[2 + 3] Cycloaddition of Nitrones to Platinum-Bound Organonitriles: Effect of Metal Oxidation State and of Nitrile Substituent

Gabriele Wagner,[†] Matti Haukka,[‡] João J. R. Fraústo da Silva,[†] Armando J. L. Pombeiro,*[,†] and Vadim Yu. Kukushkin*[,§]

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101, Joensuu, Finland, and St. Petersburg State University, 198904 Stary Petergof, Russian Federation

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The ligated benzonitriles in the platinum(II) complex $[PtCl_2(PhCN)_2]$ undergo metal-mediated [2 + 3] cycloaddition with nitrones $^{-}ON^{+}(R^3)=C(R^1)(R^2)$ [$R^1/R^2/R^3$ = H/Ph/Me, H/*p*-MeC_6H_4/Me, H/Ph/CH_2Ph] to give Δ^4-1,2,4-oxadiazoline complexes, $[PtCl_2\{N=C(Ph)O-N(R^3)-C(R^1)(R^2)\}_2]$ (**2a**, **4a**, **6a**), as a 1:1 mixture of two diastereoisomers, in 60−75% yields, while $[PtCl_2(MeCN)_2]$ is inactive toward the addition. However, a strong activation of acetonitrile was reached by application of the platinum(IV) complex $[PtCl_4(MeCN)_2]$ and both $[PtCl_4(RCN)_2]$ (R = Me, Ph) react smoothly with various nitrones to give $[PtCl_4\{N=C(R)O-N(R^3)-C(R^1)(R^2)\}_2]$ (**1b**−**6b**). The latter were reduced to the corresponding platinum(II) complexes $[PtCl_2\{N=C(R)O-N(R^3)-C(R^1)(R^2)\}_2]$ (**1a**−**6a**) by treatment with $PhCH_2NHOH$, while the reverse reaction, i.e. conversion of **1a**−**6a** to **1b**−**6b**, was achieved by chlorination with Cl_2. The diastereoisomers of $[PtCl_2\{N=C(R)O-N(R^3)-C(R^1)(R^2)\}_2]$ (**1a**−**6a**) exhibit different kinetic labilities, and liberation of the Δ^4-1,2,4-oxadiazolines by substitution with 1,2-bis(diphenylphosphino)ethane (dppe) in $CDCl_3$ proceeds at different reaction rates to give free $N=C(R)O-N(R^3)-C(R^1)(R^2)$ and $[PtCl_2(dppe)]$ in almost quantitative NMR yield. All prepared compounds were characterized by elemental analyses, FAB mass spectrometry, and IR and ^1H, $^{13}C\{^1H\}$, and ^{195}Pt (metal complexes) NMR spectroscopies; X-ray structure determination of the first (Δ^4-1,2,4-oxadiazoline)Pt(II) complexes was performed for (*S*,*S*)/(*R*,*R*)-*rac*-$[PtCl_2\{N=C(Me)O-N(Me)-C(H)Ph\}_2]$ (**1a**) (a = 9.3562(4), b = 9.8046(3), c = 13.1146(5) Å; α = 76.155(2), β = 83.421(2), γ = 73.285(2)°; V = 1117.39(7) Å^3; triclinic, $P\bar{1}$, Z = 2), (*R*,*S*)-*meso*-$[PtCl_2(N=C(Ph)O-N(Me)-C(H)Ph)_2]$ (**2a**) (a = 8.9689(9), b = 9.1365(5), c = 10.1846(10) Å; α = 64.328(6), β = 72.532(4), γ = 67.744(6)°; V = 686.82(11) Å^3; triclinic, $P\bar{1}$, Z = 1), (*S*,*S*)/(*R*,*R*)-*rac*-$[PtCl_2(N=C(Me)O-N(Me)-C(H)(p\text{-}C_6H_4Me))_2]$ (**3a**) (a = 11.6378(2), b = 19.0767(7), c = 11.5782(4) Å; β = 111.062(2)°; V = 2398.76(13) Å^3; monoclinic, $P2_1/c$, Z = 4), and (*S*,*S*)/(*R*,*R*)-*rac*-$[PtCl_2(N=C(Me)O-N(CH_2Ph)-C(H)Ph_2]$ (**5a**) (a = 10.664(2), b = 10.879(2), c = 14.388(3) Å; α = 73.11(3), β = 78.30(3), γ = 88.88(3)°; V = 1562.6(6) Å^3; triclinic, $P\bar{1}$, Z = 2).

Introduction

In organic chemistry, transformations of organonitriles play an important role in both laboratory and industry due to their chemical versatility. In particular, the addition of electrophiles[1] or nucleophiles[2−11] to the C≡N triple bond offers an attractive route for creation of novel C−C, C−N, and C−O bonds. Among the nucleophiles used, much attention has been drawn to additions of water to RCN to give carboxylic acids or amides,[2,3] alcohols to produce iminoethers or esters,[4−7] amines to give amidines,[8] and also compounds exhibiting significant C−H acidity to form the new C−C bond due to the addition.[9−11] One of the main problems encountered in reactions of nucleophilic

* Authors to whom correspondence should be addressed. Fax: +351-21-846 4455 or +7-8124286939. E-mail: pombeiro@ist.utl.pt or kukushkin@vk2100.spb.edu.
† Instituto Superior Técnico.
‡ University of Joensuu.
§ St. Petersburg State University.

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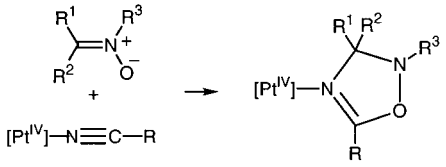
addition is insufficient electrophilic activation even by very strong electron-accepting groups R at RCN, e.g. Cl_3CCN, to perform the addition, and numerous examples of limitations of so-called pure organic chemistry in this field are illustrative.[12−16] These difficulties, however, can be overcome with the use of metal ions[9]—sometimes even in low-oxidation-states[24]—as extremely strong activators toward nucleophilic attack. This activation can result in enhancement of the rate of the addition commonly in the range of 10^6−10^8 [17] (and occasionally to 10^{18} [25]). Moreover, metal-mediated processes in many instances allow the performance of certain reactions which are not feasible without the involvement of metal ions.

Our recent results in the field of RCN ligands reactivity are relevant to (i) the observation of the fast and high-yield reaction between the platinum(IV) complexes $[PtCl_4(RCN)_2]$ and oximes, $R^1R^2C{=}NOH$,[26] and *vic*-dioximes, HON={spacer}=NOH (spacer = C(Me)C(Me), C{C_4H_8}C, C{C_5H_{10}}C, C{C_6H_{12}}C),[27] which led to the isolation of unusual iminoacylated [or (alkylideneaminooxy)imine] compounds $[PtCl_4(NH{=}C(R)ON{=}CR^1R^2)_2]$ or novel types of metallaligands $[PtCl_4(NH{=}C(R)ON{=}\{spacer\}{=}NOH)_2]$, respectively, (ii) the extension of the iminoacylation reaction involving Pt(IV) compounds to Re(IV)[28] and Rh(III)[29,30] organonitrile complexes, and (iii) the establishment of an unprecedented Ag^+- or Cu^{2+}-catalyzed coupling of dialkylcyanamides with oximes at a platinum(II) center.[31] Our interest in further exploring the metal-mediated reactions of organonitriles was recently sparked by the observation of a facile [2 + 3] cycloaddition between acetonitrile ligands in the highly reactive platinum(IV) complex $[PtCl_4(MeCN)_2]$ and various nitrones of the type $^-ON^+(R^3){=}C(R^1)(R^2)$ that gives—due to Pt(IV)-assisted cycloaddition (Scheme 1)—Δ^4-1,2,4-oxadiazoline complexes $[PtCl_4\{N{=}C(Me)O{-}N(R^3){-}C(R^1)(R^2)\}_2]$, as a 1:1 mixture of two diastereoisomers, in good to almost quantitative yields.[32]

Scheme 1. [2 + 3] Cycloaddition of Nitrones to Pt(IV)-Bound Acetonitrile Ligands



Moreover, the liberation of the newly formed ligands by reaction of $[PtCl_4\{N{=}C(Me)O{-}N(R^3){-}C(R^1)(R^2)\}_2]$ with pyridine was performed, and that opened up a route to Δ^4-1,2,4-oxadiazoline heterocyclic species whose synthesis and chemistry are very little developed. We anticipated the mild reaction conditions of the [2 + 3] cycloaddition to be a viable synthetic pathway for the preparation of that type of metal-bound heterocycles. However, the precise role of the metal oxidation state on the control of the reactivity and/or the effect of substituents R at the [Pt]−NCR center were not completely understood and we felt that further reactivity studies on the [2 + 3] cycloaddition of nitrones to metal-bound nitriles deserved additional efforts.

In the framework of our research program on the reactivity of organonitrile complexes[33−42] and as an extension of our previous work[32] on the [2 + 3] cycloaddition, it was decided to examine whether the cycloaddition is peculiar for platinum(IV) compounds or it represents a more general type of reaction of nitrones and nitrile metal complexes and also to verify factors affecting the addition. For achieving that goal, we addressed for the current work (organonitrile)Pt^{II} complexes and compared their reactivity toward the cycloaddition with that of the corresponding platinum(IV) compounds. It has been found that, for the highly reactive platinum(IV) complexes $[PtCl_4(RCN)_2]$, the cycloaddition can be performed under mild conditions starting even from a very unreactive organonitrile bearing an electron-donor substituent, e.g. R = Me, while for the much less reactive organonitriles in platinum(II) complexes $[PtCl_2(RCN)_2]$ the cycloaddition occurs only in the case of the organonitrile with an electron-acceptor substituent, i.e. R = Ph. Furthermore, it was observed that Pt(II)-bound Δ^4-1,2,4-

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Table 1. Crystallographic Data for *rac*-**1a**, *meso*-**2a**, *rac*-**3a**, and *rac*-**5a**

	rac-**1a**	*meso*-**2a**	*rac*-**3a**	*rac*-**5a**
chem formula	$C_{20}H_{24}N_4Cl_2O_2Pt$	$C_{30}H_{28}N_4Cl_2O_2Pt$	$C_{22}H_{28}N_4Cl_2O_2Pt$	$C_{32}H_{32}N_4Cl_2O_2Pt$
fw	618.41	742.54	646.46	770.60
temp, K	120	120	120	293
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.3562(4)	8.9689(9)	11.6378(2)	10.664(2)
b, Å	9.8046(3)	9.1365(5)	19.0767(7)	10.879(2)
c, Å	13.1146(5)	10.1846(10)	11.5782(4)	14.388(3)
α, deg	76.155(2)	64.328(6)	90	73.11(3)
β, deg	83.421(2)	72.532(4)	111.062(2)	78.30(3)
γ, deg	73.285(2)	67.744(6)	90	88.88(3)
V, Å^3	1117.39(7)	686.82(11)	2398.76(13)	1562.6(6)
Z	2	1	4	2
ρ_{calcd}, g/cm^3	1.838	1.795	1.790	1.638
μ(Mo Kα), mm^{-1}	6.541	5.338	6.098	4.696
R_1[a]	0.0232	0.0294	0.0316	0.0511
wR_2[b]	0.0520	0.0639	0.0664	0.1208

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

oxadiazolines can be liberated by a novel route, based on substitution with 1,2-bis(diphenylphosphino)ethane (dppe) or with PPh_3, and all these results are reported herein.

Experimental Section

Materials and Instrumentation. Aldehydes and *N*-alkylhydroxylamines were purchased from Aldrich. Solvents were obtained from commercial sources and used as received. Nitrones were synthesized by condensation of the corresponding aldehyde, and *N*-alkylhydroxylamine, according to the published methods.[43] The complexes **1b**, **3b**, **5b**,[32] $[PtCl_4(RCN)_2]$ (R = Me, Ph),[26] and *cis*-/*trans*-$[PtCl_2(PhCN)_2]$[44] were prepared as previously described. 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 have been 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. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{195}Pt NMR spectra were measured on a Varian Unity 300 spectrometer at ambient temperature. ^{31}P chemical shifts are quoted relative to 80% H_3PO_4 = 0 ppm. ^{195}Pt chemical shifts are given relative to aqueous $K_2[PtCl_4]$ = −1630 ppm, with half-height line width in parentheses.

X-ray Structure Determination of *rac*-5a. Yellow prisms of *rac*-**5a** were obtained by slow evaporation of a dichloromethane/acetone mixture. Diffraction data were collected on an Enraf-Nonius CAD 4 diffractometer. Cell parameters were obtained from 24 centered reflections with θ between 11 and 138°. Range of *hkl*: $h = -13$ to 13; $k = 0$ to 12; $l = -16$ 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[45] with profile analysis of reflections. The structure was solved by means of Fourier synthesis based upon the Pt-atom coordinates obtained from the Patterson synthesis using SHELXTL package.[46] After that, all reflections with $I < 2\sigma(I)$ were excluded from calculations. The refinement was done by full-matrix least squares based on F^2 using the SHELX-97 package.[47] All non H-atoms were treated anisotropically. H atoms were located in a difference Fourier map and refined isotropically. An extinction correction was not applied. Lorentz, polarization, and absorption corrections were made.[48] Scattering factors were from ref 49 Crystal data are given in Table 1, and bond distances and angles in Table 5.

Table 2. Bond Lengths (Å) and Angles (deg) for *rac*-**1a**

Pt(1)−Cl(1)	2.3019(10)	N(1A)−C(1A)	1.477(5)
Pt(1)−Cl(1A)	2.3019(10)	N(1A)−C(2A)	1.280(5)
Pt(1)−N(1)	1.999(3)	N(2)−C(1)	1.482(5)
Pt(1)−N(1A)	2.015(3)	N(2)−C(3)	1.476(6)
O(1)−N(2)	1.501(5)	N(2A)−C(1A)	1.490(5)
O(1)−C(2)	1.350(5)	N(2A)−C(3A)	1.467(6)
O(1A)−N(2A)	1.489(5)	C(1)−C(4)	1.515(6)
O(1A)−C(2A)	1.342(5)	C(1A)−C(4A)	1.505(5)
N(1)−C(1)	1.492(5)	C(2)−C(10)	1.473(6)
N(1)−C(2)	1.273(5)	C(2A)−C(10A)	1.462(7)
Cl(1)−Pt(1)−Cl(1A)	178.15(3)	C(1)−N(2)−C(3)	110.8(3)
Cl(1)−Pt(1)−N(1)	86.95(8)	O(1A)−N(2A)−C(1A)	103.6(3)
Cl(1)−Pt(1)−N(1A)	91.44(8)	O(1A)−N(2A)−C(3A)	103.1(3)
Cl(1A)−Pt(1)−N(1)	91.31(8)	C(1A)−N(2A)−C(3A)	112.4(4)
Cl(1A)−Pt(1)−N(1A)	90.34(8)	N(1)−C(1)−N(2)	103.7(3)
N(1)−Pt(1)−N(1A)	175.60(11)	N(1)−C(1)−C(4)	110.8(3)
N(2)−O(1)−C(2)	106.2(3)	N(2)−C(1)−C(4)	112.9(3)
N(2A)−O(1A)−C(2A)	106.6(3)	N(1A)−C(1A)−N(2A)	104.1(3)
Pt(1)−N(1)−C(1)	119.3(2)	N(1A)−C(1A)−C(4A)	112.0(3)
Pt(1)−N(1)−C(2)	132.3(2)	N(2A)−C(1A)−C(4A)	112.1(3)
C(1)−N(1)−C(2)	108.4(3)	O(1)−C(2)−N(1)	115.1(3)
Pt(1)−N(1A)−C(1A)	120.8(2)	O(1)−C(2)−C(10)	116.5(3)
Pt(1)−N(1A)−C(2A)	129.6(3)	N(1)−C(2)−C(10)	128.3(4)
C(1A)−N(1A)−C(2A)	108.8(3)	O(1A)−C(2A)−N(1A)	115.5(4)
O(1)−N(2)−C(1)	102.5(3)	O(1A)−C(2A)−C(10A)	116.1(4)
O(1)−N(2)−C(3)	103.7(3)	N(1A)−C(2A)−C(10A)	128.4(4)

X-ray Structure Determinations of *rac*-1a, *meso*-2a, and *rac*-3a. Pale yellow blocks of *rac*-**1a** and pale yellow needles of *meso*-**2a** and of *rac*-**3a** were grown by diffusion of diethyl ether into CH_2Cl_2 solutions of the corresponding complexes. X-ray diffraction data for *rac*-**1a**, *meso*-**2a**, and *rac*-**3a** were collected with a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and the ϕ-/ω-scan or ϕ-scan data collection mode with a Collect[50] collection program. Denzo and Scalepack[51] programs were used for cell refinements and data reduction. A multiscan absorption correction, based on equivalent reflections

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Table 3. Bond Lengths (Å) and Angles (deg) for *meso*-**2a**[a]

Pt−Cl(1)	2.3085(14)	N(1)−C(2)	1.281(8)
Pt−N(1)	2.000(4)	N(2)−C(1)	1.477(8)
O(1)−N(2)	1.469(7)	N(2)−C(3)	1.469(9)
O(1)−C(2)	1.356(7)	C(1)−C(4)	1.524(8)
N(1)−C(1)	1.506(7)	C(2)−C(10)	1.469(8)

Cl(1)−Pt−N(1)	92.19(14)	O(1)−N(2)−C(1)	101.9(4)
Cl(1)−Pt−Cl(1)#1	180.00	O(1)−N(2)−C(3)	103.2(5)
Cl(1)−Pt−N(1)#1	87.81(14)	C(1)−N(2)−C(3)	112.8(5)
Cl(1)#1−Pt−N(1)	87.81(14)	N(1)−C(1)−N(2)	103.9(5)
N(1)−Pt−N(1)#1	180.00	N(1)−C(1)−C(4)	109.4(5)
Cl(1)#1−Pt−N(1)#1	92.19(14)	N(2)−C(1)−C(4)	112.5(4)
N(2)−O(1)−C(2)	107.1(4)	O(1)−C(2)−N(1)	114.7(5)
Pt−N(1)−C(1)	119.0(3)	O(1)−C(2)−C(10)	115.6(5)
Pt−N(1)−C(2)	134.1(4)	N(1)−C(2)−C(10)	129.7(5)
C(1)−N(1)−C(2)	106.5(4)		

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

Table 4. Bond Lengths (Å) and Angles (deg) for *rac*-**3a**

Pt(1)−Cl(1)	2.3065(16)	N(1A)−C(1A)	1.474(8)
Pt(1)−Cl(1A)	2.3120(16)	N(1A)−C(2A)	1.275(8)
Pt(1)−N(1)	2.015(5)	N(2)−C(1)	1.498(8)
Pt(1)−N(1A)	2.007(6)	N(2)−C(3)	1.477(9)
O(1)−N(2)	1.491(7)	N(2A)−C(1A)	1.509(8)
O(1)−C(2)	1.354(7)	N(2A)−C(3A)	1.457(9)
O(1A)−N(2A)	1.496(7)	C(1)−C(4)	1.508(9)
O(1A)−C(2A)	1.352(7)	C(1A)−C(4A)	1.523(9)
N(1)−C(1)	1.484(7)	C(2)−C(10)	1.471(8)
N(1)−C(2)	1.286(8)	C(2A)−C(10A)	1.489(8)

Cl(1) −Pt(1)−Cl(1A)	177.24(5)	C(1)−N(2)−C(3)	109.7(5)
Cl(1)−Pt(1)−N(1)	87.62(15)	O(1A)−N(2A)−C(1A)	101.7(4)
Cl(1)−Pt(1)−N(1A)	92.13(17)	O(1A)−N(2A)−C(3A)	104.1(5)
Cl(1A)−Pt(1)−N(1)	92.86(15)	C(1A)−N(2A)−C(3A)	111.4(5)
Cl(1A)−Pt(1)−N(1A)	87.61(17)	N(1)−C(1)−N(2)	103.8(4)
N(1)−Pt(1)−N(1A)	175.16(19)	N(1)−C(1)−C(4)	114.3(5)
N(2)−O(1)−C(2)	106.2(4)	N(2)−C(1)−C(4)	112.6(6)
N(2A)−O(1A)−C(2A)	105.8(5)	N(1A)−C(1A)−N(2A)	103.9(5)
Pt(1)−N(1)−C(1)	125.8(4)	N(1A)−C(1A)−C(4A)	113.7(5)
Pt(1)−N(1)−C(2)	125.4(4)	N(2A)−C(1A)−C(4A)	112.0(5)
C(1)−N(1)−C(2)	107.9(5)	O(1)−C(2)−N(1)	115.1(5)
Pt(1)−N(1A)−C(1A)	125.0(4)	O(1)−C(2)−C(10)	117.0(5)
Pt(1)−N(1A)−C(2A)	126.3(5)	N(1)−C(2)−C(10)	127.9(6)
C(1A)−N(1A)−C(2A)	108.2(5)	O(1A)−C(2A)−N(1A)	115.7(5)
O(1)−N(2)−C(1)	102.0(4)	O(1A)−C(2A)−C(10A)	115.3(5)
O(1)−N(2)−C(3)	103.8(5)	N(1A)−C(2A)−C(10A)	128.9(6)

(MULABS[52] or XPREP in SHELXTL v. 5.1[53]), was applied to all data (T_{max}/T_{min} was 0.3032/0.2464, 0.7762/0.6174, and 0.4098/0.3516 for *rac*-**1a**, *meso*-**2a**, and *rac*-**3a**, respectively). Structures were solved by the Patterson method using the DIRDIF-99 program.[54] Structure refinements were carried out with the SHELXL-97 program.[47] All non-hydrogen atoms were refined anisotropically, and hydrogens were placed on idealized positions (−CH, $U_{iso} = 1.2U_{eq}(C_{CH})$; C−H, 1.00 Å; $-CH_3$, $U_{iso} = 1.5U_{eq}(C_{CH3})$; C−H, 0.98 Å; $CH_{arom.}$, $U_{iso} = 1.2U_{eq}(C_{arom.})$; C−$H_{arom}$, 0.95 Å). Crystallographic data are summarized in Table 1, and bond lengths and angles are listed in Tables 2−4.

Preparation of the Platinum(II) Oxadiazoline Complexes. (i) Via Cycloaddition. A solution of *cis*/*trans*-[$PtCl_2(PhCN)_2$] (47 mg, 0.10 mmol) and the corresponding nitrone (0.20 mmol) in CH_2Cl_2 (2 mL) are stirred for 1 d at room temperature, and the progress of the reaction is monitored by TLC. After chromatography on SiO_2/CH_2Cl_2 and evaporation of the solvent, the product (**2a**, **4a**, or **6a**) is obtained as a pale yellow powder.

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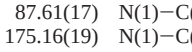
(54) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 program system*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1999.

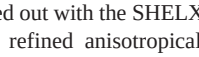
Table 5. Bond Lengths (Å) and Angles (deg) for *rac*-**5a**

Pt−Cl(1)	2.283(4)	N(2)−C(4)	1.457(17)
Pt−Cl(2)	2.295(3)	C(1)−C(11)	1.487(14)
Pt−N(1)	1.997(8)	N(3)−C(18)	1.265(11)
Pt−N(3)	1.992(9)	C(18)−O(2)	1.345(11)
N(1)−C(2)	1.298(14)	O(2)−N(4)	1.473(14)
C(2)−O(1)	1.326(13)	N(4)−C(17)	1.474(12)
O(1)−N(2)	1.506(12)	C(17)−N(3)	1.480(11)
N(2)−C(1)	1.473(15)	C(18)−C(19)	1.484(10)
C(1)−N(1)	1.453(14)	N(4)−C(20)	1.482(14)
C(2)−C(3)	1.468(16)	C(17)−C(27)	1.498(10)

Cl(1)−Pt−Cl(2)	178.89(12)	C(1)−N(2)−C(4)	113.3(10)
N(1)−Pt−Cl(1)	90.7(3)	N(2)−C(1)−C(11)	113.4(9)
N(1)−Pt−Cl(2)	88.4(3)	C(11)−C(1)−N(1)	112.8(9)
N(3)−Pt−Cl(1)	91.6(3)	Pt−N(3)−C(18)	128.9(6)
N(3)−Pt−Cl(2)	89.3(3)	Pt−N(3)−C(17)	122.9(6)
N(1)−Pt−N(3)	177.6(4)	N(3)−C(18)−O(2)	115.7(7)
Pt−N(1)−C(2)	127.9(7)	C(18)−O(2)−N(4)	105.9(7)
Pt−N(1)−C(1)	123.9(7)	O(2)−N(4)−C(17)	103.0(8)
N(1)−C(2)−O(1)	114.8(9)	N(4)−C(17)−N(3)	103.7(6)
C(2)−O(1)−N(2)	106.3(8)	C(17)−N(3)−C(18)	107.6(7)
O(1)−N(2)−C(1)	101.9(7)	N(3)−C(18)−C(19)	128.8(6)
N(2)−C(1)−N(1)	104.6(9)	O(2)−C(18)−C(19)	115.5(6)
C(1)−N(1)−C(2)	108.1(9)	O(2)−N(4)−C(20)	104.4(8)
N(1)−C(2)−C(3)	126.4(10)	C(17)−N(4)−C(20)	111.5(8)
O(1)−C(2)−C(3)	118.8(10)	N(4)−C(17)−C(27)	111.6(6)
O(1)−N(2)−C(4)	104.8(8)	C(27)−C(17)−N(3)	113.0(7)

(ii) Via Reduction. Water (one drop, ca. 0.03 mL) is added to a slurry of the platinum(IV) complex (**1b**−**6b**) (0.10 mmol), $PhCH_2$-NHOH•HCl (32 mg, 0.20 mmol), and $NaHCO_3$ (21 mg, 0.25 mmol) in CH_2Cl_2 (2 mL), and the reaction mixture is stirred at 20−25 °C for 12 h, whereafter the solvent is removed in vacuo to give an oily residue. The platinum(II) complexes **1a**−**6a** are purified by column chromatography (SiO_2/CH_2Cl_2).

[$PtCl_2$ ] (**1a**) (Two Diastereoisomers, ca. 1:1). The yield is 56% (method ii). Anal. Calcd for $C_{20}H_{24}N_4Cl_2O_2Pt$: C, 38.84; H, 3.91; N, 9.06. Found: C, 39.09; H, 4.07; N, 9.18. FAB$^+$-MS, *m*/*z*: 641 $[M + Na]^+$, 618 $[M]^+$, 581 $[M - HCl]^+$, 546 $[M - 2HCl]^+$, 410 $[M - 2HCl - PhCH{=}N(Me)O]^+$, 369 $[M - 2HCl - PhCH{=}N(Me)O - MeCN]^+$. Mp: 168 °C. TLC on SiO_2: $R_f = 0.28$ and 0.32 (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1656 and 1660 s ν(C=N). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.47 and 2.49 (two s, 3*H* of each isomer, C−N(*Me*)−O), 2.89 (s, br, 3*H* of each isomer, =C(*Me*)O), 5.68 and 5.74 (two s, br, 1*H* of each isomer, N−C*H*−N), 7.40 (m, 4*H*) and 7.59 (m, 6*H*) (*Ph*). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, δ: 13.25 and 13.30 (N=C(*Me*)O), 46.4 (C−N(*Me*)−O), 91.9 and 92.0 (br, N−*C*H−N), 128.1 and 128.2 (*o*-Ph), 128.4 and 128.5 (*m*-Ph), 129.3 (*p*-Ph), 135.7 and 136.2 (*ipso*-Ph), 167.0 and 167.3 (C=N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −2210 (400 Hz) and −2203 (400 Hz).

[$PtCl_2$ ] (**2a**) (Two Diastereoisomers, ca. 1:1). The total yield is 75% (method i). Anal. Calcd for $C_{30}H_{28}N_4Cl_2O_2Pt$: C, 48.53; H, 3.80; N, 7.55. Found: C, 48.63; H, 3.81; N, 7.48. FAB$^+$-MS, *m*/*z*: 765 $[M + Na]^+$, 742 $[M]^+$, 706 $[M - HCl]^+$, 670 $[M - 2HCl]^+$, 535 $[M - 2HCl - PhCH{=}N(Me)O]^+$, 431 $[M - 2HCl - PhCH{=}N(Me)O - PhCN]^+$. Recrystallization from $CHCl_3$/diethyl ether gave a mixture of colorless and yellow crystals which were separated mechanically. Data follow for the colorless isomer. Mp: 191 °C. TLC on SiO_2: $R_f = 0.65$ (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1645 vs ν(C=N) + ν(C=C). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.96 (s, 3*H*, C−N(*Me*)−O), 5.94 (s, br, 1*H*, N−C*H*−N), 7.40 (t, 7.8 Hz, 2*H*), 7.50 (m, 3*H*), 7.65 (m, 3*H*), and 8.68 (d, 7.5 Hz, 2*H*) (two *Ph*). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, δ: 46.0 (br, C−N(*Me*)−O), 94.7 (br, N−*C*H−N), 122.3, 128.2, 128.6, 128.8, 129.7, 130.4, 133.4 and 136.0 (two Ph), 164.1 (C=N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −2109 (380 Hz). Data follow for the yellow isomer. Mp: 184 °C. TLC on SiO_2: $R_f = 0.60$ (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1} 1623 vs ν(C=N) + ν(C=C). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.99 (s, 3*H*, C−N(*Me*)−O), 5.89 (s, br, 1*H*, N−C*H*−N), 7.37 (t, 7.6 Hz, 2*H*), 7.50 (m, 3*H*), 7.59 (m, 3*H*), and 8.84 (d, 7.6 Hz, 2*H*)

(two *Ph*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 46.3 (br, C−N(*Me*)−O), 94.8 (br, N−*C*H−N), 122.5, 128.3, 128.6, 128.7, 129.6, 130.6, 133.6 and 136.1 (two Ph), 163.5 (C═N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: − 2121 (480 Hz).

[$PtCl_2$(N═C(Me)O−N(Me)−C(H)(p-C_6H_4Me)$_2$] (**3a**) (Two Diastereoisomers, ca. 1:1). The yield is 54% (method ii). Anal. Calcd for $C_{22}H_{28}N_4Cl_2O_2Pt$: C, 40.87; H, 4.37; N, 8.67. Found: C, 41.00; H, 4.38; N, 8.63. FAB$^+$-MS, *m*/*z*: 669 [M + Na]$^+$, 646 [M]$^+$, 610 [M − HCl]$^+$, 574 [M − 2Cl]$^+$, 425 [M − 2HCl − (MeC_6H_4)CH═N(Me)O]$^+$, 384 [M − 2HCl − (MeC_6H_4)CH═N(Me)O − MeCN]$^+$. Recrystallization from CH_2Cl_2/diethyl ether/pentane gave a mixture of pale yellow needles and yellow plates which were separated mechanically. Data follow for the pale yellow needles. Mp: 131 °C. TLC on SiO_2: R_f = 0.31 (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1660 and 1651 s ν(C═N), 322 m ν(Pt−Cl). ^1H NMR spectrum in $CDCl_3$, δ: 2.40 (s, 3*H*, C_6H_4*Me*), 2.47 (s, 3*H*, C−N(*Me*)−O), 2.87 (s, br, 3*H*, ═C(*Me*)O), 5.63 (s, br, 1*H*, N−CH−N), 7.22 (d, 7.2 Hz, 2H) and 7.48 (d, 7.8 Hz, 2H) (C_6H_4Me). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 13.25 (N═C(*Me*)O), 21.4 (C_6H_4*Me*), 46.3 (C−N(*Me*)−O), 91.9 (br, N−*C*H−N), 128.1 (CH), 129.2 (CH), 135.5 (Cq), 139.0 (Cq) (C_6H_4Me), 166.8 (C═N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −2205 (350 Hz). Data follow for the yellow plates. Mp: 157 °C. TLC on SiO_2: R_f = 0.38 (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1647 s ν(C═N), 335 m ν(Pt−Cl). ^1H NMR spectrum in $CDCl_3$, δ: 2.40 (s, 3*H*, C_6H_4*Me*), 2.49 (s, 3*H*, C−N(*Me*)−O), 2.87 (s, br, 3*H*, ═C(*Me*)O), 5.69 (s, br, 1*H*, N−CH−N), 7.20 (d, 7.2 Hz, 2H) and 7.48 (d, 7.8 Hz, 2H) (C_6H_4Me). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 13.30 (N═C(*Me*)O), 21.4 (C_6H_4*Me*), 46.3 (C−N(*Me*)−O), 91.8 (br, N−*C*H−N), 128.0 (CH), 129.1 (CH), 135.5 (Cq), 139.1 (Cq), 166.8 (C═N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −2200 (350 Hz).

[$PtCl_2${N═C(Ph)O−N(Me)−C(H)(p-C_6H_4Me)}$_2$] (**4a**) (Two Diastereoisomers, ca. 1:1). The yields are 71% (method i) and 45% (method ii). Anal. Calcd for $C_{32}H_{32}N_4Cl_2O_2Pt$: C, 49.87; H, 4.19; N, 7.27. Found: C, 49.64; H, 4.11; N, 7.16. FAB$^+$-MS, *m*/*z*: 793 [M + Na]$^+$, 770 [M]$^+$, 735 [M − Cl]$^+$, 698 [M − 2HCl]$^+$, 549 [M − 2HCl − (MeC_6H_4)CH═N(Me)O]$^+$, 446 [M − 2HCl − (MeC_6H_4)CH═N(Me)O − PhCN]$^+$. Mp: 178 °C (dec). TLC on SiO_2: R_f = 0.54 and 0.62 (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1641 and 1627 s ν(C═N) + ν(C═C). ^1H NMR spectrum in $CDCl_3$, δ: 2.43 and 2.46 (two s, 3*H* each, C_6H_4*Me*), 2.95 and 2.98 (two s, 3*H* each, C−N(*Me*)−O), 5.87 and 5.91 (two s, broad, 1*H* each, N−C*H*−N), 7.29 (m, 2*H* of each isomer) 7.48 and 7.56 (two d, 7.6 Hz, 2*H* of each isomer) (C_6H_4Me), 7.40 (m, 2*H* of each isomer), 7.63 (m, 1*H* of each isomer), 8.70 and 8.83 (two d, 7.5 Hz, 1*H* of each isomer) (Ph). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 21.5 (C_6H_4*Me*), 45.9 and 46.1 (C−N(*Me*)−O), 94.7 (N−*C*H−N), 122.4 and 122.6 (N═C*Ph*), 128.2 (C_6H_4Me), 128.6 and 128.7 (N═C*Ph*), 129.2 and 129.3 (C_6H_4Me), 130.5 and 130.7 (N═C*Ph*), 133.1 and 133.2 (C_6H_4Me), 133.4 and 133.5 (N═C*Ph*), 139.3 and 139.5 (C_6H_4Me), 163.4 and 163.9 (C═N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −2104 (650 Hz) and −2113 (420 Hz).

[$PtCl_2$(N═C(Me)O−N(CH_2Ph)−C(H)Ph)$_2$] (**5a**) (Two Diastereoisomers, ca. 2:1). The yield is 70% (method ii). Anal. Calcd for $C_{32}H_{32}N_4Cl_2O_2Pt$: C, 49.88; H, 4.19; N, 7.27. Found: C, 50.32; H, 4.20; N, 7.43. FAB$^+$-MS, *m*/*z*: 792 [M + Na]$^+$, 770 [M + H]$^+$, 734 [M − HCl]$^+$. Mp: 180 °C. TLC on SiO_2: R_f = 0.71 (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1653 s ν(C═N). ^1H NMR spectrum in $CDCl_3$, δ: 2.53 (minor) and 2.56 (major) (two s, 3*H* of each isomer, ═C(*Me*)O), 4.08 (d, 12.3 Hz, 1*H* of each isomer), 4.30 (d, 12.3 Hz, 1*H* of each isomer) (CH_2Ph), 6.00 and 6.04 (two s, br, 1*H* of each isomer, N−*CH*−N), 7.32−7.50 (m, 10*H* of each isomer, *Ph* and CH_2*Ph*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 13.3 (minor) and 13.4 (major) (N═C(*Me*)O), 62.5 (major) and 62.7 (minor) (CH_2Ph), 88.9 (major) and 89.1 (minor) (br, N−*C*H−N), 127.8 (major) and 127.9 (minor) (*o*-Ph), 128.3 (*m*-Ph), 128.4 and 128.7 (*p*-Ph and *p*-*Ph*CH_2), 129.0 (*Ph*CH_2), 129.67 (minor) and 129.73 (major) (*Ph*CH_2), 133.73 (major) and 133.75 (minor) (*ipso*-*Ph*CH_2), 136.3 (major) and 136.4 (minor) (*ipso*-Ph), 167.6 (major) and 167.8 (minor) (C═N). ^{195}Pt NMR spectrum $CDCl_3$, δ: −2204 (640 Hz).

[$PtCl_2${N═C(Ph)O−N(CH_2Ph)−C(H)Ph}$_2$] (**6a**) (Two Diastereoisomers 1:1). The yield is 60% (method i). Anal. Calcd for $C_{42}H_{36}N_4Cl_2O_2Pt$: C, 56.38; H, 4.06; N, 6.26. Found: C, 56.52; H, 4.14; N, 6.19. FAB$^+$-MS, *m*/*z*: 917 [M + Na]$^+$, 895 [M]$^+$, 859 [M − Cl]$^+$, 822 [M − 2HCl]$^+$, 611 [M − 2HCl − PhCH═N(CH_2Ph)O]$^+$, 507 [M − 2HCl − PhCH═N(CH_2Ph)O − PhCN]$^+$. Mp: 164 °C. TLC on SiO_2: R_f = 0.60 and 0.73 (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 1622 s ν(C═N) + ν(C═C). ^1H NMR spectrum in $CDCl_3$, δ: 4.17, 4.19, 4.39, and 4.40 (four d, 12.7 Hz each, 4*H*, CH_2Ph), 6.18 and 6.21 (two s, 1*H* each, N−C*H*−N), 7.30−7.74 (m, 26*H*), 8.73 (d, 7.2 Hz, 2*H*), and 8.82 (d, 7.4 Hz, 2*H*)(Ph, CH_2Ph and N═C(*Ph*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 62.4 and 62.6 (*C*H_2Ph), 92.0 (N−*C*H−N), 122.1 and 122.4, 128.3, 128.4, 128.5, 128.6, 129.3, 129.8, 129.9, 130.7, 132.0 and 132.1, 133.5 and 133.6, 136.0 (N═C*Ph*, Ph and CH_2*Ph*), 163.9 (C═N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −2115 (380 Hz) and −2129 (520 Hz).

Preparation of the Platinum(IV) Oxadiazoline Complexes. (i) Via Cycloaddition. A mixture of [$PtCl_4$(PhCN)$_2$] (42 mg, 0.10 mmol) with the corresponding nitrone (0.20 mmol) in CH_2Cl_2 (2 mL) is stirred for 1.5 h at room temperature, whereupon the initial suspension became a homogeneous yellow solution. After chromatography on SiO_2/CH_2Cl_2 and evaporation of the solvent, the product is obtained as a pale yellow powder. Yields given below are relevant to this method.

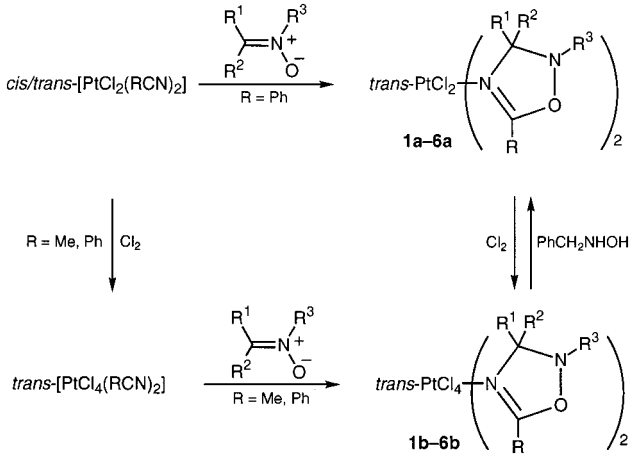
(ii) Via Chlorination of Pt(II) Complexes. Chlorination of **1a**−**6a** is performed by passing an excess of Cl_2 through a $CDCl_3$ solution of 0.03 mmol of the corresponding complex at room temperature for 10−15 s, and after 5 min the reaction mixture is monitored by ^1H NMR spectroscopy. The formation of **1b**−**6b** is almost quantitative.

[$PtCl_4${N═C(Ph)O−N(Me)−C(H)Ph}$_2$] (**2b**) (Two Diastereoisomers 1:1). The yield is 82%. Anal. Calcd for $C_{30}H_{28}N_4Cl_4O_2Pt$: C, 44.30; H, 3.47; N, 6.89. Found: C, 44.20; H, 3.31; N, 6.89. FAB$^+$-MS, *m*/*z*: 671 [M − 4Cl − 2H]$^+$. Mp: 173 °C. TLC on SiO_2: R_f = 0.56 (eluent pentane/CH_2Cl_2, 1:2). IR spectrum (selected bands), cm^{-1}: 1607 and 1573 s ν(C═N) + ν(C═C). ^1H NMR spectrum in $CDCl_3$, δ: 3.09 and 3.10 (two s, 3*H* each, C−N(*Me*)−O), 6.65 and 6.66 (two s + d, $^3J_{PtH}$ 13.2 Hz each, 2*H*, N−C*H*−N), 7.35−7.51 (m, 14*H*), 7.66 (m, 2*H*), and 8.18 (m, 4*H*) (Ph and N═C(*Ph*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 46.5 (C−N(*Me*)−O), 92.56 and 92.73 ($^2J_{PtC}$ 20.3 Hz, N−*C*H−N), 123.61 and 123.68 (N═C*Ph*), 126.03 (*o*-Ph), 127.70 (N═C*Ph*), 128.34 and 128.37 (*m*-Ph), 128.77 and 128.81 (*p*-Ph), 131.90 and 131.96 (N═C*Ph*), 133.97 and 134.04 (N═C*Ph*), 138.30 and 138.45 (*ipso*-Ph), 172.56 and 172.40 (C═N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −126 (390 Hz).

[$PtCl_4${N═C(Ph)O−N(Me)−C(H)(p-C_6H_4Me)}$_2$] (**4b**) (Two Diastereoisomers 1:1). The yield is 71%. Anal. Calcd for $C_{32}H_{32}N_4Cl_4O_2Pt$: C, 45.67; H, 3.83; N, 6.66. Found: C, 45.53; H, 3.82; N, 6.60. FAB$^+$-MS, *m*/*z*: 863 [M + Na]$^+$, 841 [M + H]$^+$, 805 [M − Cl]$^+$, 792 [M − 2Cl + Na]$^+$, 770 [M − 2Cl]$^+$, 735 [M − 3Cl]$^+$, 698 [M − 4Cl − 2H]$^+$. Mp: 169 °C (dec). TLC on SiO_2: R_f = 0.59 (eluent pentane/CH_2Cl_2, 1:2). IR spectrum (selected bands), cm^{-1}: 1608 and 1577 s ν(C═N) + ν(C═C). ^1H NMR spectrum in $CDCl_3$, δ: 2.33 and 2.34 (two s, 3*H* each, C_6H_4*Me*), 3.07 and 3.08 (two s, 3*H* each, C−N(*Me*)−O), 6.60 and 6.61 (two s + d, $^3J_{PtH}$ 12.6 Hz each, 2*H*, N−C*H*−N), 7.17 (m, 2*H* of each isomer) and 7.31 (m, 2*H* of each isomer) (C_6H_4Me), 7.45 (m, 2*H* of each isomer), 7.65 (m, 1*H* of each isomer), 8.17 (m, 2*H* of each isomer) (Ph). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 21.2 (C_6H_4*Me*), 46.4 (C−N(*Me*)−O), 92.6 and 92.7 (N−*C*H−N), 123.7 (N═C*Ph*), 125.9 (C_6H_4Me), 127.7 (N═C*Ph*), 129.09, and 129.13 (C_6H_4Me), 131.88 and 131.92 (N═C*Ph*), 133.89 and 133.97 (N═C*Ph*), 134.0 (C_6H_4Me), 138.6 (C_6H_4Me), 172.2 (C═N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −123 (420 Hz).

[$PtCl_4${N═C(Ph)O−N(CH_2Ph)−C(H)Ph}$_2$] (**6b**) (Two Diastereoisomers 1:1). The yield is 84%. Anal. Calcd for $C_{42}H_{36}N_4Cl_4O_2Pt$: C, 52.24; H, 3.76; N, 5.80. Found: C, 51.95; H, 3.79; N, 5.68. FAB$^+$-MS, *m*/*z*: 966 [M + H]$^+$, 917 [M − 2HCl + Na]$^+$, 894 [M − 2Cl − H]$^+$, 857 [M − 3Cl − 2H]$^+$, 822 [M − 4Cl − 2H]$^+$, 610 [M − 4Cl − 2H − PhCH═N(CH_2Ph)O]$^+$, 507 [M − 4Cl − 2H − PhCH═N(CH_2Ph)O − PhCN]$^+$. Mp: 136 °C. TLC on SiO_2: R_f = 0.42 (eluent

Scheme 2. Observed Transformations[a]



[a] R/R^1/R^2/R^3 = Me/H/Ph/Me (**1**), Ph/H/Ph/Me (**2**), Me/H/*p*-MeC$_6$H$_4$/Me (**3**), Ph/H/*p*-MeC$_6$H$_4$/Me (**4**), Me/H/Ph/CH$_2$Ph (**5**), and Ph/H/Ph/CH$_2$Ph (**6**). For syntheses of **1b**, **3b**, and **5b**, see ref 32.

pentane/CH_2Cl_2, 1:1). IR spectrum (selected bands), cm^{-1}: 1607 and 1574 s ν(C=N) + ν(C=C). ^{1}H NMR spectrum in $CDCl_3$, δ: 4.44, 4.46, 4.51 and 4.52 (four d, 12.5 Hz each, 4*H*, C*H*$_2$Ph), 6.78 and 6.79 (two s + d, $^3J_{PtH}$ 13.0 Hz each, 1*H*, N−C*H*−N), 7.28−7.50 (m, 20*H*), 7.59 (m, 4*H*), 7.66 (m, 2*H*) and 8.20 (m, 4*H*)(Ph, CH_2Ph and N=C(*Ph*). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, δ: 61.5 and 61.6 (*C*H$_2$Ph), 90.5 and 90.6 (N−*C*H−N), 123.66 and 123.70 (N=C*Ph*), 126.08 (Ph), 127.72 (N=C*Ph*), 128.30 and 128.38 (Ph), 128.65, 128.68, and 128.81 (Ph and CH_2*Ph*), 129.81 and 129.86 (CH_2*Ph*), 131.98 and 132.05 (N=C*Ph*), 133.61 and 133.67 (CH_2*Ph*), 134.00 and 134.10 (N=C*Ph*), 138.34 and 138.60 (Ph), 172.7 (C=N). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −112 (420 Hz).

Results and Discussion

Cycloaddition Reaction. For this study we choose the platinum(II) complexes *cis*/*trans*-[$PtCl_2(RCN)_2$], containing donor (R = Me) and acceptor (R = Ph) radicals attached to the nitrile group, and the nitrones $^-$ON$^+$(R^3)=C(R^1)(R^2) [R^1/R^2/R^3 = H/Ph/Me, H/*p*-MeC$_6$H$_4$/Me or H/Ph/CH$_2$Ph] (see Scheme 2). For comparative purposes, we have also investigated if the [2 + 3] cycloaddition occurs in the case of the corresponding platinum(IV) complexes [$PtCl_4(PhCN)_2$].

Couplings of nitrones and free organonitriles RCN bearing electron-withdrawing groups R are known from organic chemistry.[55−63] In particular, it has been reported that the reaction of $^-$ON$^+$(Me)=C(H)(Ph) and neat benzonitrile requires rather harsh reaction conditions (10 d, 110 °C) to give the corresponding 2-methyl-3,5-diphenyl-Δ^4-1,2,4-oxadiazoline in moderate yield (57%).[64] Our experiments indicate that benzonitrile is activated toward the [2 + 3] cycloaddition with the same and other nitrones by its ligation to the platinum(II) center and the formation of (Δ^4-1,2,4-oxadiazoline)Pt^{II} complexes **2a**, **4a**, and **6a** (Scheme 1) was achieved faster than in the case of free PhCN and under much milder conditions. In particular, the process takes only 1 d at 20−25 °C to furnish **2a**. Furthermore, an additional strong activation of benzonitrile was reached by application of the platinum(IV) complex [$PtCl_4(PhCN)_2$] in the reaction with $^-$ON$^+$(Me)=C(H)(Ph), and the end point in the formation of the oxadiazoline compound **2b**, under conditions similar to the preparative ones, was detected by ^{1}H NMR spectroscopy already after 1 h at room temperature. The final products from the cycloaddition to both platinum(II) and platinum(IV) nitrile complexes were purified by chromatography on SiO_2 and obtained in the solid state as *meso*-(*R*,*S*) and *rac*-(*S*,*S*)/(*R*,*R*) diastereoisomers.

It is remarkable that the alteration of the substituent R at RCN (from acceptor Ph to donor Me)−like the change in the oxidation state of the metal ion−plays a dramatic role on the reactivity. Thus, the acetonitrile complex [$PtCl_4(MeCN)_2$] and $^-$ON$^+$(Me)=C(H)(Ph) give the appropriate oxadiazoline complex after 6 h at room temperature,[32] while the corresponding platinum(II) compound [$PtCl_2(MeCN)_2$] does not react with the nitrone for 2 weeks at room temperature, whereas on heating at 56 °C for 2 d a variety of unidentified products, with no oxadiazoline compound, were observed by ^{1}H and ^{13}C{^{1}H} NMR monitoring. In connection to these experiments attention should be drawn to the work by Hermkens et al.,[64] who established that free acetonitrile does not react with nitrones even under harsh conditions (high pressure, reflux, 3 d).

Mutual Redox Interconversions of Pt(II) and Pt(IV) Oxadiazoline Complexes. In the current work, two types of synthetic strategy to obtain platinum(II) Δ^4-1,2,4-oxadiazoline complexes, i.e. [2 + 3] cycloaddition of nitrones to (organonitrile)Pt^{II} species (described above) and reduction of [$PtCl_4$-{N=C(R)O−N(R^3)-C(R^1)(R^2)}$_2$] to give the appropriate Pt(II) derivatives, were tested. Whereas (oxadiazoline)Pt^{II} complexes derived from acetonitrile are not accessible by direct cycloaddition of a nitrone to [$PtCl_2(MeCN)_2$], we succeded (Scheme 2) in their synthesis by a selective reduction of the corresponding Pt(IV) complexes with $PhCH_2NHOH$ as the reducing agent (other reducing agents, e.g. cyclopentadiene, triphenylphosphine, trimethyl phosphite, or cysteine, gave the (oxadiazoline)Pt^{II} compounds contaminated with a large amount of unidentified byproducts). The reverse reaction−conversion of [$PtCl_2$-{N=C(R)O−N(R^3)−C(R^1)(R^2)}$_2$] to afford the platinum(IV) complexes **1b**−**6b** (Scheme 2)−was carried out by addition of Cl_2 to solutions of **1a**−**6a** in $CDCl_3$, and products were identified by ^{1}H NMR spectroscopy.

All isolated complexes derived from both the direct addition of nitrones (see previous section) and from the reduction experiments were characterized by elemental analyses, FAB mass spectrometry, and IR and ^{1}H, ^{13}C{^{1}H}, and ^{195}Pt NMR spectroscopies (see Experimental Section); X-ray structure determinations were performed for four oxadiazoline Pt(II) complexes (*meso*-2a was obtained from the addition, while *rac*-**1a**, *rac*-**3a**, and *rac*-**5a** were from the reduction experiments). In all these compounds, the coordination polyhedron of platinum is slightly distorted square-planar with the oxadiazoline ligands in trans positions to each other. In the *meso*-(*R*,*S*)-**2a** complex (Figure 1) and in *rac*-(*S*,*S*)+(*R*,*R*)-**5a** (Figure 4), the oxadiazoline rings, similar to the Pt(IV) complex of our previous study,[32] adopt half-chair conformations that are slightly twisted around

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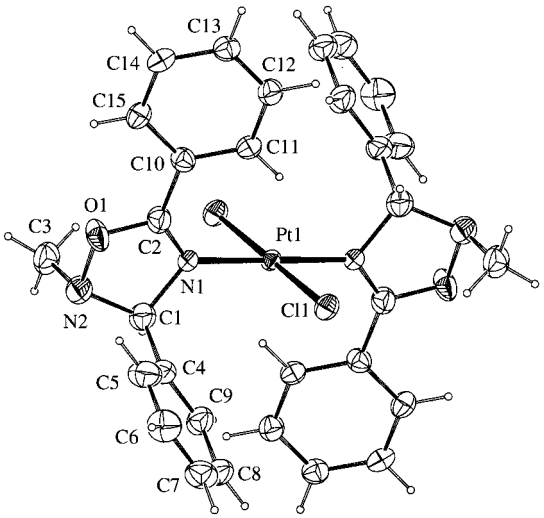

Figure 1. PLATON view of (*R,S*)-*meso*-[$PtCl_2$(N=C(Ph)O−N(Me)−C(H)Ph)$_2$] (**2a**) with atomic numbering scheme.

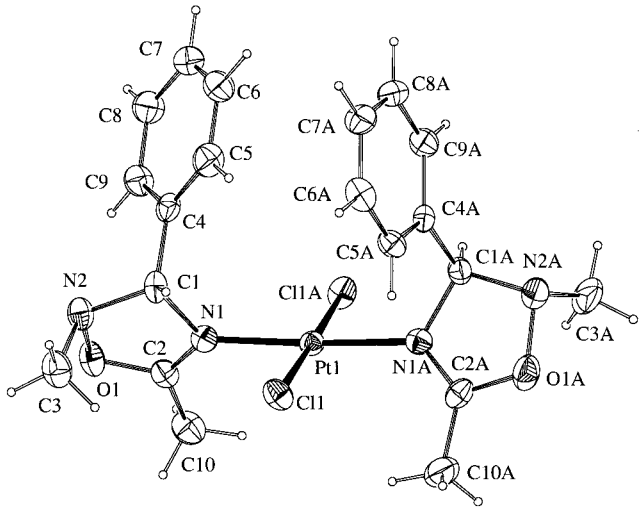

Figure 2. PLATON view of *rac*-[$PtCl_2${N=C(Me)O−N(Me)−C(H)Ph}$_2$] (**1a**) with atomic numbering scheme. The (*S,S*)-enantiomer is shown.

the N(2)−C(1) (for **2a**) or the N(2)−C(1) or N(4)−C(17) (for **5a**) bonds. The *rac*-(*S,S*)+(*R,R*)-**1a** complex (Figure 2) occupies an intermediate position with only one ring twisted on N(2)−C(1), whereas the other ring is in the envelope conformation on N(2A). In the *rac*-(*S,S*)+(*R,R*)-**3a** complex (Figure 3), even both oxadiazoline rings, similar to the few structurally characterized purely organic oxadiazoline compounds,[61−63] were found in an envelope conformation with the N(2) or N(2A) atom at the "flap". This shows that there is no general preference for one conformation in the Pt(II)−oxadiazoline complexes, and interconversion between the conformers can occur easily.

The geometrical parameters of the oxadiazoline rings in the four Pt(II) complexes are the same within 3σ as those in the previously described Pt(IV) complex[32] and also in a few known examples of structurally characterized uncoordinated Δ^4-1,2,4-oxadiazolines.[61−63] All other bonds and angles (Tables 2−5) are also of normal values.[65,66]

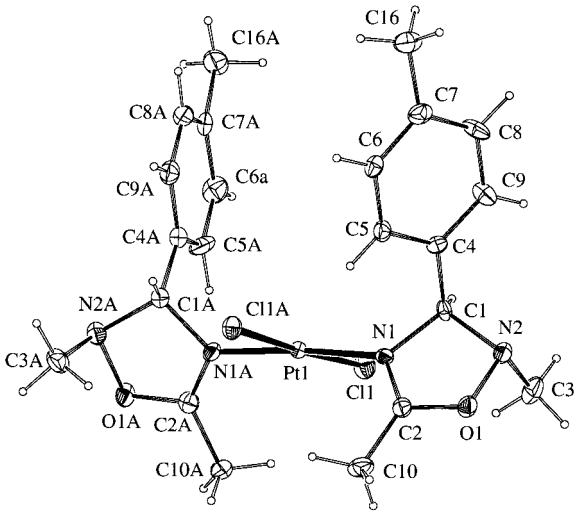

Figure 3. PLATON view of *rac*-[$PtCl_2$(N=C(Me)O−N(Me)−C(H)(*p*-C_6H_4Me)$_2$] (**3a**) with atomic numbering scheme. The (*S,S*)-enantiomer is shown.

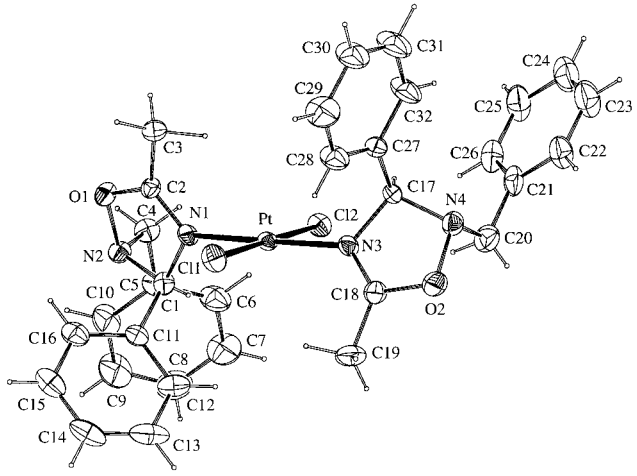

Figure 4. PLATON view of *rac*-[$PtCl_2$(N=C(Me)O−N(CH_2Ph)−C(H)Ph)$_2$] (**5a**) with atomic numbering scheme. The (*S,S*)-enantiomer is shown.

Liberation of Δ^4-1,2,4-Oxadiazolines from the Platinum(II) Complexes. Although liberation of the Δ^4-1,2,4-oxadiazoline is facile when the platinum(IV) complexes [$PtCl_4$-{N=C(Me)O−N(R^3)−C(R^1)(R^2)}$_2$] are treated with pyridine,[32] it does not proceed easily in the case of corresponding platinum(II) derivatives, thus indicating a stronger Pt−N(imine) bond in the latter group of compounds. Indeed, we were unable to substitute the heterocyclic ligands from the [$PtCl_2$(Δ^4-1,2,4-oxadiazoline)$_2$] with pyridine, thiourea, and also with such strong chelating agents as 2,2′-bipyridine and cycloheptanedione dioxime under heating conditions. The release was successful, however, with dppe or PPh_3 though slow even on heating in the presence of a large excess of the ligand.

For example, in the case of **2a** two diastereoisomers were mechanically separated and in $CDCl_3$ gave distinct ^{1}H NMR spectra. It was observed that the isomers do not interconvert to each other on heating in this solvent for 2 d at 56 °C. Addition of 1 equiv of dppe to a mixture of the two isomers (1 equiv each), followed by heating to ca. 56 °C of the solution formed, resulted (as revealed by ^{1}H and ^{31}P{^{1}H} NMR monitoring of the progress of the reaction) in a slow substitution to generate the previously characterized[64] oxadiazoline (^{1}H NMR spectrum,

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δ: 5.77 N−CH−N, 8.04 Ph; remaining Ph's signals overlapping with peaks due to dppe) along with the well-known [$PtCl_2$(dppe)][67,68] complex. Interestingly, the reactivity of the isomers toward the substitution is different and one (^{1}H NMR spectrum, δ: 5.94 N−CH−N, 8.68 Ph) reacts more readily than the other one (^{1}H NMR spectrum, δ: 5.89 N−CH−N, 8.84 Ph; the *trans*-(*R*,*S*)-structure of this complex was determined). To speed up the reaction, a further 10 equiv of dppe was added, and the completion of the substitution is observed after 8 d at 56 °C.

Concluding Remarks. By extension to a platinum(II) center the previously observed activation, by a platinum(IV) site, of organonitriles toward nucleophilic addition of a nitrone, this work demonstrates a considerable generality for this reaction showing that it can occur for a much weaker activating (and more easily available) metal center than the initially applied rather strong Lewis acid Pt(IV) system. The expected weaker activation of the organonitrile by the platinum(II) center is corroborated by the lower ν(N≡C) shift experienced on coordination (e.g. for platinum(II) complexes $\Delta = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$ = ca. 50 cm^{-1}, while for the appropriate platinum(IV) complexes Δ = ca. 100 cm^{-1}), which, nevertheless, is sufficient for such a type of activation, suggesting that the cycloaddition reaction can occur at a much wider variety of binding transition-metal centers. The reduced activation by the platinum(II) site is also indicated by the lower reaction rate and by the emergence of a selectivity toward the type of organonitrile substituent R group, which becomes a controlling factor of the reaction that is then prevented by an electron-donor R moiety such as an alkyl.

The reaction can be applied to the convenient synthesis, under mild conditions and using easily prepared platinum(II) compounds, of the still rare and previously inaccessible (or difficult to obtain) Δ^4-1,2,4-oxadiazoline compounds whose chemistry can then be further developed. However, for optically pure products, the enantioselectivity has to be promoted, and for this purpose the studies now reported on the basic factors controlling the reaction constitute an important basis and starting stage to be further developed. The different kinetic lability, now recognized, of the ligated oxadiazoline toward displacement at the diastereoisomers of its complexes should be further explored with the aim of getting pure diastereoisomers.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes [$PtCl_2${N═C(Me)O−N(Me)−C(H)Ph}$_2$] (*rac*-**1a**), [$PtCl_2$(N═C(Ph)O−N(Me)−C(H)Ph)$_2$] (*meso*-**2a)**, [$PtCl_2$-(N═C(Me)O−N(Me)−C(H)(*p*-C_6H_4Me))$_2$] (*rac*-**3a)**, and [$PtCl_2$-(N═C(Me)O−N(CH_2Ph)−C(H)Ph)$_2$] (*rac*-**5a)**. This material is available free of charge via the Internet at http://pubs.acs.org.

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