N−H); 150.73 (C=N−Ph); 129.53 (C$_{ipso}$); 127.71, 127.56, 127.41, 125.31 (carbons in Ph's); 118.08 (C≡N); 32.75 and 11.20 (*Et*C=N); 11.63 and 9.03 (*Et*C≡N). ^{195}Pt NMR (CDCl$_3$, δ): −2295 (811 Hz).

[PtCl(NCCH$_2$Ph)\{NH=C(CH$_2$Ph)NC(Ph)=NPh\}] (9). Anal. Calcd for C$_{29}$H$_{25}$N$_4$ClPt: C, 52.69; H, 3.96; N, 8.48. Found: C, 52.25; H, 4.16; N, 8.87%. FAB$^+$ MS, m/z: 660 [M]$^+$, 624 [M − Cl]$^+$, 543 [M − PhCH$_2$CN]$^+$, 506 [M − HCl − PhCN]$^+$. mp = 127 °C. TLC: R_f = 0.53 (eluent Et$_2$O/CH$_2$Cl$_2$ = 1:3). IR (KBr, selected bands, cm^{-1}): 3320 (m), ν(N−H); 1559 (ms), ν(C=N and C=C from Ar); 1449 (s), ν(C=C from Ar); 698 (m), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.29 and 7.09−6.93 (m, 20H, Ph's), 6.74 (s, br, 1H, NH), 3.69 (s, 2H, N=CCH$_2$Ph), 3.48 (m, 4.5 Hz, 2H, N≡CCH$_2$-Ph). ^{13}C\{^{1}H\} NMR (CDCl$_3$, δ): 159.50 (C=N−H); 150.34 (C=N−Ph); 134.95 (C$_{ipso}$); 129.66, 129.16, 128.98, 128.76, 128.48, 127.95, 127.58, 127.46, 125.35 (carbons in Ph's); 115.65 (N≡C); 45.35 (Ph*CH$_2$*C=N); 23.90 (Ph*CH$_2$*C=N). ^{195}Pt NMR (CDCl$_3$, δ): −2296 (1151 Hz).

[PtCl(NCPh)\{NH=C(Ph)NHC(Ph)=NPh\}] (10). Anal. Calcd for C$_{27}$H$_{22}$N$_4$ClPt: C, 51.31; H, 3.35; N, 8.86. Found: C, 51.38; H, 3.48; N, 8.70%. FAB$^+$ MS, m/z: 632 [M]$^+$, 596 [M − Cl]$^+$, 529 [M − PhCN]$^+$, 492 [M − HCl − PhCN]$^+$. mp = 213 °C (dec). TLC: R_f = 0.50 (eluent CH$_2$Cl$_2$). IR (KBr, selected bands, cm^{-1}): 3359 (m), 3340 (m), ν(N−H); 2281 (w), ν(C≡N); 1540 (ms), ν(C=N and C=C from Ar); 1456 (s), ν(C=C from Ar); 698 (m), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.95 (d, 2H, o-PhC≡N from nitrile), 7.81 (d, 2H, PhC=N from nitrile), 7.57−7.11 (m, 15H, Ph's), 6.88 (t, 1H, p-Ph). ^{13}C\{^{1}H\} NMR (CDCl$_3$, δ): 158.66 (C=N−H); 150.93 (C=N−Ph); 134.23, 132.92, 130.45, 128.95, 128.57, 127.95, 127.76, 127.44, 127.26, 126.93, 125.48 (carbons in Ph's); 109.65 (C≡N). ^{195}Pt NMR (CDCl$_3$, δ): −2256 (1029 Hz).

[PtCl(NCNEt$_2$)\{NH=C(NEt$_2$)NC(Ph)=NPh\}] (11). Anal. Calcd for C$_{23}$H$_{31}$N$_6$ClPt: C, 44.34; H, 5.18; N, 13.49. Found: C, 44.46; H, 5.32; N, 13.29%. FAB$^+$ MS, m/z: 622 [M]$^+$, 593 [M − Et]$^+$, 587 [M − Cl]$^+$. mp = 199 °C (dec). TLC: R_f = 0.54 (eluent CH$_2$Cl$_2$). IR (KBr, selected bands, cm^{-1}): 3395 (m), ν(N−H); 2287 (sm),

Nitrile−Amidine Coupling at Pt(IV) and Pt(II) Centers

Table 1. Crystal Data for Compounds **4**, **6**, **8**, and **15**

	4	**6**	**8**	**15**
empirical formula	$C_{36}H_{44}Cl_4N_8Pt$	$C_{36}H_{42}Cl_2N_8Pt$	$C_{19}H_{21}ClN_4Pt$	$C_{72}H_{84}N_{16}Pt_2$
fw	925.68	852.77	535.94	1563.73
temp (K)	110(2)	100(2) K	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	10.9802(16)	9.3749(3)	12.1385(8)	12.3627(3)
b (Å)	19.4181(18)	9.6825(4)	10.4006(8)	12.9400(4)
c (Å)	9.6964(11)	19.2244(7)	15.0235(10)	22.0075(6)
a (deg)	90	90	90	77.720(2)
β (deg)	112.080(10)	103.766(3)	90.997(6)	83.761(2)
γ (deg)	90	90	90	71.5490(10)
V (Å^3)	1915.8(4)	1694.92(11)	1896.4(2)	3259.97(16)
Z	2	2	4	2
ρ_{calc} (Mg/m^3)	1.605	1.671	1.877	1.593
μ(Mo Kα) (mm^{-1})	3.979	4.337	7.549	4.343
R1^a ($I \geq 2\sigma$)	0.0308	0.0239	0.0165	0.0323
wR2^b ($I \geq 2\sigma$)	0.0558	0.0576	0.0355	0.0734

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

ν(C≡N); 1559 (s), ν(C=N and C=C from Ar); 1469 (s), ν(C=C from Ar); 701 (m), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.02 (m, 9*H*, Ph), 6.83 (t, 1*H*, *o*-Ph), 7.10 (t, 2*H*, *m*-Ph), 7.07 (m, 5*H*, Ph), 5.56 (s, br, 1*H*, NH), 3.41 (q, 4*H*) and 1.17 (t, 6*H*) (Et$_2$NC=N), 2.75 (q, 4*H*) and 1.01 (t, 6*H*) (Et$_2$NC≡N). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 187.03 (C=N−H); 151.82 (C=N−Ph); 129.53 (C$_{ipso}$); 128.63, 128.13, 127.17, 126.85, 126.60, 124.20 (carbons in Ph's); 45.19 and 12.76 (Et$_2$NC=N); 42.85 and 13.51 (Et$_2$NC≡N). ^{195}Pt NMR (CDCl$_3$, δ): −2273 (788 Hz).

Reaction of *trans*-[PtCl$_2$(RCN)$_2$] and the Amidine (4 Equiv). General Method B. *trans*-[PtCl$_2$(RCN)$_2$] (0.053 mmol) (R = Et, NEt$_2$) and PhC(=NH)NHPh (42 mg, 0.212 mmol) were dissolved in CH$_2$Cl$_2$ (0.5 mL) and left at 40 °C. For R = Et, the pale-yellow needles appeared on the top of the vial after 3 d. They were filtered off and mechanically separated from the colorless crystals of byproduct PhC(=NH)NHPh·HCl. For R = Et, crystals can be dissolved in warm CH$_2$Cl$_2$; the solvent was separated from the colorless crystals and evaporated to give the product. For R = NEt$_2$, after 5 d, a yellow solution with colorless crystals of PhC(=NH)-NHPh·HCl (**7**) was obtained, the crystals were filtered off, and the filtrate was evaporated to half of its volume, whereupon Et$_2$O (0.2 mL) was added dropwise. The released yellow precipitate was filtered off, washed with Et$_2$O (0.5 mL), and dried. Yields: 50 and 35% for R = Et and NEt$_2$, respectively. The complexes with R = CH$_2$Ph (**13**) and Ph (**14**) are prepared analogously.

[Pt{*N*H=C(Et)NC(Ph)*N*Ph}$_2$] (12). Anal. Calcd for C$_{32}$H$_{32}$N$_6$-Pt·Et$_2$O: C, 55.73; H, 5.09; N, 11.47%. Found: C, 55.75; H, 4.87; N, 11.41%. FAB$^+$ MS, *m/z*: 696 [M + H]$^+$. mp = 207 °C (dec). TLC: R_f = 0.47 (eluent CH$_2$Cl$_2$/acetone = 1:1). IR (KBr, selected bands, cm^{-1}): 3347 (m), ν(N−H); 1632 (m), ν(C=N); 1561 (ms), ν(C=N and C=C from Ar); 1446 (s), 1430 (s), ν(C=C from Ar); 697 (ms), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.22 (t, 2*H*, *m*-Ph), 7.05 (m, 8*H*, Ph), 5.77 (s, br, 1*H*, NH), 2.04 (q, 7.5 Hz, 2*H*) and 0.56 (t, 7.5 Hz, 3*H*) (EtC=N). ^{13}C{^{1}H}NMR (CDCl$_3$, δ): 163.03 (C=N−H); 145.86 (C=N−Ph); 128.85, 128.29, 127.47, 127.24, 125.99 (carbons in Ph's); 32.92 and 9.48 (*Et*C=N). ^{195}Pt NMR (CDCl$_3$, δ): −2145 (538 Hz).

[Pt{*N*H=C(CH$_2$Ph)NC(Ph)=*N*Ph}$_2$] (13). Anal. Calcd for C$_{42}$H$_{36}$N$_6$Pt: C, 61.53; H, 4.43; N, 10.25. Found: C, 61.49; H, 4.80; N, 10.26%. FAB$^+$ MS, *m/z*: 820 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3339 (ms), ν(N−H); 1558 (s), ν(C=N and C=C from Ar); 1448 (s), ν(C=C from Ar); 697 (ms), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.22 and 7.01 (m, 15*H*, Ph), 5.61 (s, br, 1*H*, NH), 3.30 (m, 4.5 Hz, 2*H*, N=CC*H*$_2$Ph). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 129.26, 128.57, 127.60, 127.47, 127.31, 126.88, 126.20 (carbons in Ph) (Ph*C*H$_2$C=N and C=N were not detected). ^{195}Pt NMR (CDCl$_3$, δ): −2261 (540 Hz).

[Pt{*N*H=C(Ph)NC(Ph)=*N*Ph}$_2$] (14). Anal. Calcd for C$_{40}$H$_{32}$N$_6$-Pt: C, 60.68; H, 4.07; N, 10.61. Found: C, 60.54; H, 4.52; N, 10.60%. FAB$^+$ MS, *m/z*: 792 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3350 (ms), ν(N−H); 1540 (s), ν(C=N and C=C from Ar); 1465 (ms), ν(C=C from Ar); 702 (m), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.30 (m, 4*H*), 7.16 (m, 8*H*) and 7.08 (m, 3*H*) (Ph), 6.38 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 156.15 and 156.05 (2 C=N); 129.11, 128.40, 128.06, 127.59, 127.22, 126.39, 125.85 (carbons in Ph). ^{195}Pt NMR (CDCl$_3$, δ): −2270 (520 Hz).

[Pt{*N*H=C(NEt$_2$)NC(Ph)=*N*Ph}$_2$] (15). Anal. Calcd for C$_{36}$H$_{42}$N$_8$Pt: C, 55.30; H, 5.41; N, 14.33. Found: C, 55.46; H, 5.61; N, 13.93%. FAB$^+$ MS, *m/z*: 783 [M + H]$^+$. mp = 209 °C. TLC: R_f = 0.47 (eluent Et$_2$O/CH$_2$Cl$_2$ = 1:4). IR (KBr, selected bands, cm^{-1}): 3392 (ms), ν(N−H); 1541 (s), ν(C=N and C=C from Ar); 1471 (s), ν(C=C from Ar); 695 (m), δ(C−H). ^{1}H NMR (CDCl$_3$, δ): 7.11 and 7.08 (2 m, 10*H*, Ph), 3.84 (s, br, 1*H*, NH), 2.81 (q, 4*H*) and 0.79 (t, 6*H*) (Et$_2$NC=N). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 160.82 (C=N−H); 150.57 and 147.79 (C=N−Ph); 129.52, 129.28, 128.70, 128.53, 127.77, 127.17, 126.75, 126.09, 124.87, 122.32 (carbons in Ph's); 41.85 and 13.70 (Et$_2$NC=N). ^{195}Pt NMR (CDCl$_3$, δ): −2259 (441 Hz).

Reaction of *cis*-[PtCl$_2$(RCN)$_2$] and the Amidine (2 Equiv). A solution of the amidine HN=C(Ph)NHPh (106.8 mg, 0.54 mmol) in CHCl$_3$ (2 mL) was added dropwise to a suspension of *cis*-[PtCl$_2$-(EtCN)$_2$] (100 mg, 0.27 mmol) in CHCl$_3$ (3 mL) {or *cis*-[PtCl$_2$-(MeCN)$_2$] in MeCN}. The reaction mixture was left to stand for 1 h at 40 °C; during this time, a pale-yellow powder of the product started to release. The product was filtered off, washed with Et$_2$O (three 4-mL portions), and dried in the air. Yield is 50−60%.

[PtCl$_2${*N*H=C(Me)N=C(Ph)*N*HPh}] (16). Anal. Calcd for C$_{15}$H$_{15}$N$_3$Cl$_2$Pt: C, 35.80; H, 3.00; N, 8.35. Found: C, 36.14; H, 3.36; N, 8.50%. FAB$^+$ MS, *m/z*: 503 [M]$^+$, 468 [M − Cl + H]$^+$. The compound has no characteristic mp; upon heating, it decomposes above 255 °C. TLC: R_f = 0.70 (eluent CH$_2$Cl$_2$/acetone = 1:1). IR (KBr, selected bands, cm^{-1}): 3345 (m), 3230 (m), 3187 (m), ν(N−H); 1685 (s), 1629 (ms), ν(C=N); 1527 (s), ν(C=C from Ar); 696 (m), δ(C−H). ^{1}H NMR (DMSO-*d*$_6$, δ): 10.07 (s, br, 1*H*, NH), 7.39 (s, br, 1*H*, NH), 6.8−7.2 (m, 10*H*, two Ph), 1.99 (s, 3*H*, Me).

[PtCl₂{*N*H=C(Et)N=C(Ph)*N*HPh}] (17). Anal. Calcd for $C_{16}H_{17}N_3Cl_2Pt$: C, 37.15; H, 3.31; N, 8.12. Found: C, 37.27; H, 3.33; N, 7.84%. FAB$^+$ MS, m/z: 517 [M]$^+$, 482 [M − Cl + H]$^+$, 444 [M − 2HCl]$^+$. The compound has no characteristic mp, and upon heating, it decomposes above 285 °C. TLC: R_f = 0.60 (eluent CH₂Cl₂/acetone = 3:1). IR (KBr, selected bands, cm^{-1}): 3349 (m), 3230 (m), 3188 (m), ν(N−H); 1688 (s), 1628 (ms), ν(C=N); 1529 (s), ν(C=C from Ar); 807 (m), 695 (m), δ(C−H). ^{1}H NMR (DMSO-d_6, δ): 11.33 (s, br, 1H, NH), 9.98 (s, br, 1H, NH), 6.3−7.3 (m, 10H, 2 Ph), 3.32 (q, 7.4 Hz, 2H, CH₂), 1.14 (t, 7.4 Hz, 3H, CH₃).

X-ray Structure Determinations. The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer. The Denzo-Scalepack[29] or EvalCCD[30] program packages were used for cell refinements and data reduction. Structures were solved by direct methods using the SHELXS-97 or SIR-2002 programs.[31,32] A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL version 6.12 or SADABS version 2.05)[33,34] was applied to all data (T_{min}/T_{max} values were 0.5345/0.8168, 0.14737/0.22322, 0.22453/0.26323, 0.3136/0.7040, and 0.12102/0.20939 for **4**, **6−8**, and **15**, respectively). All structures were refined with SHELXL-97[35] and the WinGX graphical user interface.[36] In **4**, NH hydrogens were located from the difference Fourier map and refined isotropically. In **8**, NH hydrogens were also located from the difference Fourier map but not refined. All other hydrogens were placed in idealized positions and constrained to ride on their parent atom. The asymmetric unit of **15** contains a complete molecule and two halves, which have been labeled as molecules B and C. The crystallographic details for **4**, **6**, **8**, and **15** are summarized in Table 1, and the selected bond lengths and angles are found in the figure captions. The crystallographic details of **7** are given as Supporting Information.

Supporting Information Available: Crystallographic data in CIF format. Tables of crystallographic data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles, and hydrogen bonds for **4**, **6**, **7**, **8**, and **15**. Thermal ellipsoid view of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. *Methods in Enzymology, Macromolecular Crystallography, Part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276, pp 307−326.

(30) Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr.* **2003**, *36*, 220.

(31) Sheldrick, G. M. *SHELXS-97*; University of Göttingen, Göttingen, Germany, 1997.

(32) Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2003**, *36*, 1103.

(33) Sheldrick, G. M. *SHELXTL*, version 6.14; Bruker AXS, Inc.: Madison, WI, 2003.

(34) Sheldrick, G. M. *SADABS*, version 2.05; Bruker Axs, Inc.: Madison, WI, 2002.

(35) Sheldrick, G. M. *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

(36) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.