Platinum(IV)-Assisted [2 + 3] Cycloaddition of Nitrones to Coordinated Organonitriles. Synthesis of Δ^4-1,2,4-Oxadiazolines

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Abstract: [2 + 3] cycloaddition between acetonitrile ligands in the platinum(IV) complex $[PtCl_4(MeCN)_2]$ and the nitrones $^-O^+N(R^3)=C(R^1)(R^2)$ [R^1 = H, R^2 = Ph, *o*-C_6H_4OH, *p*-C_6H_4Me, *p*-C_6H_4OMe, *p*-$C_6H_4NO_2$, *p*-$C_6H_4NMe_2$, *p*-$C_6H_4NMe_2$·HCl, R^3 = Me; R^1 = H, R^2 = Ph, ^{t}Bu, R^3 = CH_2Ph] proceeds smoothly under mild conditions and gives the first examples of Δ^4-1,2,4-oxadiazoline complexes, $[PtCl_4\{\overline{N=C(Me)O-N(R^3)-C(R^1)(R^2)}\}_2]$, as a 1:1 mixture of two diastereoisomers, in 70−90% yields. The heterocyclic ligands were liberated almost quantitatively by reaction at room temperature of the complexes with a slight excess of pyridine in chloroform giving free $\overline{N=C(Me)O-N(R^3)-C(R^1)(R^2)}$ and *trans*-$[PtCl_4(pyridine)_2]$; subsequent workup allowed the isolation of the novel Δ^4-1,2,4-oxadiazolines. All prepared compounds were characterized by elemental analyses, FAB or EI mass spectrometry, and IR and ^{1}H, $^{13}C\{^1H\}$, and ^{195}Pt (metal complexes) NMR spectroscopies; X-ray structure determination was performed for the (*R*,*S*) diastereoisomer of *trans*-$[PtCl_4\{\overline{N=C(Me)ON(Me)-CH(p\text{-}C_6H_4OMe)}\}_2]$.

Introduction

Although the effect of the ligands upon a metal ion is often relatively well understood and many aspects are fairly well *quantified*, similar quantitative theories are unavailable for investigating the effect of coordination to a metal upon the ligand. However, *qualitative* models to justify the changes which result from coordination of a ligand to a metal allow the description and sometimes the prediction of metal-mediated processes which can form the basis for the use of metal complexes as *stoichiometric reagents* and *homogeneous catalysts* in organic chemistry. In this context, ligands containing double or triple bonds were shown to be the most useful and versatile materials whose metal-mediated reactions[1] give a tremendous variety of new organic compounds. Qualitative models describing these, very often, ionic-type processes suggest polarization of the double and triple bond species and appearance of new electrophilic or nucleophilic centers which promote ligand reactions.

Among these species, organonitriles are of paramount importance in the formation of C−C, C−N, and C−O bonds in organic chemistry,[2] and metal-ion control of their reactivity[3] offers an attractive way to promote or inhibit such reactions or perform synthetic routes which are not feasible for so-called *pure* organic chemistry. Our own research in the field of reactivity of organonitrile ligands[4] has recently got the second breath when we observed the reaction between the platinum(IV) complexes $[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph, Ph) and oximes, $R^1R^2C=NOH$ ($R^1 = R^2 = Me$; $R^1R^2 = C_4H_8$, $R^1R^2 = C_5H_{10}$, R^1R^2 = (H)Ph, R^1R^2 = (H)C_6H_4(OH)-*o*), which led to isolation of unusual and unexpectedly stable iminoacylated compounds $[PtCl_4(NH=C(R)ON=CR^1R^2)_2]$, Scheme 1.[5]

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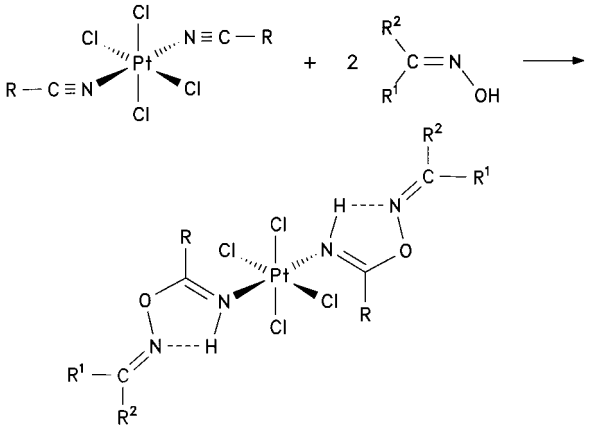
Scheme 1. Addition of Oximes to Coordinated Nitriles



This route was then extended to *N*-alkylated hydroxylamines to observe unprecedented O-addition of R_2NOH to the metal-bound MeCN[6] and to additions of sterically hindered alcohols which do not react with free nitriles under the Pinner reaction conditions,[7] but they do react with Pt(IV)-bound ones.[8] Eventually, in contrast to the classic substitution processes, we discovered occurrence of a facile one-end addition of *vic*-dioximes to the nitrile species in $[PtCl_4(RCN)_2]$ that generated Pt(IV)-based metallaligands of a novel type.[9]

All of these iminoacylation reactions, giving rather unusual metal-bound organic species, proceeded rapidly, typically under mild conditions and gave final coordination products in high and sometimes almost quantitative yields. All this together pointed out that a very reactive starting material containing highly electrophilically activated RCN ligands is at our disposal, and we became much interested in initiating the utilization of $[PtCl_4(RCN)_2]$ for generation of organic species. We now report on an extension of the addition reaction to completely different reagents, i.e., nitrones, that brings about platinum(IV)-assisted [2 + 3] cycloaddition, followed by liberation of newly formed ligands by reaction with pyridine, and this opens up an easy route to Δ^4-1,2,4-oxadiazoline heterocyclic species whose synthesis and further chemistry are still little explored.

In fact, Δ^4-1,2,4-oxadiazolines represent a class of compounds that, although known, is rather limited in the number of heterocycles synthesized. All methods of their preparation involve [2 + 3] cycloadditions and include reactions of nitrosobenzene with nitrile ylides[10] or oxazolinones[11] and reactions of *electron-deficient* organonitriles,[12,13] for example, Cl_3CCN[14,15] or $NCCH_2CN$,[16] or aryl cyanates, ROCN,[17] with nitrones. Consequently, the latter method allows the preparation of Δ^4-1,2,4-oxadiazolines, but only with strong electron-withdrawing groups R. Indeed, preparation of the compounds with the electron-donor group R = Me was achieved only in one case when an extremely reactive nitrone was employed and also harsh reaction conditions (150 °C, neat acetonitrile, 10 days) were applied.[13] In contrast, the platinum(IV)-assisted reaction we now describe offers broad possibilities for derivatization of Δ^4-1,2,4-oxadiazolines. In fact, the electrophilic activation by the metal center of organonitriles RCN, even with electron-donor substituents R, such as methyl, is so strong that the cycloaddition is determined only by the reactivity of a nitrone and occurs smoothly under mild conditions.

Results and Discussion

Cycloaddition Reaction and Characterization of Products. Examples of cycloaddition reactions, although these and also in situ metal-catalyzed processes are well-known in organic chemistry,[18] are rather scarce in coordination chemistry. Among them attention should be drawn to (i) the cycloaddition of dipolar reagents to alkynyl Fischer carbene complexes,[19] coordinated CS_2,[20] or dinuclear metal complexes across the metal−metal multiple bond;[21] (ii) cyclization of metal allyl, allenyl, propargyl, or related compounds with organic isocyanides, ketenes, SO_2, or S_2O;[22] (iii) reactions of coordinated organoazides with

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isonitriles,[23] activated alkynes,[24] olefins,[25] CS_2,[26] or isothiocyanates;[27] (iv) the cycloadditions due to the reaction between isonitrile complexes and azide ion,[28] isocyanates, or isothiocyanates;[29] (v) formation of metallacycles originating from the cycloaddition between low-valent metal carbonyls and organonitrile *N*-oxides;[30] (vi) the cycloadditions of *free* CF_3CN to metallaisonitrile ylides which lead to metal-bound imidazoles.[31] As far as the cycloaddition to *coordinated* organonitrile species is concerned, to the best of our knowledge, there is only one example of such a process, i.e., the [2 + 3] addition of azide ion to cobalt-bound nitriles or, at least formally, the reverse reaction between azido complexes and RCN giving, in either case, coordinated tetrazolates.[32] The restricted amount of these reactions described in coordination chemistry is somehow surprising if one takes into account significant and sometimes tunable, e.g., by variation of other supporting ligands or of the overall charge on a complex ion, electrophilic activation of ligands by their ligation to a metal center making the reactions with electron-rich dipolar reagents favorable and controllable.

For this study we addressed the platinum(IV) complex $[PtCl_4(MeCN)_2]$ since it has been proved that the acetonitrile ligands are highly activated and they are logical candidates for investigations of cycloaddition reactions with electron-rich dipoles such as nitrones. The reaction between the complex and a nitrone in a molar ratio 1:2 proceeds smoothly in a suspension of CH_2Cl_2 (with its gradual homogenization) at room temperature and completes after 4−6 h (Scheme 1). The final products were purified by chromatography on SiO_2 and obtained as solids [(*R*,*S*) + (*S*,*S*)/(*R*,*R*) diastereoisomers] in good yields (70−90%). All isolated complexes were characterized by elemental analyses, FAB mass spectrometry, and IR and ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectroscopies; X-ray structure determination was performed for (*R*,*S*)-*trans*-$[PtCl_4\{\overline{N{=}C(Me)ON(Me){-}CH}(p\text{-}C_6H_4OMe)\}_2]$. The coordination polyhedron of the complex is a slightly distorted octahedron (Figure 1). The Pt atom is situated at an inversion center, and all bonds and angles around the platinum are of normal values.[33] The spectroscopic data additionally support the formulations and indicate the presence of two heterocyclic ligands bound to the Pt atom via their imino nitrogens. Only three structures of uncoordinated Δ^4-1,2,4-oxadiazolines are known,[15] and, to the best of our knowledge, the complexes relevant to this study represent the first example of Δ^4-1,2,4-oxadiazoline species coordinated to a metal center

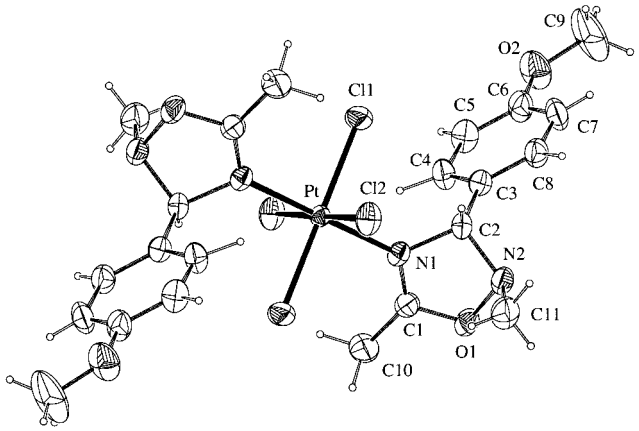
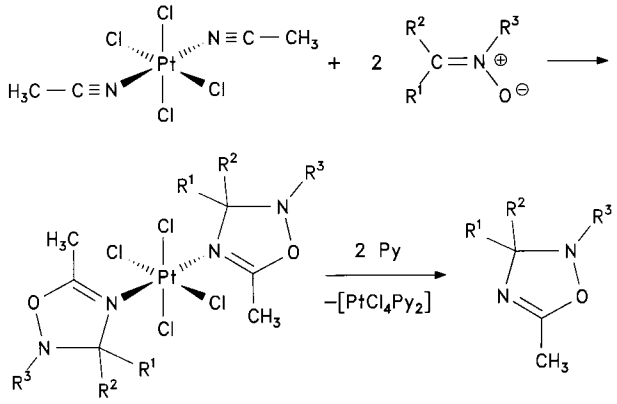


Figure 1. ORTEP view of *trans*-$[PtCl_4\{\overline{N{=}C(Me)ON(Me){-}CH}(p\text{-}C_6H_4OMe)\}_2]$ with atomic numbering scheme.

Scheme 2. [2 + 3] Cycloaddition between Coordinated Acetonitrile and Nitrones (R^1 = H, R^2 = Ph, *o*-C_6H_4OH, *p*-C_6H_4Me, *p*-C_6H_4OMe, *p*-$C_6H_4NO_2$, *p*-$C_6H_4NMe_2$, *p*-$C_6H_4NMe_2$·HCl, R^3 = Me; R^1 = H, R^2 = Ph, ^{t}Bu, R^3 = CH_2Ph)



and, consequently, *trans*-$[PtCl_4\{\overline{N{=}C(Me)ON(Me){-}CH}(p\text{-}C_6H_4OMe)\}_2]$ is the first example of a structurally characterized (Δ^4-1,2,4-oxadiazoline)metal compound. Surprisingly, geometrical parameters of the ring are almost unaffected by its ligation to the platinum(IV) center. Indeed, all bond lengths and angles in the cycle within 3σ correspond to those in the three purely organic 1,2,4-oxadiazolines.[15] However, in contrast to the envelope conformation found for the organic compounds,[15] the coordinated heterocycle is a half-chair that is twisted around the N2−C2 bond with deviations of 0.307(6) Å for N2 and −0.209(6) Å for C2 from the plane passed through the atoms N1, C1, and O1. The methyl group at N2 and the aromatic substituent at C2 are mutually trans, and both occupy axial positions on the ring.

The results obtained (for IR and NMR spectroscopic results see below) indicate the cycloaddition of the nitrones to the acetonitrile species to give Δ^4-1,2,4-oxadiazolines coordinated to the platinum(IV), Scheme 2. The newly formed organic ligands can be easily liberated by reaction of the (Δ^4-1,2,4-oxadiazoline)platinum(IV) complexes with a slight excess of pyridine in chloroform (Scheme 2). The formation of *trans*-$[PtCl_4(pyridine)_2]$,[34] highly insoluble in $CHCl_3$, in the course of the substitution, its separation by filtration, and evaporation of the solvent to dryness allowed us to obtain individual Δ^4-1,2,4-oxadiazolines. All isolated compounds were characterized

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by NMR and IR spectroscopies and EI mass spectrometry. The mass spectra show, in addition to the molecular ions, a typical fragmentation pattern that indicates loss of CH_3CN as a consequence of retrocycloaddition reaction. In IR spectra, the heterocycles show strong bands due to ν(C═N) stretch at 1670−1680 cm^{-1}. In ^1H NMR spectra, the ═C(Me)O protons were detected in the range 2.11−2.68 and the N−CH−N proton appears in the range 4.72−5.80 ppm. In $^{13}C\{^1H\}$ NMR spectra, signals of ═C(*Me*)O and N−CH−N carbons emerge in intervals from 12.0 to 13.4 and 90.4 to 94.7 ppm, correspondingly, while carbons of the C═N groups were observed in the very narrow range 160.0−161.6 ppm.

We were unable to isolate or to characterize in situ N═C(Me)O−N(Me)-CH(*p*-$C_6H_4NMe_2$) because the appropriate complex [$PtCl_4$(N═C(Me)O−N(Me)-CH(*p*-$C_6H_4NMe_2$))$_2$] is rather unstable in solutions and its degradation occurs much faster than the substitution of the heterocycle by pyridine.

IR and NMR Spectroscopic Results for the Platinum(IV) Complexes. Comparison of IR spectra of the products with that of [$PtCl_4$(MeCN)$_2$] shows disappearance of the C≡N stretching vibrations at 2354 cm^{-1} and appearance of one strong ν(C═N) band in the range 1597−1612 cm^{-1}. These values are considerably lower than those found for the uncoordinated Δ^4-1,2,4-oxadiazolines (1670 cm^{-1}), indicating a weakening of the C═N double bond by coordination to the metal. In the course of the cycloaddition reaction, a new stereocenter is generated at the nitrone carbon atom, thus giving rise to two diastereomeric platinum complexes which display two sets of signals in a ratio of 1:1 and with small difference in chemical shifts in both ^1H ($\Delta\delta$ ca. 0.01 ppm) and $^{13}C\{^1H\}$ NMR spectra ($\Delta\delta$ ca. 0.05 ppm). The N−C*H*−N group appears in ^1H NMR typically at a chemical shift of 5.25−6.75 ppm and displays a coupling ($^3J_{PtH}$ of 12−13 Hz), whereas the corresponding ^{13}C signal is in the range 87.3−94.3 ppm with $^2J_{PtC}$ from 20 to 21 Hz. For the ═C(*Me*)O group, a ^1H chemical shift of 2.80 to 3.06 ppm ($^4J_{PtH}$ of 3.0−4.5 Hz) was observed, while the ^{13}C signal appears in the range 15.0−17.4 ppm ($^3J_{PtC}$ of 3.0−4.2 Hz). The fact that both groups display coupling constants to platinum and also the values of the coupling constants indicate that the heterocyclic ligands in all complexes are coordinated to platinum via their iminoacyl nitrogens. An additional argument in favor of coordination by the imino N atom is the chemical shift of the N═C carbon itself (174.6−177.5 ppm), which appears at considerably lower field than the corresponding carbon in the free ligands (160.0−161.6 ppm).

The ^{195}Pt NMR spectra of the diastereoisomers, in contrast to the ^1H and $^{13}C\{^1H\}$ ones, show only one broad signal with a half-height peak width in the range 520−800 Hz. The chemical shifts range from −98 to −190 ppm, depending on the structure of the heterocyclic ligand and solvent employed for NMR measurements. This interval agrees well with that observed for *trans*-[$PtCl_4$(iminoacyl)$_2$] complexes,[5,6,9] thus giving additional arguments in favor of trans arrangement of the oxadiazoline ligands. No evidence for the presence of the other geometrical isomer was obtained from the NMR data.

Concluding Remarks. Our results show that nonactivated organonitriles can be readily activated toward [2 + 3] cycloaddition reactions with nitrones by coordination to a platinum(IV) center, thus giving easy access to Δ^4-1,2,4-oxadiazoline complexes, from which the oxadiazoline ligands can be liberated almost quantitatively under mild conditions using pyridine, and providing a novel and simple synthetic route for such a rare type of heterocycle. Attention additionally should be drawn to the fact that the success of the metal-mediated reaction is a consequence of coordination of the nitrile ligand to the platinum atom in a *high oxidation state*, i.e., the Pt(IV) ion. Indeed, all attempts to perform the same reaction with the platinum(II) acetonitrile compound [$PtCl_2$(MeCN)$_2$]—even under harsh reaction conditions—failed. Further studies on better understanding the factors determining the progress of the reaction, on its extension to other metal ions, and on making the [2 + 3] cycloaddition metal-catalyzed are on the way in our group.

Experimental Section

Materials and Instrumentation. Aldehydes and *N*-alkylhydroxylamines were puchased from Aldrich. Solvents were obtained from commercial sources and used as received. The complex [$PtCl_4$(MeCN)$_2$][35] was prepared as previously described. Nitrones were synthesized by condensation of the corresponding aldehyde and *N*-alkylhydroxylamine according to the published methods.[36] C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Kofler table. For TLC, Merck UV 254 SiO_2 plates were used. 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 (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectra were measured on Varian UNITY 300 and Bruker AMX 300 spectrometers at ambient temperature. ^{195}Pt chemical shifts are given relative to aqueous $K_2[PtCl_4] = -1630$ ppm, and half-height line widths are shown in parentheses.

X-ray Structure Determination of *trans*-[$PtCl_4${N═C(Me)ON-(Me)−CH(*p*-C_6H_4OMe)}$_2$]. Light-yellow plates of the complex were grown from dichloromethane solution upon addition of diethyl ether. Diffraction data were collected on an Enraf-Nonius CAD 4 diffractometer. Cell parameters were obtained from 24 centered reflections with Θ between 10° and 13°. Range of *hkl*: $h = 0$ to 15, $k = 0$ to 9, $l = -17$ to 17. Standard reflections were measured every 60 min and showed practically no change with time (±1%). Diffractometer data were processed by the program PROFIT[37] with profile analysis of reflections. The structures were solved by means of Fourier synthesis based upon the Pt-atom coordinates obtained from the Patterson synthesis using the SHELXTL package.[38] After that, all reflections with $I < 2\sigma(I)$ were excluded from calculations. Refinement was done by full-matrix least squares based on F^2 using the SHELX-97 package.[39] All non-H atoms were treated anisotropically. H atoms were located in a difference Fourier map and refined isotropically. An extinction correction has been applied. Lorentz, polarization, and absorption corrections were made.[40] Scattering factors are from *International Tables for X-ray Crystallography*.[41] Crystal data are given in Table 1, bond distances and angles in Table 2.

Preparation of the Oxadiazoline Platinum(IV) Complexes. A mixture of [$PtCl_4$(MeCN)$_2$] (42 mg, 0.10 mmol) and the corresponding nitrone (0.20 mmol) in CH_2Cl_2 (2.0 mL) was stirred for 4 h at room temperature, whereupon the initial suspension became a homogeneous

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Table 1. Crystal Data and Structure Refinement for *trans*-[$PtCl_4${N=C(Me)ON(Me)−CH(*p*-C_6H_4OMe)}$_2$]

empirical formula	$C_{22}H_{28}Cl_4N_4O_4Pt$
fw	749.36
temp, K	293(2)
wavelength, Å	0.71073
cryst syst	monoclinic
space group	$P2_1/a$ (No. 14)
a, Å	12.6010(10)
b, Å	7.572(5)
c, Å	14.497(2)
α, deg	90
β, deg	102.83(3)
γ, deg	90
V, Å^3	1348.7(9)
Z	2
ρ_{calcd}, Mg m^{-3}	1.845
μ(Mo Kα), mm^{-1}	5.634
reflns collected/unique	1934/1844 [*R*(int) = 0.053]
data/restraints/params	1844/0/205
goodness-of-fit on F^2	1.155
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0287$
	$wR2 = 0.0755$

Table 2. Bond Lengths (Å) and Angles (deg) for *trans*-[$PtCl_4${N=C(Me)ON(Me)−CH(*p*-C_6H_4OMe)}$_2$]

Pt−Cl(1)	2.305(2)	C(2)−C(3)	1.513(9)
Pt−Cl(2)	2.321(2)	C(3)−C(4)	1.399(10)
Pt−N(1)	2.047(6)	C(4)−C(5)	1.381(11)
N(1)−C(1)	1.265(9)	C(5)−C(6)	1.367(10)
C(1)−O(1)	1.350(7)	C(6)−C(7)	1.386(10)
O(1)−N(2)	1.488(7)	C(7)−C(8)	1.382(10)
N(2)−C(2)	1.473(9)	C(8)−C(3)	1.374(9)
C(2)−N(1)	1.499(9)	C(6)−O(2)	1.367(8)
C(1)−C(10)	1.480(10)	O(2)−C(9)	1.393(15)
N(2)−C(11)	1.473(10)		
N(1)#1−Pt−N(1)[a]	180.00	O(1)−C(1)−C(10)	112.6(6)
N(1)−Pt−Cl(1)	89.77(17)	O(1)−N(2)−C(11)	105.8(6)
N(1)−Pt−Cl(2)	88.55(16)	C(2)−N(2)−C(11)	113.6(6)
N(1)#1−Pt−Cl(1)	90.23(17)	N(2)−C(2)−C(3)	109.6(5)
N(1)#1−Pt−Cl(2)	91.45(16)	N(1)−C(2)−C(3)	112.9(5)
Cl(1)−Pt−Cl(2)	91.36(6)	C(2)−C(3)−C(4)	122.8(6)
Cl(1)#1−Pt−Cl(2)	88.64(6)	C(3)−C(4)−C(5)	119.9(6)
Cl(1)#1−Pt−Cl(1)	180.00	C(4)−C(5)−C(6)	121.3(7)
Pt−N(1)−C(1)	130.8(5)	C(5)−C(6)−C(7)	119.4(6)
Pt−N(1)−C(2)	122.7(4)	C(6)−C(7)−C(8)	119.3(7)
N(1)−C(1)−O(1)	115.1(6)	C(7)−C(8)−C(3)	122.0(6)
C(1)−O(1)−N(2)	105.7(5)	C(8)−C(3)−C(2)	119.0(6)
O(1)−N(2)−C(2)	100.2(5)	C(5)−C(6)−O(2)	115.4(6)
N(2)−C(2)−N(1)	102.7(5)	C(7)−C(6)−O(2)	125.2(6)
C(2)−N(1)−C(1)	106.1(5)	C(6)−O(2)−C(9)	119.6(7)
N(1)−C(1)−C(10)	132.2(6)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1$, $-y + 1$, $-z + 1$.

yellow solution. After chromatography on SiO_2/CH_2Cl_2 and evaporation of the solvent, the product was obtained as a pale yellow powder.

[$PtCl_4$(N=C(Me)O−N(Me)−C(H)Ph)$_2$] (Two Diastereoisomers, 1:1). Yield: 72%. Anal. Calcd for $C_{20}H_{24}N_4Cl_4O_2Pt$: C, 34.85; H, 3.51; N, 8.13. Found: C, 34.82; H, 3.40; N, 7.83. FAB$^+$-MS, *m*/*z*: 689 [M]$^+$, 619 [M − 2Cl]$^+$, 583 [M − 3Cl − H]$^+$, 547 [M − 4Cl − 2H]$^+$. Mp: 173 °C. TLC on SiO_2: $R_f = 0.77$ (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1604 s *ν*(C=N). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 2.93 and 2.94 (two s, 3H each, C−N(*Me*)−O), 2.98 and 2.99 (s + d each, $^4J_{PtH}$ 4.2 Hz, 3H each, =C(*Me*)O), 6.45 (s + d, $^3J_{PtH}$ 12.1 Hz, 2H, N−C*H*−N), 7.22 (m, 4H) and 7.36 (m, 6H) (*Ph*). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, *δ*: 15.50 and 15.54 ($^3J_{PtC}$ 4 Hz, N=C(*Me*)O), 46.0 (C−N(*Me*)−O), 90.57 and 90.62 ($^2J_{PtC}$ 20 Hz, N−*C*H−N), 125.81 and 125.83 (*o*-Ph), 128.4 (*m*-Ph), 128.79 and 128.82 (*p*-Ph), 137.66 and 137.69 (*ipso*-Ph), 174.83 and 174.90 (C=N). ^{195}Pt NMR spectrum in $CDCl_3$, *δ*: −192 (800 Hz).

[$PtCl_4$(N=C(Me)O−N(CH_2Ph)−C(H)Ph)$_2$] (Two Diastereoisomers, 1:1). Yield: 81%. Anal. Calcd for $C_{32}H_{32}N_4Cl_4O_2Pt$: C, 45.67; H, 3.83; N, 6.66. Found: C, 45.47; H, 3.76; N, 6.45. FAB$^+$-MS, *m*/*z*: 771 [M − 2Cl]$^+$, 698 [M − 4Cl − 2H]$^+$. Mp: 176 °C. TLC on SiO_2: $R_f = 0.85$ (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1607 s *ν*(C=N). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 3.04 and 3.06 (s + d each, $^4J_{PtH}$ 4.5 Hz, 3H each, =C(*Me*)O), 4.19, 4.20, 4.30, and 4.31 (four d, 12.3 Hz, 1H each, *CH*$_2$Ph), 6.52 and 6.55 (two s + d, $^3J_{PtH}$ 12.0 Hz, 1H each, N−*CH*−N), 7.00 (m, 2H) and 7.32 (m, 3H) (Ph), 7.40 (m, 3H) and 7.53 (m, 2H) (CH$_2$*Ph*). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, *δ*: 15.60 and 15.67 ($^3J_{PtC}$ 4.2 Hz, N=C(*Me*)O), 60.84 and 60.92 (*CH*$_2$-Ph), 87.98 and 88.08 ($^2J_{PtC}$ 20.6 Hz, N−*C*H−N), 125.79 and 125.83 (*o*-Ph), 128.3 (*m*-Ph), 128.5 and 128.6 (*p*-Ph and *p*-*Ph*CH$_2$), 128.7 (*Ph*CH$_2$), 130.0 (*Ph*CH$_2$), 132.93 and 132.97 (*ipso*-*Ph*CH$_2$), 137.74 and 137.78 (*ipso*-Ph), 175.25 and 175.38 (C=N). ^{195}Pt NMR spectrum $CDCl_3$, *δ*: −180 (775 Hz).

[$PtCl_4$(N=C(Me)O−N(Me)−C(H)(*p*-C_6H_4Me))$_2$] (Two Diastereoisomers, 1:1). Yield: 70%. Anal. Calcd for $C_{22}H_{28}N_4Cl_4O_2Pt$: C, 36.83; H, 3.93; N, 7.80. Found: C, 36.68; H, 3.90; N, 7.79. FAB$^+$-MS, *m*/*z*: 669 [M − 2Cl + Na]$^+$, 646 [M − 2Cl]$^+$, 611 [M − 3Cl]$^+$, 575 [M − 4Cl − 2H]$^+$. Mp: 190 °C (dec). TLC on SiO_2, $R_f = 0.73$ (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1606 s *ν*(C=N). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 2.30 (s, 6H, C_6H_4*Me*), 2.87 and 2.89 (two s, 3H each, C−N(*Me*)−O), 2.93 and 2.94 (s + d each, $^4J_{PtH}$ 4.2 Hz, 3H each, =C(*Me*)O), 6.38 (s + d, $^3J_{PtH}$ 11.9 Hz, 2H, N−C*H*−N), 7.05 (d, 8.1 Hz, 4H) and 7.13 (d, 8.1 Hz, 4H) (C_6H_4Me). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, *δ*: 15.54 and 15.58 ($^3J_{PtC}$ 4 Hz, N=C(*Me*)O), 21.2 (C_6H_4*Me*), 46.0 (C−N(*Me*)−O), 90.59 and 90.64 ($^2J_{PtC}$ 20 Hz, N−*C*H−N), 125.70 and 125.90 (CH), 129.2 (CH), 134.83 and 134.86 (Cq), 138.7 (Cq) (C_6H_4Me), 174.65 (C=N). ^{195}Pt NMR spectrum in $CDCl_3$, *δ*: −194 (700 Hz).

[$PtCl_4$(N=C(Me)O−N(Me)−C(H)(*p*-C_6H_4OMe))$_2$] (Two Diastereoisomers, 1:1). Yield: 67%. Anal. Calcd for $C_{22}H_{28}N_4Cl_4O_4Pt$: C, 35.26; H, 3.77; N, 7.48. Found: C, 35.75; H, 3.86; N, 7.33. FAB$^+$-MS, *m*/*z*: 701 [M − 2Cl + Na]$^+$, 678 [M − 2Cl]$^+$, 643 [M − 3Cl − H]$^+$, 607 [M − 4Cl − 2H]$^+$. Mp: 176 °C. TLC on SiO_2: $R_f = 0.77$ (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1612 s *ν*(C=N). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 2.86 and 2.87 (two s, 3H each, C−N(*Me*)−O), 2.92 and 2.93 (s + d each, $^4J_{PtH}$ 3.0 Hz, 3H each, =C(*Me*)O), 3.75 (s, 6H, OMe), 6.35 (s + d, $^3J_{PtH}$ 11.7 Hz, 2H, N−C*H*−N), 6.84 (d, 8.8 Hz, 4H) and 7.10 (d, 8.8 Hz, 4H) (C_6H_4OMe). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, *δ*: 15.59 and 15.64 ($^3J_{PtC}$ 4 Hz, N=C(*Me*)O), 45.9 (C−N(*Me*)−O), 55.2 (OMe), 90.38 and 90.46 ($^2J_{PtC}$ 21 Hz, N−*C*H−N), 113.8 (CH), 127.17 and 127.19 (CH), 129.85 and 129.90 (Cq), 159.9 (Cq), 174.7 (C=N). ^{195}Pt NMR spectrum in $CDCl_3$, *δ*: −190 (600 Hz).

[$PtCl_4$(N=C(Me)O−N(Me)−C(H)(*p*-$C_6H_4NO_2$))$_2$]. Yield: 91%. Anal. Calcd for $C_{20}H_{22}N_6Cl_4O_6Pt$: C, 30.82; H, 2.85; N, 10.78. Found: C, 30.96; H, 2.75; N, 10.41. FAB$^+$-MS in NBA matrix shows no signals characteristic for the compound. The compound has no defined melting point: on heating, it decomposes above 270 °C. TLC on SiO_2: $R_f = 0.60$ (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1603 s *ν*(C=N), 1524 s $\nu_{as}(NO_2)$, 1350 $\nu_s(NO_2)$. In 300 MHz NMR spectra we observed only one set of signals and were unable to distinguish diastereoisomers. ^{1}H NMR spectrum in $CDCl_3$, *δ*: 2.76 (s, 3H, C−N(*Me*)−O), 2.80 (s + d, $^4J_{PtH}$ 3.9 Hz, 3H, =C(*Me*)O), 6.32 (s + d, $^3J_{PtH}$ 12.3 Hz, 1H, N−C*H*−N), 7.26 (d, 8.5 Hz, 2H) and 8.00 (d, 8.6 Hz, 2H) (C_6H_4). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, *δ*: 15.0 ($^3J_{PtC}$ 4 Hz, N=C(*Me*)O), 45.6 (C−N(*Me*)−O), 88.9 ($^2J_{PtC}$ 21 Hz, N−*C*H−N), 122.9 (CH), 126.9 (CH), 144.2 (Cq) and 147.5 (Cq) (C_6H_4), 175.4 (C=N). ^{195}Pt NMR spectrum in $CDCl_3$, *δ*: −198 (600 Hz).

[$PtCl_4$(N=C(Me)O−N(Me)−C(H)(*o*-C_6H_4OH))$_2$] (Two Diastereoisomers, 1:1). Yield: 94%. Anal. Calcd for $C_{20}H_{24}N_4Cl_4O_4Pt$: C, 33.30; H, 3.35; N, 7.77. Found: C, 31.22; H, 3.35; N, 7.22. FAB$^+$-MS, *m*/*z*: 722 [M + H]$^+$, 651 [M − 2Cl]$^+$, 615 [M − 3Cl − H]$^+$, 579 [M − 4Cl − 2H]$^+$. Mp: 157 °C dec. TLC on SiO_2: $R_f = 0.50$ (eluent 9:1 CH_2Cl_2:acetone). IR spectrum (selected bands), cm^{-1}: 3367 s *ν*(OH), 1610 s *ν*(C=N). ^{1}H NMR spectrum in acetone-d_6, *δ*: 2.85 and 2.86 (two s,

3H each, C−N(*Me*)−O), 2.96 (s + d, $^4J_{PtH}$ 4.1 Hz, 6H, =C(*Me*)O), 6.75 (m, 2H, N−C*H*−N), 6.75 (m, 2H), 6.85 (ddd, 7.8 Hz, 3.3 Hz, 1.2 Hz, 2H), 6.96 (d, 7.5 Hz, 2H) and 7.11 (m, 2H) (C_6H_4O). $^{13}C\{^1H\}$ NMR spectrum in acetone-d_6, δ: 15.80 and 15.85 ($^3J_{PtC}$ 4 Hz, N=C(*Me*)O), 45.8 (C−N(*Me*)−O), 87.3 (broad, N−CH−N), 115.9, 119.6, 125.9, 127.3, 130.1, and 154.8 (C_6H_4OH), 176.3 (C=N). ^{195}Pt NMR spectrum in acetone-d_6, δ: −142 (520 Hz).

[$PtCl_4$(N=C(Me)O−N(Me)−C(H)(*p*-$C_6H_4NMe_2$)•HCl)$_2$] (Two Diastereoisomers, 1:1). This complex precipitates directly from the reaction mixture. It is washed with 10 mL of CH_2Cl_2 and 5 mL of ether and dried in air. Yield: 98%. Anal. Calcd for $C_{24}H_{36}N_6Cl_6O_2Pt$: C, 33.98; H, 4.28; N, 9.91. Found: C, 33.35; H, 4.24; N, 9.00. FAB$^+$-MS, *m*/*z*: 704 [$PtCl_4$(NC(Me)ON(Me)C(H)$C_6H_4NHMe_2$)$_2$ − 2Cl]$^+$. Mp: 141 °C dec. IR spectrum (selected bands), cm^{-1}: 1597 s ν(C=N). ^{1}H NMR spectrum in DMSO-d_6, δ: 2.84 and 2.91 (two s, 3H each, C−N(*Me*)−O and =C(*Me*)O), 2.98 (s, 6H, NMe_2), 6.40 (s + d, $^3J_{PtH}$ 11.8 Hz, 1H, N−C*H*−N), 7.23 (m, 4H, $C_6H_4NMe_2$). The complex is rather unstable in DMSO-d_6 and poorly soluble in most other common deuterated solvents to measure the $^{13}C\{^1H\}$ NMR spectrum. ^{195}Pt NMR spectrum in DMSO-d_6, δ: −98 (560 Hz).

[$PtCl_4$(N=C(Me)O−N(Me)−C(H)(*p*-$C_6H_4NMe_2$))$_2$]. The complex is liberated from the corresponding hydrochloride adduct by stirring a suspension of [$PtCl_4$(N=C(Me)O−N(Me)−C(H)(*p*-$C_6H_4NMe_2$)•HCl)$_2$] and Na_2CO_3 in CH_2Cl_2, followed by filtration and evaporation of the solvent. Yield: 70%. The complex is very unstable, even in the solid state, and its degradation is already significant within 1 h after isolation. Elemental analyses obtained were unsatisfactory. However, spectrosopy data presented below give arguments in favor of the proposed structure. IR spectrum (selected bands), cm^{-1}: 1611 s ν(C=N). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.86 (s, 3H, C−N(*Me*)−O), 2.91 (s, 6H, NMe_2), 2.96 (s, 3H, =C(*Me*)O), 6.33 (s + d, $^3J_{PtH}$ 12.0 Hz, 1H, N−C*H*−N), 6.73 (m, 2H) and 7.04 (d, 7.2 Hz, 2H) ($C_6H_4NMe_2$). The complex is rather unstable in $CDCl_3$ to measure the $^{13}C\{^1H\}$ NMR spectrum. ^{195}Pt NMR spectrum in $CDCl_3$, δ: −173 (650 Hz).

[$PtCl_4$(N=C(Me)O−N(CH_2Ph)−C(H)^{t}Bu)$_2$] (Two Diastereoisomers, 1:1). Yield: 50%. Anal. Calcd for $C_{28}H_{40}N_4Cl_4O_2Pt$: C, 41.96; H, 5.03; N, 6.99. Found: C, 40.98; H, 4.41; N, 6.65. FAB$^+$-MS, *m*/*z*: 753 [M − 2Cl + Na]$^+$, 731 [M − 2Cl]$^+$. Mp: 214 °C dec. TLC on SiO_2: R_f = 0.90 (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1567 s ν(C=N). ^{1}H NMR spectrum in $CDCl_3$, δ: 1.03 and 1.04 (two s, 9H each, ^{t}Bu), 2.85 and 2.87 (s + d each, $^4J_{PtH}$ 3.5 Hz, 3H each, =C(Me)O), 4.11 (d, 13.1 Hz, 2H), 4.20 (d, 13.1 Hz, 1H) and 4.21 (d, 13.1 Hz, 1H) (CH_2Ph), 5.25 and 5.26 (two s + d, $^3J_{PtH}$ 13.0 Hz, 1H each, N−CH−N), 7.38 (m, 3H) and 7.51 (m, 2H) (CH_2Ph). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 17.36 and 17.42 ($^3J_{PtC}$ 3.0 Hz, N=C(Me)O), 27.67 and 27.72 ((CH_3)$_3$C), 37.8 ((CH_3)$_3$*C*), 61.30 and 61.37 (*C*H_2Ph), 94.20 and 94.34 ($^2J_{PtC}$ 20.2 Hz, N−CH−N), 128.0 (*p*-PhCH_2), 128.4 (PhCH_2), 129.72 and 129.75 (PhCH_2), 134.1 (*ipso*-PhCH_2), 177.5 (C=N). ^{195}Pt NMR spectrum $CDCl_3$, δ: +107 (775 Hz).

Liberation of Coordinated Δ^4-1,2,4-Oxadiazolines by Reaction with Pyridine. A solution of the corresponding platinum(IV) complex (0.060 mmol) and pyridine (10.4 mg, 0.13 mmol) in $CHCl_3$ (2.0 mL) was stirred for 6 h at room temperature. In the course of reaction the [$PtCl_4$(pyridine)$_2$] precipitates from the starting yellow solution as a yellow powder. After filtration, the filtrate is evaporated to dryness in vacuo and the residue formed analyzed without further purification.

N=C(Me)O−N(Me)−C(H)Ph. Yield: 78%. Oil. EI-MS, *m*/*z*: 175 [M − 1], 134 [M − 1 − CH_3CN], 118 [M − 1 − CH_3CN − O]. TLC on SiO_2: R_f = 0.32 (eluent 9:1 CH_2Cl_2:Et_2O). IR spectrum (selected bands), cm^{-1}: 1673 s ν(C=N). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.11 (s, 3H, =C(*Me*)O), 2.89 (s, 3H, C−N(*Me*)−O), 5.55 (s, 1H, N−C*H*−N), 7.32−7.39 (m, 5H, *Ph*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 12.0 (N=C(*Me*)O), 47.5 (C−N(*Me*)O), 93.5 (N−*C*H−N), 126.3, 128.3, 128.5 and 140.0 (Ph), 161.2 (C=N).

N=C(Me)O−N(CH_2Ph)−C(H)Ph. Yield: 89%. Oil. EI-MS, *m*/*z*: 252 [M], 211 [M − CH_3CN], 193 [M − CH_3CN − H_2O]. TLC on SiO_2: R_f = 0.32 (eluent 9:1 CH_2Cl_2:Et_2O). IR spectrum (selected bands), cm^{-1}: 1677 s ν(C=N). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.12 (s, 3H, =C(*Me*)O), 4.14 (d, 12.6 Hz, 1H) and 4.29 (d, 12.9 Hz, 1H) (CH_2Ph), 5.80 (s, 1H, N−C*H*−N), 7.31−7.42 (m, 10H, Ph and CH_2*Ph*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 12.1 (N=C(*Me*)O), 63.3 (*C*H_2Ph), 90.4 (N−*C*H−N), 126.4, 128.4, 128.5, and 140.2 (Ph), 128.2, 128.6, 129.4 and 135.3 (CH_2*Ph*), 161.6 (C=N).

N=C(Me)O−N(Me)−C(H)(*p*-C_6H_4Me). Yield: 88%. Oil. EI-MS, *m*/*z*: 189 [M − 1], 148 [M − 1 − CH_3CN], 131 [M − CH_3CN − H_2O]. TLC on SiO_2: R_f = 0.28 (eluent 9:1 CH_2Cl_2:Et_2O). IR spectrum (selected bands), cm^{-1}: 1676 s ν(C=N). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.11 (s, 3H, =C(*Me*)O), 2.35 (s, 3H, C_6H_4*Me*), 2.88 (s, 3H, C−N(*Me*)−O), 5.52 (s, 1H, N−C*H*−N), 7.18 (d, 7.8 Hz, 2H), 7.29 (d, 7.8 Hz, 2H) (C_6H_4Me). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 12.1 (N=C(*Me*)O), 21.2 (C_6H_4*Me*), 47.0 (C−N(*Me*)O), 93.4 (N−*C*H−N), 125.8, 126.2, 129.2 and 138.1 (C_6H_4Me), 161.1 (C=N).

N=C(Me)O−N(Me)−C(H)(*p*-C_6H_4OMe). Yield: 73%. Oil. EI-MS, *m*/*z*: 206 [M], 164 [M − 1 − CH_3CN], 146 [M − 1 − CH_3CN − H_2O]. TLC on SiO_2: R_f = 0.28 (eluent 9:1 CH_2Cl_2:Et_2O). IR spectrum (selected bands), cm^{-1}: 1674 s ν(C=N). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.11 (s, 3H, =C(*Me*)O), 2.87 (s, 3H, C−N(*Me*)−O), 3.79 (s, 3H, C_6H_4O*Me*), 5.50 (s, 1H, N−C*H*−N), 6.89 (d, 8.7 Hz, 2H), 7.31 (d, 8.4 Hz, 2H) (C_6H_4OMe). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 12.1 (N=C(*Me*)O), 47.0 (C−N(*Me*)O), 55.3 (C_6H_4O*Me*), 93.3 (N−*C*H−N), 113.9, 123.8, 127.6 and 149.8 (C_6H_4Me), 160.0 (C=N).

N=C(Me)O−N(Me)−C(H)(*p*-$C_6H_4NO_2$). Yield: 65%. Oil. EI-MS, *m*/*z*: 221 [M], 180 [M − CH_3CN]. TLC on SiO_2: R_f = 0.26 (eluent 9:1 CH_2Cl_2:Et_2O). IR spectrum (selected bands), cm^{-1}: 1672 s ν(C=N), 1519 s ν_{as}(NO_2), 1346 ν_s(NO_2). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.11 (s, 3H, =C(*Me*)O), 2.91 (s, 3H, C−N(*Me*)−O), 5.64 (s, 1H, N−C*H*−N), 7.61 (d, 9.0 Hz, 2H) and 8.23 (d, 8.7 Hz, 2H) (C_6H_4). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 12.0 (N=C(*Me*)O), 47.0 (C−N(*Me*)−O), 92.2 (N−*C*H−N), 127.3 (CH), 129.2 (CH), 139.2 (Cq) and 147.1 (Cq) (C_6H_4), 160.2 (C=N).

N=C(Me)O−N(Me)−C(H)(*o*-C_6H_4OH). Yield: 72%. Oil. EI-MS, *m*/*z*: 191 [M − 1], 151 [M − CH_3CN]. TLC on SiO_2: R_f = 0.13 (eluent 9:1 CH_2Cl_2:Et_2O). IR spectrum (selected bands), cm^{-1}: 3374 s ν(OH), 1675 s ν(C=N). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.06 (s, 3H, =C(*Me*)O), 2.93 (s, 3H, C−N(*Me*)−O), 5.92 (s, 1H, N−C*H*−N), 6.93 (m, 1H), 7.03 (m, 1H) and 7.32 (m, 2H) (C_6H_4O). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 13.3 (N=C(*Me*)O), 46.5 (C−N(*Me*)−O), 88.9 (N−CH−N), 117.6, 120.5, 125.2, 126.9, 130.8, and 153.7 (C_6H_4OH), 160.0 (C=N).

N=C(Me)O−N(CH_2Ph)−C(H)^{t}Bu. Yield: 53%. Oil. EI-MS, *m*/*z*: 232 [M], 191 [M − CH_3CN], 173 [M − CH_3CN − H_2O]. TLC on SiO_2: R_f = 0.31 (eluent 9:1 CH_2Cl_2:Et_2O). IR spectrum (selected bands), cm^{-1}: 1670 s ν(C=N). ^{1}H NMR spectrum in $CDCl_3$, δ: 1.08 (s, 9H, ^{t}Bu), 2.68 (s, 3H, =C(*Me*)O), 3.82 (dd, 13.2 Hz, 2.1 Hz, 1H) and 4.72 (d, 13.2 Hz, 1H) (CH_2Ph), 4.72 (s, 1H, N−C*H*−N), 7.30−7.40 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 13.4 (N=C(*Me*)O), 25.3 (C(*C*H_3)$_3$), 35.6 (*C*(CH$_3$)$_3$), 62.9 (*C*H_2Ph), 94.7 (N−*C*H−N), 128.2, 129.0, 130.2 and 134.4 (CH_2*Ph*), 160.0 (C=N).

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Supporting Information Available: Tables of crystal data and refinement, atomic coordinates, bond length, angles, and anisotropic parameters (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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