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Pop-the-Cork Strategy in Synthetic Utilization of Imines: Stabilization by Complexation and Activation via Liberation of the Ligated Species

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Treatment of *trans*-$[PtCl_4(RCN)_2]$ (R = Me, Et) with ethanol allowed the isolation of *trans*-$[PtCl_4\{E\text{-}NH{=}C(R)OEt\}_2]$. The latter were reduced selectively, by the ylide $Ph_3P{=}CHCO_2Me$, to *trans*-$[PtCl_2\{E\text{-}NH{=}C(R)OEt\}_2]$. The complexed imino esters NH=C(R)OEt were liberated from the platinum(II) complexes by reaction with 2 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) in chloroform; the cationic complex $[Pt(dppe)_2]Cl_2$ precipitates almost quantitatively from the reaction mixture and can be easily separated by filtration to give a solution of NH=C(R)OEt with a known concentration of the imino ester. The imino esters efficiently couple with the coordinated nitriles in *trans*-$[PtCl_4(EtCN)_2]$ to give, as the dominant product, $[PtCl_4\{NH{=}C(Et)N{=}C(R)OEt\}_2]$ containing a previously unknown linkage, i.e., ligated *N*-(1-imino-propyl)-alkylimidic acid ethyl esters. In addition to $[PtCl_4\{NH{=}C(Et)N{=}C(Et)OEt\}_2]$, another compound was generated as the minor product, i.e., $[PtCl_4(EtCN)\{NH{=}C(Et)N{=}C(Et)OEt\}]$, which was reduced to $[PtCl_2(EtCN)\{NH{=}C(Et)N{=}C(Et)OEt\}]$, and this complex was characterized by X-ray single-crystal diffraction. The platinum(IV) complexes $[PtCl_4\{NH{=}C(Et)N{=}C(R)OEt\}_2]$ are unstable toward hydrolysis and give EtOH and the acylamidine complexes *trans*-$[PtCl_4\{Z\text{-}NH{=}C(Et)NHC(R){=}O\}_2]$, where the coordination to the Pt center results in the predominant stabilization of the imino tautomer NH=C(Et)NHC(R)=O over the other form, i.e., $NH_2C(Et){=}NC(R){=}O$, which is the major one for free acylamidines. The structures of *trans*-$[PtCl_4\{Z\text{-}NH{=}C(Et)NHC(R){=}O\}_2]$ (R = Me, Et) were determined by X-ray studies. The complexes $[PtCl_4\{NH{=}C(Et)N{=}C(R)OEt\}_2]$ were reduced to the appropriate platinum(II) compounds $[PtCl_2\{NH{=}C(Et)N{=}C(R)OEt\}_2]$, which, similarly to the appropriate Pt(IV) compounds, rapidly hydrolyze to yield the acylamidine complexes $[PtCl_2\{NH{=}C(Et)NHC(R){=}O\}_2]$ and EtOH. The latter acylamidine compounds were also prepared by an alternative route upon reduction of the corresponding platinum(IV) complexes. Besides the first observation of the platinum(IV)-mediated nitrile–imine ester integration, this work demonstrates that the application of metal complexes gives new opportunities for the generation of a great variety of imines (sometimes unreachable in pure organic chemistry) in metal-mediated conversions of organonitriles, the "storage" of imino species in the complexed form, and their synthetic utilization after liberation.

Introduction

In general, imines RR′C=NR″ are rather reactive species and often unstable toward hydrolysis and also involved in di-, tri-, and polymerizations and in various redox type conversions. In particular, the imines RR′C=NH with two donor substituents are usually so reactive in hydrolysis and trimerizations that some of these compounds are commonly treated as *elusive*.[1]

Even though it has since long been known that most of the imine reactions are affected by metal ions, surprisingly, a fundamental theory predicting metal control on the reactivity of imines has not yet been devised.[2] Indeed, the reactions of coordinated imines strongly depend on a delicate (and in

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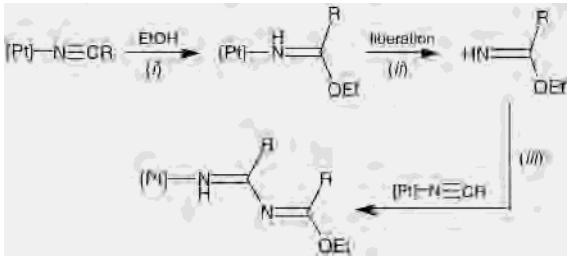
many instances unpredictable) balance between such factors as fine structure of the ligand and nature of the metal center. Thus, imines with very close structural characteristics being ligated to a metal center can exhibit even the opposite reactivity modes, for example, stabilization vs activation toward hydrolysis.[2]

Recently we (see reviews[3]) and others[4] found explicit evidence that platinum group metals,[5−9] rhenium,[10] gold,[11a,b] or silver[11c] centers provide enormous stabilization of the potentially unstable imines RR′C═NH, and these ligands can be "stored" without changes in the coordinated form under normal conditions for a prolonged time. Moreover, it appears that the formation of imines is one of the major driving forces for some reactions, e.g., condensation of complexed ammonia with ketones,[11] reductions of oximes,[12] oxidative dehydration of amines (e.g., at Fe,[13] Ru,[14,15] Os,[16] Re,[17] and Pt[18] centers), and nucleophilic additions to metal-bound nitriles.[3,4] We expected that the combination of the inertness of *coordinated* imines RR′C═NH with their high reactivity in the *free state* could have some intrinsic practical, albeit not yet explored, implications. Indeed, if the imine complex forms and if the further replacement of the ligated imines is carried out in nonaqueous dried solvents and the new complex (without imine) precipitates and is removed by filtration, the liberated reactive imines present in the filtrate can be immediately used in situ for further reactions, and we felt that this methodology warranted investigation.

Scheme 1



Taking into account our interest in the reactions of metal-activated organonitriles in general and the interest in the nitrile−imine coupling[3] in particular, the suggested research plan of the present work was the following (Scheme 1): (i) To use a metal center as the promoter for the formation of imines which are unstable in the free state. For this part of the study we addressed $[PtCl_4(RCN)_2]$ (R = Me, Et) compounds and EtOH insofar as it has been demonstrated[8] that the Pt(IV) center provides the facile hydroxide-free nitrile−alcohol coupling to achieve imino ester complexes. The latter species contain the imines unreactive in the complexed form, while the free imino esters are quite reactive in acid-free media.[19] (ii) To perform the liberation of the coordinated imines. Despite the overall inertness of the imino ester complexes toward substitution, some specific displacement methods have been previously developed,[8,9,20,21] and it was anticipated to apply them for the liberation. (iii) To employ the released imines in situ for further reactions by studying the yet unknown Pt(IV)-mediated nitrile−imino ester coupling giving 1,3-diaza-1,3-dienes. All these results—indicating new directions in the synthetic utilization of imines and their complexes and showing novel routes to 1,3-diaza-1,3-diene and acylamidine species—are reported herein.

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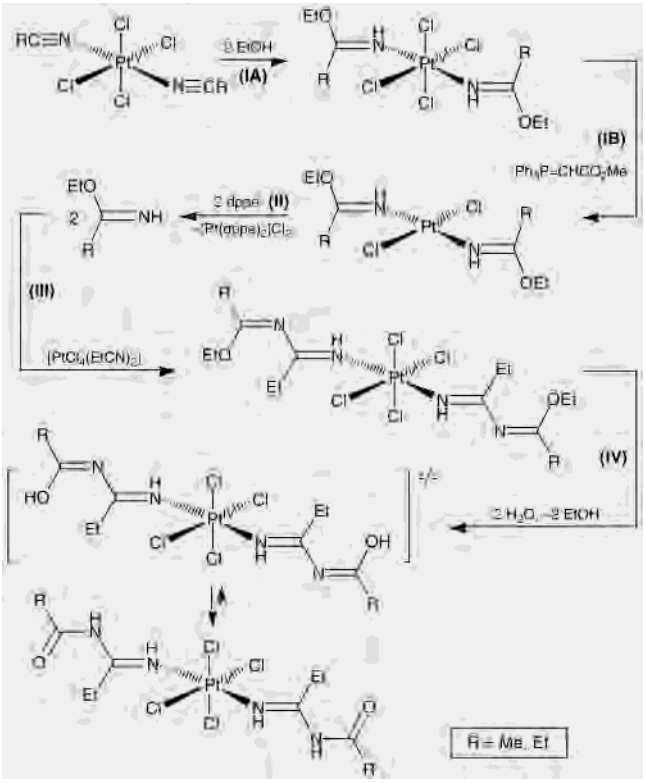
Scheme 2



Results and Discussion

Steps I and II: Complexed Imino Esters and Their Liberation. We have recently reported that, in contrast to the well-known (nitrile)Pt(II) systems,[3] the addition of alcohols to organonitrile platinum(IV) complexes occurs under mild conditions and does not require a base as a catalyst.[8] Thus, treatment of *trans*-$[PtCl_4(RCN)_2]$ (R = Me, Et) with ethanol at 45 °C allowed the isolation of the *trans*-$[PtCl_4\{E\text{-}NH{=}C(R)OEt\}_2]$ imino ester complexes (Scheme 2, step IA). These complexes were reduced selectively, by the ylide $Ph_3P{=}CHCO_2Me$ in accord with a recently described method,[7b] to the corresponding isomers of (imino ester)Pt(II) species *trans*-$[PtCl_2\{E\text{-}NH{=}C(R)OEt\}_2]$ (R = Me **1**, R = Et **2**) without change in configuration of the imino ester ligands (step IB). The coordinated imino ester species exhibit significant stability and the solid complexes remain intact for at least 6 months. In step II, the imino esters NH=C(R)OEt (R = Me **3**, R = Et **4**) were liberated from the platinum(II) complexes **1** and **2** by reaction with 2 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) in chloroform. The cationic complex $[Pt(dppe)_2]Cl_2$ precipitates almost quantitatively from the reaction mixture and can be easily separated by filtration to give a solution of NH=C(R)OEt (**3** or **4**) with a known concentration of the imino ester. The liberated imino esters were used in step III for the coupling.

Step III: Nitrile−Imine Ester Coupling. In spite of the wealth of reports on the metal-mediated RCN−amine integration[3] (recent examples of the C−N bond making include molybdenum-[22] and platinum-mediated[23] amine−nitrile coupling, and the formation of amidines from conversions of alkyl nitriles at a Pt(II) center[24] or on $Re_4Te_4(TeCl_2)_4Cl_8$ clusters[25] or imidoylamidines at a Ni(II) center[26]), only a few works deal with nitrile−imine (or heteroimine) coupling, i.e., the addition of $Ph_2C{=}NH$ to Pt(IV)-bound nitriles[27] and of $Ph_2S{=}NH$ to organonitriles at Pt(II)[28] and Pt(IV)[29] centers; both $Ph_2C{=}NH$ and $Ph_2S{=}NH$ exhibit substantial *stability* toward hydrolysis and dimerization. The coupling between complexed nitriles and *unstable* (or reactive) imines in general and imino esters in particular is yet an uncovered area of nitrile chemistry. In the present work, it has been found that the imino esters efficiently couple in step III with the nitriles in *trans*-$[PtCl_4(EtCN)_2]$ to give complexed 1,3-diaza-1,3-diene species, and this is the first observation of nitrile−imine ester integration.

Thus, to achieve 1,3-diaza-1,3-diene complexes, a ca. 10-fold excess of the imino ester (prepared in step II) is added to *trans*-$[PtCl_4(EtCN)_2]$ in $CHCl_3$ at room temperature, and the solvent is evaporated almost immediately to give $[PtCl_4\{NH{=}C(Et)N{=}C(R)OEt\}_2]$ (R = Me **5**, R = Et **6**) as the dominant product (Scheme 2, step III). Both **5** and **6** gave satisfactory C, H, N elemental analyses and expected fragmentation/isotopic patterns in FAB^+ mass spectra. IR spectra display two stretching vibrations due to the different C=N bonds [1699 and 1613 cm^{-1} for **5** and 1698 and 1617 cm^{-1} for **6**], and also two C=N carbons [179.6 and 159.9 ppm for **5** and 178.8 and 162.4 ppm for **6**] from the NH=C(Et)N=C(R)OEt species were observed in the $^{13}C\{^1H\}$ NMR spectra. The imino hydrogen was identified by the characteristic IR ν(N−H) stretching vibrations and for **6** a broad ^1H NMR signal from *H*N displayed at 7.11 ppm (this signal was not observed for **5** probably due to the line broadening).

In addition to **6**, another compound was generated as the minor product, i.e., $[PtCl_4(EtCN)\{NH{=}C(Et)N{=}C(Et)OEt\}]$ (**7**). The latter has been separated after column chromatography on silica gel. Despite the small isolated amount, we succeeded to characterize **7** by FAB-MS and ^1H NMR spectroscopy (see Experimental Section) and also to reduce this compound to the platinum(II) complex $[PtCl_2(EtCN)\{NH{=}C(Et)N{=}C(Et)OEt\}]$ (**8**) and to perform the X-ray crystallographic study (Figure 1). The X-ray single-crystal diffraction study of **8** revealed a planar environment around the metal center and the overall trans geometry with the NH=C(Et)N=C(Et)OEt ligand in the *Z* configuration having bond

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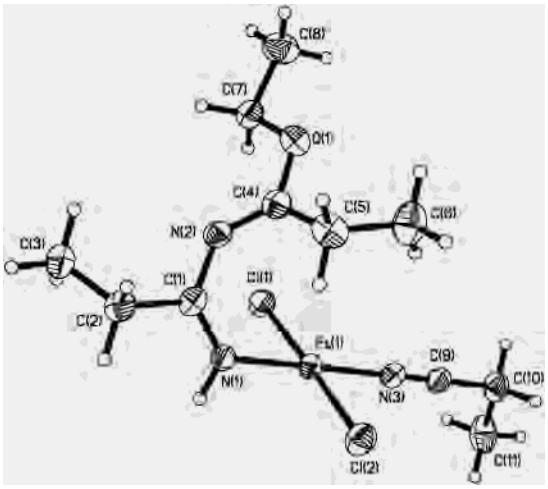

Figure 1. Molecular structure of **8**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt(1)−Cl(1) 2.305(2), Pt(1)−Cl(2) 2.299(2), Pt(1)−N(1) 1.987(5), Pt(1)−N(3) 1.983(5), N(1)−C(1) 1.287(7), C(1)−N(2) 1.364(8), N(2)−C(4) 1.283(8), C(4)−O(1) 1.337(8), C(4)−C(5) 1.488(9), O(1)−C(7) 1.452(8), N(3)−C(9) 1.125(8), C(9)−C(10) 1.466(9), Pt(1)−N(1)−C(1) 130.2(4), C(1)−N(2)−C(4) 125.8(6), N(2)−C(4)−O(1) 118.8(6), N(2)−C(4)−C(5) 128.3(6), C(4)−O(1)−C(7) 117.2(5).

lengths and angles of normal values.[27−30] In **8**, the newly formed ligand [*N*-(1-imino-propyl)-alkylimidic acid ethyl esters] represents the previously unknown linkage.

It was proved that both **3** and **4** do not react with EtCN under the reaction conditions. Furthermore, no side reactions were reported for the first step of the Pinner synthesis[3] when imino esters are formed (in the absence of any activating metal center) from nitriles and both species are jointly present in the reaction mixture. All this implies that the nitrile−imine ester coupling is metal mediated. We believe that the (1,3-diaza-1,3-diene)Pt(IV) complexes are presumably formed by nucleophilic attack of the imine N atom on the electrophilically activated carbon atom of the organonitrile.

One further point deserves discussion. In many instances, the synthetic utilization of imines involves their hydrochlorides insofar as the protonation stabilizes RR′C═NH from other reactions. Step III illustrates some advantages of the application of metal-bound imines over their HCl salts. Indeed, careful neutralization of 1 equiv of HCl in *nonaqueous* media is often a technically complicated task especially when the synthesis is performed in microscales. Moreover, products of neutralization, e.g., H_2O, can affect the condition of either the imines or a product of its transformation. Similarly to protonation, coordination to a metal center stabilizes imines and they can be stored in the complexed form for a prolonged time, but their liberation in many instances is easier to perform than that of dehydrochlorination. If the substitution is conducted in nonaqueous dried solvents and the complex formed is separated (e.g., by filtration), the liberated imines can be used in situ for further reactions.

Step IV: Hydrolysis of the Coordinated 1,3-Diaza-1,3-dienes. The complexes $[PtCl_4\{NH{=}C(Et)N{=}C(R)OEt\}_2]$ (**5**, **6**), prepared in step III, are unstable toward hydrolysis. When **5** or **6** was dissolved in $CDCl_3$ containing traces of water, the formation of both EtOH and a new platinum complex was observed. The latter was isolated upon column chromatography with nondried eluents. Physicochemical data along with X-ray crystallography (Figures 2 and 3) for the complexes *trans*-$[PtCl_4\{Z\text{-}NH{=}C(Et)NHC(R){=}O\}_2]$ (R = Me **9**, R = Et **10**) allowed the establishment of the acylamidine structure of the ligated imino species. Indeed,

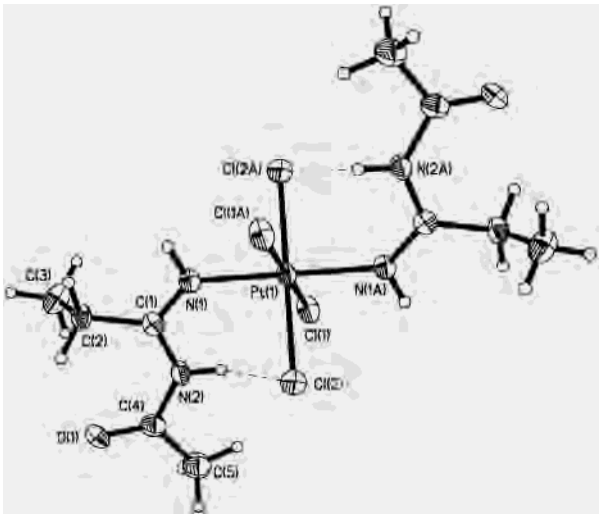

Figure 2. Molecular structure of **9**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt(1)−Cl(1) 2.3201(11), Pt(1)−Cl(2) 2.3239(11), Pt(1)−N(1) 2.022(4), N(1)−C(1) 1.293(6), C(1)−C(2) 1.508(6), C(1)−N(2) 1.360(6), N(2)−C(4) 1.388(6), C(4)−O(1) 1.215(6), C(4)−C(5) 1.497(7), Cl(1)−Pt(1)−Cl(2) 90.43(5), N(1)−Pt(1)−Cl(1) 94.15(11), N(1)−Pt(1)−Cl(2) 92.11(12), Pt(1)−N(1)−C(1) 134.2(3), N(1)−C(1)−N(2) 119.7(4), N(1)−C(1)−C(2) 119.2-(4), C(1)−N(2)−C(4) 129.6(4), N(2)−C(4)−O(1) 122.5(5), N(2)−C(4)−C(5) 114.2(4), N(2)···Cl(1) 3.150(4), N(2)−H(2)···Cl(2) 149.8.

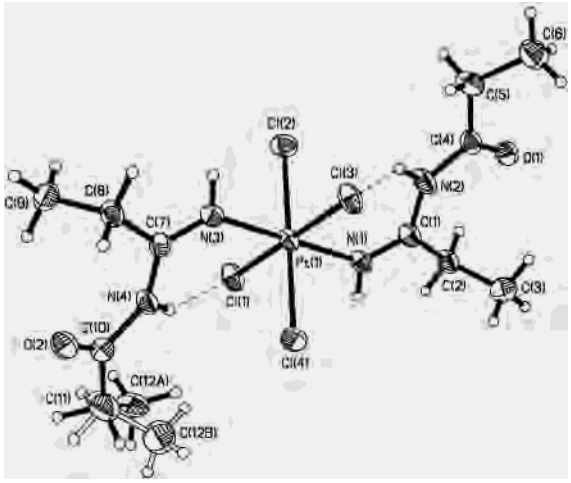

Figure 3. Molecular structure of **10**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt(1)−Cl(1) 2.3192(9), Pt(1)−Cl(2) 2.3207(10), Pt(1)−Cl(3) 2.3300(9), Cl(4)−Pt(1) 2.3145(10), Pt(1)−N(1) 2.025(3), Pt(1)−N(3) 2.031(3), C(1)−N(1) 1.291(5), C(1)−N(2) 1.369(5), N(2)−C(4) 1.382(5), C(4)−O(1) 1.212(5), N(3)−C(7) 1.291(5), C(7)−N(4) 1.370(5), N(4)−C(10) 1.400(5), C(10)−O(2) 1.205(5), C(10)−C(11) 1.492(7), C(11)−C(12A) 1.371(10), C(11)−C(12B) 1.439(12), Cl(1)−Pt(1)−Cl(3) 179.08(4), Cl(2)−Pt(1)−Cl(4) 179.18(4), N(1)−Pt(1)−N(3) 179.52(13), N(3)−C(7)−N(4) 119.0(3), N(4)−C(10)−O(2) 121.9(4), N(1)−C(1)−C(2) 120.6(3), N(2)−C(4)−O(1) 122.3(4), N(2)···Cl(3) 3.126(3), N(2)−H(2)···Cl(3) 143.3, N(4)···Cl(1) 3.238(3), N(4)−H(4)···Cl(1) 150.9.

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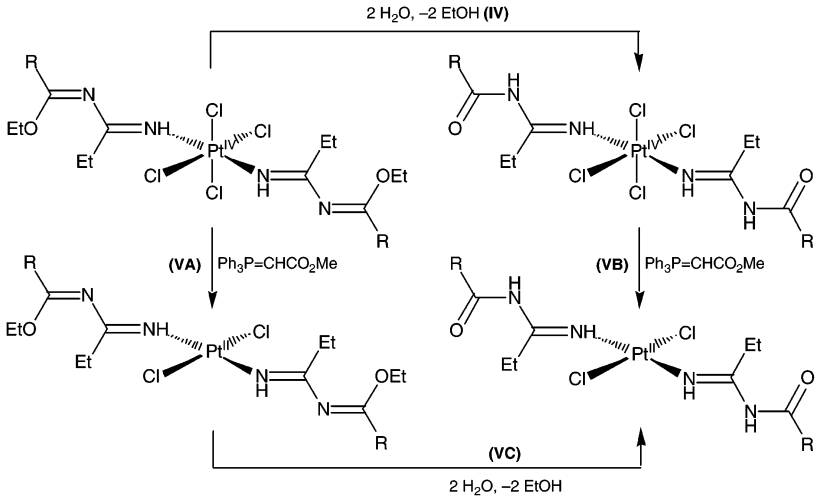
Scheme 3



the N═C bonds in the Pt−N(H)═C moieties and the C═O bonds have typical double-bond character, while the two bonds in the C−N(H)−C moiety are single ones. Coordination to the Pt center results in the predominant stabilization of the imino tautomer NH═C(Et)NHC(R)═O over the other form, i.e., $NH_2C(Et)$═NC(R)═O. The imino tautomer is the minor one when the acylamidines are free.[31] Presumably **9** and **10** are formed via the $[PtCl_4\{NH═C(Et)N═C(R)OH\}_2]$ intermediate (Scheme 2) followed by its conversion to *trans*-$[PtCl_4\{NH═C(Et)NHC(R)═O\}_2]$.

It is worthwhile to mention that although acylamidines are well-known species,[32,33] their coordination chemistry is still poorly investigated and reported examples are restricted only to copper(II)[31] and nickel(II)[34] complexes where acylamidines form *N,O-chelates*. Structures **9** and **10** are the first ones where these ligands are involved in the *monodentate* coordination.

Step V: Synthesis of 1,3-Diaza-1,3-diene Pt(II) Complexes and Hydrolysis of the 1,3-Diaza-1,3-diene Ligands. We endeavored to verify an oxidation state dependence of the hydrolysis, and for this reason complexes $[PtCl_4\{NH═C(Et)N═C(R)OEt\}_2]$ (**5**, **6**) were reduced, by the ylide $Ph_3P═CHCO_2Me$ (Scheme 3, step VA), to the appropriate platinum(II) compounds $[PtCl_2\{NH═C(Et)N═C(R)OEt\}_2]$ (R = Me **11**, R = Et **12**). The latter have physicochemical characteristics similar to those of the parent platinum(IV) compounds; the most significant difference was observed in the ^{195}Pt NMR spectra, which display a ca. 2000 ppm shift. Both **11** and **12** are unstable toward hydrolysis in the presence of traces of water and give, in step VC, the acylamidines $[PtCl_2\{NH═C(Et)NHC(R)═O\}_2]$ (**13**, **14**) and EtOH. The complexes **13** and **14** were also prepared by the alternative route VB upon reduction of the corresponding platinum(IV) complexes. In the NMR experiments, we do not feel the difference in the hydrolysis rates of the Pt(IV) and Pt(II) complexes.

Final Remarks. The results from this work may be considered from two perspectives. From a *narrower*, specific point of view it demonstrates that the addition of imino esters to coordinated organonitriles is Pt(IV)-mediated and leads to ligated previously unknown 1,3-diaza-1,3-dienes and the reaction represents the first example of nitrile−imino ester coupling. We are continuing to explore the metal-mediated nitrile−imine integration and to apply for that purpose more labile systems, e.g., involving high oxidation state hard metal centers, on one hand, to achieve a high metal-activation effect for such reactions with an easier liberation of the 1,3-diaza-1,3-diene ligands and, on the other hand, to discover novel routes for generation of aza compounds and/or nitrogen heterocycles under catalytic conditions, and this work will be reported in due course. The possibility of stepwise assembly of imines and nitriles, namely, by a sequence of double steps as those achieved in this work consisting of the liberation of the coupled ligand followed by its new coupling to a nitrile ligand, appears particularly promising to the metal-mediated synthesis of polyimines or aza heterocycles formed upon secondary conversions of the polyimines.

In a *broader sense*, the work shows that the application of metal complexes gives new opportunities for (i) the generation of a great variety of imines (sometimes unreachable in pure organic chemistry) in the metal-mediated conversions of organonitriles,[3] (ii) the "storage" of imino species in the complexed form, and (iii) their synthetic utilization after liberation. It is anticipated that all these issues combined together might have a further impact on both coordination and organic chemistries of imines.

Experimental Section

Materials and Instrumentation. Solvents were obtained from commercial sources and used as received. $[PtCl_4(RCN)_2]$ (R = Me, Et) were prepared accordingly to the published method.[35] C, H,

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(33) For recent works on acylamidines see: Cunha, S.; Kascheres, A. *J. Braz. Chem. Soc.* **2001**, *12*, 481; *Chem. Abstr.* **2001**, *135*, 303742. Thiagarajan, K.; Puranik, V. G.; Deshmukh, A. R. A. S.; Bhawal, B. M. *Tetrahedron* **2000**, *56*, 7811.
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Table 1. Crystal Data for Compounds **8**−**10**

	8	**9**	**10**
empirical formula	$C_{11}H_{21}N_3Cl_2OPt$	$C_{10}H_{20}N_4Cl_4O_2Pt$	$C_{12}H_{24}N_4Cl_4O_2Pt$
fw	477.30	569.19	593.24
temp (K)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	tetragonal	tetragonal
space group	$P2_1/c$	$P4_2/n$	$I4_1/a$
a (Å)	7.7388(3)	14.9692(2)	21.2748(2)
b (Å)	12.3831(5)	14.9692(2)	21.2748(2)
c (Å)	17.0456(8)	8.6265(2)	17.5715(2)
β (deg)	97.886(3)	90	90
V (Å^3)	1618.04(12)	1933.00(6)	7953.16(14)
Z	4	4	16
ρ_{calc} (Mg/m^3)	1.959	1.942	1.982
μ(Mo Kα) (mm^{-1})	8.995	7.818	7.606
R1[a] ($I \geq 2\sigma$)	0.0321	0.0300	0.0216
wR2[b] ($I \geq 2\sigma$)	0.0696	0.0519	0.0512

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

and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. ^{1}H, ^{13}C{^{1}H}, and ^{195}Pt NMR spectra were measured on Varian UNITY 300 spectrometer at ambient temperature. ^{195}Pt chemical shifts are given relative to $Na_2[PtCl_6]$ (by using $K_2[PtCl_4]$, $\delta = -1630$ ppm, as a standard), and the half-height line width is given in parentheses.

X-ray Structure Determinations. The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The Denzo-Scalepack[36] program package was used for cell refinements and data reduction. All structures were solved by direct methods using the SHELXS97 program and the WinGX graphical user interface.[37,38] A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL v5.1)[39] was applied to all data (T_{min}/T_{max} values were 0.11842/0.15193, 0.11160/ 0.17024, and 0.25637/0.33691 for **9**, **10**, and **11**, respectively). Structural refinements were carried out with SHELXL97.[40] In structure **10**, one of the ethyl groups was disordered in two positions with occupation parameters 0.51/0.49. All hydrogens were placed in idealized positions and were constrained to ride on their parent atom. The crystallographic data are summarized in Table 1. Selected bond lengths and angles are shown in Figures 1−3.

Synthetic Work. Step I. The platinum(IV) complexes *trans*-$[PtCl_4\{NH{=}C(Me)OEt\}_2]$ and *trans*-$[PtCl_4\{NH{=}C(Et)OEt\}_2]$ were prepared by addition of ethanol to the nitrile complexes $[PtCl_4(RCN)_2]$ (R = Me, Et) in accord with the published method.[8] The reduction of *trans*-$[PtCl_4\{NH{=}C(R)OEt\}_2]$ with the ylide $Ph_3P{=}CHCO_2Me$[7b] gave the platinum(II) complexes *trans*-$[PtCl_2\{NH{=}C(R)OEt\}_2]$. *trans*-$[PtCl_2\{NH{=}C(Me)OEt\}_2]$ (**1**) has been previously characterized.[8]

***trans*-[PtCl$_2${NH=C(Et)OEt}$_2$] (2).** Anal. Calcd for $C_{10}H_{20}N_4Cl_2O_2Pt$: C, 25.65; H, 4.74; N, 5.98. Found: C, 25.54; H, 4.86; N, 5.98. FAB$^+$-MS, *m*/*z*: 466 [M]$^+$, 432 [M − Cl]$^+$, 395 [M − 2Cl − 2H]$^+$. IR spectrum, selected bands, cm^{-1}: 3246 m ν(N−H), 2985 and 2943 m-w ν(C−H), 1641 s ν(C=N). ^{1}H NMR in $CDCl_3$, δ: 7.72 (s, br, 1*H*, C=NH), 4.02 (q, 6.9 Hz, 2*H*) and 1.35 (t, 6.9 Hz, 3*H*) (OCEt), 3.11 (q, 7.7 Hz, 2*H*) and 1.26 (t, 7.7 Hz, 3*H*) (N=CEt). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 173.32 (C=N), 63.82 and 13.56 (OEt), 28.82 (J_{Pt-C} 25.4 Hz) and 10.22 (N=C*Et*). ^{195}Pt NMR in $CDCl_3$, δ: −1894.7 (590 Hz).

Step II. Dppe (40 mg, 0.10 mmol) is added to *trans*-$[PtCl_2\{NH{=}C(R)OEt\}_2]$ (25 mg, 0.05 mmol) in $CHCl_3$ (2 mL) and the reaction mixture left to stand at 0 °C for 20 min, whereupon the colorless precipitate of $[Pt(dppe)_2]Cl_2$ is removed by filtration and the filtrate is used in step III. For characterization of NH=C(Me)OEt (**3**) see ref 8.

NH=C(Et)OEt (4). ^{1}H NMR in $CDCl_3$, δ: 6.64 (s, br, 1*H*, C=NH), 4.08 (q, 7.2 Hz, 2*H*) and 1.25 (t, 7.2 Hz, 3*H*) (OCEt), 2.21 (q, 7.5 Hz, 2*H*) and 1.08 (t, 7.5 Hz, 3*H*) (N=CEt). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 174.25 (C=N), 61.19 and 14.13 (OEt), 26.16 and 10.08 (N=C*Et*).

Step III. A significant excess of the imino ester prepared in the step II (0.50 mmol or more) is added to $[PtCl_4(EtCN)_2]$ (20 mg, 0.045 mmol) in $CHCl_3$ at room temperature, and almost immediately the solvent is evaporated and the mixture obtained is separated by column chromatography (first fraction; eluent is CH_2Cl_2:Et_2O = 4:1, v/v, silica gel 70−230 mesh; 60 Å, Aldrich).

[PtCl$_4${NH=C(Et)N=C(Me)OEt}$_2$] (5). Anal. Calcd for $C_{14}H_{28}N_4Cl_4O_2Pt$: C, 27.07; H, 4.54; N, 9.02. Found: C, 26.75; H, 4.02; N, 9.15. FAB$^+$-MS, *m*/*z*: 665 [M + 2Na − H]$^+$, 629 [M − Cl + 2Na − 2H]$^+$, 593 [M − 2Cl + 2Na − 3H]$^+$. IR spectrum, selected bands, cm^{-1}: 3291 and 3215 m-w ν(N−H), 2979 m-w, 2934 w ν(C−H), 1699 m and 1613 s ν(C=N), 1292 s ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 4.26 (q, 7.1 Hz, 2*H*) and 1.27 (t, 7.1 Hz, 3*H*) (OEt), 2.61 (q, 7.5 Hz, 2*H*) and 1.18 (t, 7.4 Hz, 3*H*) (=CEt), 2.02 (s, 3*H*, =CMe). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 179.6 (C=N−Pt), 159.9 (C=N−C), 64.4 and 13.9 (OEt), 33.4 and 10.1 (=CEt), 20.6 (=CMe). ^{195}Pt{^{1}H} NMR in $CDCl_3$, δ: −99.8 (880 Hz).

[PtCl$_4${NH=C(Et)N=C(Et)OEt}$_2$] (6). Anal. Calcd for $C_{16}H_{32}N_4Cl_4O_2Pt$: C, 29.30; H, 4.97; N, 8.63. Found: C, 29.32; H, 5.02; N, 8.54. FAB$^+$-MS, *m*/*z*: 687 [M + K]$^+$, 617 [M − 2Cl + K]$^+$, 578 [M − 2Cl]$^+$. IR spectrum, selected bands, cm^{-1}: 3356 m ν(N−H), 2979 w, 29334 m ν(C−H), 1698 s and 1617 m-s ν(C=N). ^{1}H NMR in $CDCl_3$, δ: 7.11 (s, br, 1*H*, NH), 4.30 (q, 7.2 Hz, 2*H*) and 1.31 (t, 7.2 Hz, 3*H*) (OEt), 2.64 (q, 7.5 Hz, 2*H*) and 1.20 (t, 7.5 Hz, 3*H*) (PtN=CEt), 2.39 (q, 7.5 Hz, 2*H*), and 1.20 (t, 7.5 Hz, 3*H*) (N=CEt). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 178.80 (C=N−Pt), 162.38 (C=N), 64.30 and 13.90 (OEt), 33.57 and 10.24 (Pt−N=C*Et*), 28.21 and 9.73 (N=C*Et*). ^{195}Pt{^{1}H} NMR in $CDCl_3$, δ: −100.6 (719 Hz).

[PtCl$_4$(EtCN){NH=C(Et)N=C(Et)OEt}] (7). This complex formed as a minor byproduct in step III and can be isolated in pure form after column chromatography on silica gel. Despite instability and the small isolated amount, we succeeded in characterizing the complex by FAB-MS and ^{1}H NMR spectroscopy, reducing it to the platinum(II) complex $[PtCl_2(EtCN)\{NH{=}C(Et)N{=}C(Et)OEt\}]$ (**8**; see later), and determining the X-ray structure of the latter (Figure 1). FAB$^+$-MS, *m*/*z*: 512 [M − Cl]$^+$, 477 [M − 2Cl]$^+$. ^{1}H NMR in $CDCl_3$, δ: 6.85 (s, br, 1*H*, NH), 4.33 (q, 2*H*, CH_2 from OEt), 3.20 (q, 2*H*, CH_2 from N≡CEt), 2.72 (q, 2*H*, CH_2 from

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Pt−N=CEt), and 2.42 (q, 2*H*, CH_2 from N=CEt), 1.47, 1.32, 1.21, and 1.22 (four t, 12*H*, CH_3 from Et).

Step IV. The imino ester prepared in step II (0.10 mmol) is added to $[PtCl_4(EtCN)_2]$ (20 mg, 0.045 mmol) in $CHCl_3$, and the reaction mixture is left to stand for 2 h, whereupon the product (**9** or **10**) is separated by column chromatography (first fraction; eluent is CH_2Cl_2:Et_2O = 4:1, v/v, silica gel 70−230 mesh; 60 Å, Aldrich). In the case of using well-dried solvents and a high rate of the elution, a mixture of $[PtCl_4\{NH=C(Et)N=C(R)OEt\}_2]$ and **9** or **10** is obtained. If the reaction mixture is eluted at a lower rate, pure **9** or **10** is isolated. The latter can also be obtained from the mixture of the two products after its recrystallization at 45 °C from commercial nondried solvents (CH_2Cl_2 and Et_2O).

$[PtCl_4\{NH=C(Et)NHC(Me)=O\}_2]$ (9). Anal. Calcd for $C_{10}H_{20}N_4Cl_4O_2Pt$: C, 21.25; H, 3.57; N, 9.91. Found: C, 21.46; H, 3.77; N, 9.57. FAB^+-MS, *m*/*z*: 565 $[M + H]^+$, 529 $[M - Cl]^+$, 496 $[M - 2Cl + 2H]^+$, 459 $[M - 3Cl]^+$, 423 $[M - 4Cl]^+$. IR spectrum, selected bands, cm^{-1}: 3284 and 3220 m-w ν(N−H), 2920 w, 2851 m ν(C−H), 1738 s ν(C=O), 1629 vs ν(C=N). ^1H NMR in $CDCl_3$, δ: 10.13 (s, br, 1*H*, =CNH), 6.83 (s, br, 1*H*, C=NH), 3.17 (q, 7.5 Hz, 2*H*) and 1.30 (t, 7.4 Hz, 3*H*) (=CEt), 2.21 (s, 3*H*, =CMe). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 173.21 (C=N), 168.23 (C=O), 29.80 (s + d, J_{PtC} 25.0 Hz) and 9.84 (Et), 25.17 (Me). $^{195}Pt\{^1H\}$ NMR in $CDCl_3$, δ: −236.3 (410 Hz).

$[PtCl_4\{NH=C(Et)NHC(Et)=O\}_2]$ (10). Anal. Calcd for $C_{12}H_{24}N_4Cl_4O_2Pt$: C, 24.30; H, 4.08; N, 9.44. Found: C, 24.58; H, 4.31; N, 9.19. FAB^+-MS, *m*/*z*: 617 $[M + Na]^+$, 594 $[M]^+$, 559 $[M - Cl + H]^+$, 523 $[M - 2Cl + H]^+$. IR spectrum, selected bands, cm^{-1}: 3358 m-w and 3214 m-w ν(N−H), 2980 w, 2936 m ν(C−H), 1698 s ν(C=O), 1621 vs ν(C=N). ^1H NMR in $CDCl_3$, δ: 10.05 (s, br, 1*H*, =CNH), 6.81 (s, br, 1*H*, C=NH), 3.17 (q, 7.4 Hz, 2*H*) and 1.29 (t, 7.5 Hz, 3*H*) (N=CEt), 2.46 (q, 7.5 Hz, 2*H*) and 1.20 (t, 7.5 Hz, 3*H*) (O=CEt). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 173.19 (C=N), 172.07 (C=O), 31.42 and 9.90 (O=C*Et*), 29.87 (J_{Pt-C} 25.4 Hz) and 8.38 (N=C*Et*). $^{195}Pt\{^1H\}$ NMR in $CDCl_3$, δ: −244.5 (707 Hz).

Step V. The ylide $Ph_3P=CHCO_2Me$ (4 mg, 0.01 mmol) is added to a solution of **9** or **10** (0.01 mmol) in CH_2Cl_2 (2 mL) and left to stand at room temperature for 12 h, whereupon the solvent is evaporated and the yellow residue of the corresponding Pt(II) complex formed is washed with two 2-mL portions of Et_2O, dissolved in a minimum amount of CH_2Cl_2 at room temperature, and purified on a column filled with silica gel (70−230 mesh; 60 Å, Aldrich). Complexes **8**, **11**, and **12** were reduced analogously but at 45 °C for 6 h and with monitoring of the reaction by TLC.

$[PtCl_2\{NH=C(Et)N=C(Me)OEt\}_2]$ (11). Anal. Calcd for $C_{14}H_{28}N_4Cl_2O_2Pt$: C, 30.55; H, 5.13; N, 10.18. Found: C, 30.09; H, 5.15; N, 9.97. FAB^+-MS, *m*/*z*: 665 $[M + 2Na - H]^+$, 629 $[M - Cl + 2Na - 2H]^+$, 593 $[M - 2Cl + 2Na - 3H]^+$. IR spectrum, selected bands, cm^{-1}: 3224 m ν(N−H), 2978 m-w ν(C−H), 1692 m and 1625 m-s ν(C=N). ^1H NMR in $CDCl_3$, δ: 7.06 (s, br, 1*H*, C=NH), 4.30 (q, 7.20 Hz, 2*H*) and 1.36 (t, 7.20 Hz, 3*H*) (OEt), 2.45 (q, 7.46 Hz, 2*H*) and 1.11 (t, 7.46 Hz, 3*H*) (N=CEt), 2.28 (s, 3*H*, Me). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 178.80 (C=N at Pt), 160.57 (C=N), 63.41 and 13.99 (OEt), 32.07 and 9.98 (N=C*Et*), 19.15 (Me). ^{195}Pt NMR in $CDCl_3$, δ: −2038.4 (420 Hz). The complex is unstable toward hydrolysis and gives $[PtCl_2\{NH=C(Et)NHC(Me)=O\}_2]$ and EtOH. In nondried $CDCl_3$ (Aldrich), ca. 50% hydrolytic conversion was observed after 12 h at room temperature.

$[PtCl_2\{NH=C(Et)N=C(Et)OEt\}_2]$ (12). Anal. Calcd for $C_{16}H_{32}N_4Cl_2O_2Pt$: C, 33.22; H, 5.58; N, 9.69. Found: C, 33.36; H, 5.60; N, 9.38. IR spectrum, selected bands, cm^{-1}: 3247 m ν(N−H), 2979 and 2938 m ν(C−H), 1686 s and 16189 m ν(C=N). FAB^+-MS, *m*/*z*: 506 $[M - 2Cl]^+$. ^1H NMR in $CDCl_3$, δ: 7.22 (s, br, 1*H*, C=NH), 4.28 (q, 7.1 Hz, 2*H*) and 1.36 (t, 7.1 Hz, 3*H*) (OEt), 2.66 (q, 7.4 Hz, 2*H*, CH_2) and 1.23 (t, 7.4 Hz, 3*H*, CH_3) (N=CEt), 2.44 (q, 7.4 Hz, 2*H*, CH_2) and 1.13 (t, 7.4 Hz, 3*H*, CH_3) (Pt−N=CEt). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 178.68 (C=N−Pt), 163.69 (C=N), 63.37 and 13.96 (OEt), 32.29 (J_{PtH} 37.03 Hz) and 10.02 (Pt−N=C*Et*), 26.65 and 10.27 (CN*Et*). ^{195}Pt NMR in $CDCl_3$, δ: −2076.7 (583 Hz). The complex is unstable toward hydrolysis and gives $[PtCl_2\{NH=C(Et)NHC(Et)=O\}_2]$ and EtOH. In nondried $CDCl_3$ (Aldrich), ca. 50% hydrolytic conversion was observed after 12 h at room temperature.

$[PtCl_2(EtCN)\{NH=C(Et)N=C(Et)OEt\}]$ (8). For preparation of this complex see above, i.e., step III. IR spectrum, selected bands, cm^{-1}: 3251 m ν(N−H), 2946 m-w ν(C−H), 1688 and 1678 s ν(C=N). ^1H NMR in $CDCl_3$, δ: 6.75 (s, br, 1*H*, NH), 4.30 (q, CH_2 from OEt), 2.76 (q, CH_2 from Pt−N≡CEt), 2.65 (q, CH_2 from Pt−N=CEt), 2.47 (q, CH_2 from N=CEt), 1.32 and 1.20 (four t, CH_3 from Et). Crystals suitable for X-ray crystallography were obtained by evaporation of a CH_2Cl_2−Et_2O solution.

$[PtCl_2\{NH=C(Et)NHC(Me)=O\}_2]$ (13). Anal. Calcd for $C_{10}H_{20}N_4Cl_2O_2Pt$: C, 24.30; H, 4.08; N, 11.34. Found: C, 24.78; H, 4.40; N, 10.92. FAB^+-MS, *m*/*z*: 457 $[M - Cl]^+$, 422 $[M - 2Cl - H]^+$. IR spectrum, selected bands, cm^{-1}: 3336 m-w, 3267 w and 3198 m-w ν(N−H), 2945 w ν(C−H), 1732 m ν(C=O), 1637 s ν(C=N). ^1H NMR in $CDCl_3$, δ: 10.25 (s, br, 1*H*, =CNH), 6.97 (s, br, 1*H*, C=NH), 2.92 (q, 7.5 Hz, 2*H*) and 1.15 (t, 7.5 Hz, 3*H*) (N=CEt), 2.16 (s, 3*H*, Me). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 172.47 (C=N), 168.53 (C=O), 29.29 (J_{Pt-C} 25.4 Hz) and 9.64 (N=C*Et*), 24.97 (Me). ^{195}Pt NMR in $CDCl_3$, δ: −2083.5 (824 Hz).

$[PtCl_2\{NH=C(Et)NHC(Et)=O\}_2]$ (14). Anal. Calcd for $C_{12}H_{24}N_4Cl_2O_2Pt$: C, 27.59; H, 4.63; N, 10.73. Found: C, 27.88; H, 4.55; N, 10.52. IR spectrum, selected bands, cm^{-1}: 3314 m-w, 3268 m-w ν(N−H), 2981 and 29.39 w ν(C−H), 1732 m ν(C=O), 1633 s ν(C=N). FAB^+-MS, *m*/*z*: 522 $[M]^+$. ^1H NMR in $CDCl_3$, δ: 10.23 (s, br, 1*H*, =CNH), 6.90 (s, br, 1*H*, C=NH), 2.95 (q, 7.4 Hz, 2*H*, CH_2 from N=C*Et*), 2.40 (two q, 7.4 Hz, 2*H*, CH_2 from C(=O)*Et*), 1.18 (t, 7.4 Hz, 6*H*, both CH_3). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 172.64 (C=N), 172.40 (C=O), 31.09 and 9.70 (N=C*Et*), 29.48 (J_{Pt-C} 25.4 Hz) and 8.60 (C(=O)*Et*). ^{195}Pt NMR in $CDCl_3$, δ: −2092.0 (803 Hz).

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Supporting Information Available: Tables of crystallographic data for **8**−**10**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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