Iminoacylation. 3. Formation of Platinum(IV)-Based Metallaligands Due to Facile One-End Addition of *vic*-Dioximes to Coordinated Organonitriles[1−3]

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The reaction of *vic*-dioximes with the organonitrile platinum(IV) complexes *trans*-$[PtCl_4(RCN)_2]$ (R = Me, CH_2-Ph, Ph, *vic*-dioxime = dimethylglyoxime; R = Me, *vic*-dioxime = cyclohexa-, cyclohepta-, and cyclooctanedione dioximes) proceeds rapidly under relatively mild conditions and affords products of one-end addition of the dioximes to the nitrile carbon, i.e. $[PtCl_4(NH{=}C(R)ON{=}\{spacer\}{=}NOH)_2]$ (**1**−**6**) (R = Me, CH_2Ph, Ph, spacer = C(Me)C-(Me) for dimethylglyoxime; R = Me, spacer = $C\{C_4H_8\}C$, $C\{C_5H_{10}\}C$, $C\{C_6H_{12}\}C$ for the other dioximes), giving a novel type of metallaligand. All addition compounds were characterized by elemental analyses (C, H, N, Cl, Pt), FAB mass spectrometry, and IR and ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectroscopy. X-ray structure determination of the dimethylformamide bis-solvate $[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]\cdot 2DMF$ (**1a**) disclosed its overall trans geometry with the dimethylglyoxime part in anti configuration and the amidine one-end (rather than N,N-bidentate) coordination mode of the N-donor ligands. When a mixture of *cis*- and *trans*-$[PtCl_4(MeCN)_2]$ in MeCN was treated with dimethylglyoxime, the formation of, correspondingly, *cis*- and *trans*-$[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]$ (**1**) was observed and cis-to-trans isomerization in DMSO-d_6 solution was monitored by ^1H, 2D [^1H,^{15}N] HMQC, and ^{195}Pt NMR spectroscopies. Although performed ab initio calculations give evidence that the trans geometry is the favorable one for the iminoacylated species $[PtCl_4(ligand)_2]$, the platinum(IV) complex $[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\}C{=}NOH)_2]$ (**4**) was isolated exclusively in cis configuration with the two metallaligand "arms" held together by intramolecular hydrogen bonding between the two peripheral OH groups, as it was proved by single-crystal X-ray diffractometry. The classic substitution products, e.g. $[PtCl_2(N,N\text{-dioximato})_2]$ (**12**−**15**), are formed in the addition reaction as only byproducts in minor yield; two of them, $[PtCl_2(C_7H_{11}N_2O_2)_2]$ (**14**) and $[PtCl_2(C_8H_{13}N_2O_2)_2]$ (**15**), were structurally characterized. Complexes (**12**−**15**) were also prepared by reaction of the *vic*-dioximes with $[PtCl_4L(Me_2SO)]$ (L = Me_2SO, MeCN), but monoximes ($Me_2C{=}NOH$, $\{C_4H_8\}C{=}NOH$, $\{C_5H_{10}\}C{=}NOH$, PhC(H)=NOH, $(OH)C_6H_4C(H){=}$NOH) react differently adding to $[PtCl_4(MeCN)(Me_2SO)]$ to give the corresponding iminoacylated products $[PtCl_4(NH{=}C(Me)ON{=}CRR')(Me_2SO)]$ (**7**−**11**).

Introduction

The metal-assisted reactions of oximes and reactivity of oxime ligands is an area of tremendous variety as it has been demonstrated in reviews published recently by two of us.[5,6] Our own research in the area of (oxime)Pt chemistry has so far centered on the preparation of precursors for further synthetic works,[7] investigation of self-assembly of (oxime/oximato)Pt^{II} species by hydrogen bonding,[8] oxidation of oximes to give nitrosoalkanes,[9,10] studies on the redox duality of oxime species toward platinum complexes,[11] chlorination of coordinated oxime ligands,[12] and additions of coordinated oximes to ketones upon oxidation of (oxime)Pt^{II} compounds.[13]

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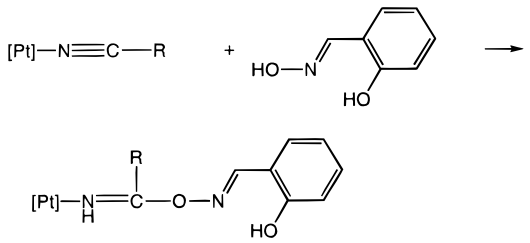
Scheme 1. Iminoacylation of Salicylaldoxime



Recently we reported on the metal-mediated iminoacylation reaction of ketoximes or aldoximes, $HON{=}CR_1R_2$, upon treatment with the organonitrile platinum(IV) complexes *trans*-$[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph, Ph) that proceeds under relatively mild conditions to give *trans*-$[PtCl_4(NH{=}C(R)ON{=}CR_1R_2)_2]$ ($R_1 = R_2 = Me$; $R_1R_2 = C_4H_8$, $R_1R_2 = C_5H_{10}$, $R_1R_2 = (H)Ph$, $R_1R_2 = (H)C_6H_4(OH)$-*o*) in almost quantitative yield.[2] Our interest in further investigation of the platinum(IV)-assisted iminoacylation is driven by the following main reasons. First, the reaction opened up a route for preparation of complexes containing unusual iminoacylated oxime ligands whose chemistry is not yet developed. Second, these species were proved to be exceptionally stable toward hydrolysis and this property allows us to assume that the complexes might be useful in coordination chemistry for modeling elusive monodentate imino ligands[14−16] and in organic chemistry as models of highly unstable intermediates in a nitrilium ion catalyzed Beckmann rearrangement.[17,18]

One more result[2] has stimulated our current work. It appeared that salicylaldoxime, although being a well-known chelating reagent employed in both synthetic and analytical chemistry for many years, added to *trans*-$[PtCl_4(RCN)_2]$ to give a Pt(IV)-based metallaligand (Scheme 1).

The chemistry of so-called multimetal-centered complexes or metal complex assemblies is of current intrinsic interest since it was demonstrated that metallaligands are proved to be useful in the design of multimetal systems and the control of their properties (for reviews see refs 19−23; for recent experimental work see refs 24−36). In view of the apparent success on the addition of salicylaldoxime to coordinated acetonitrile species in *trans*-$[PtCl_4(MeCN)_2]$, we wondered whether this synthetic method might represent a general route to the new type metallaligands. For this study we addressed *vic*-dioximes (Figure 1) a representative of which, viz. dimethylglyoxime, is probably one of the most classical bidentate chelating ligand. Indeed, in complete contrast to the traditional views on the reactivity of dimethylglyoxime and other *vic*-dioxime species, we have isolated compounds of their one-end *addition* to the nitriles giving Pt(IV)-based metallaligands rather than the ordinary *substitution* products, and these results are reported in this article.

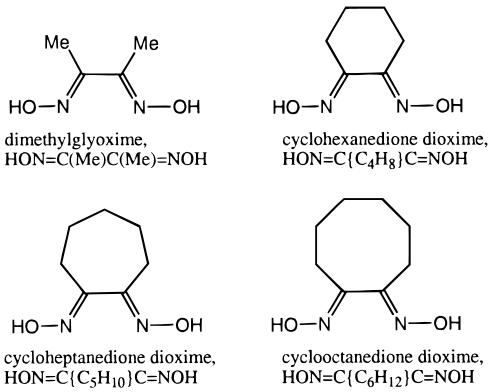


Figure 1. *vic*-Dioximes employed for the iminoacylation.

Experimental Section

Materials and Instrumentation. Dimethylglyoxime and cyclohexanedione dioxime were purchased from Aldrich and Reakhim, respectively. Solvents were obtained from commercial sources and used as received. C, H, and N elemental analyses were carried out by Microanalytical Services of the Instituto Superior Técnico and St. Petersburg Technological Institute, while Cl and Pt were analyzed by the authors. Decomposition points were determined on a Kofler table. For TLC, Silufol 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 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 3000 Mx instrument in KBr pellets. ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature. ^{195}Pt spectra were recorded without ^1H decoupling at a frequency of 64.507 MHz and a spectral width of 100 kHz, using a 90° pulse (12.2 μs), an acquisition time of 0.64 s, and a delay of 0.05 s. Chemical shifts were measured relative to aqueous $K_2[PtCl_4]$ (−1630 ppm), and half-height line widths are given in parentheses. 2D [^1H,^{15}N] HMQC spectra were recorded on a Bruker Avance DPX 400 instrument in 5 mm tubes at 24 °C using standard pulse programs supplied by Bruker (2D $^1H/^{15}N$ correlation via heteronuclear zero and double quantum coherence, gradient selected version with decoupling (GARP sequence) during aquisition in a phase sensitive mode using TPPI). The chemical shifts are reported relative to external $^{15}NH_4Cl$ (0 ppm).

Synthetic Work and Characterization. Complexes *trans*-$[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph, Ph),[2] $[PtCl_4(MeCN)(Me_2SO)]$,[37] and $[PtCl_4(Me_2SO)_2]$[38] were prepared according to the published methods. A mixture of cis and trans isomers of $[PtCl_4(MeCN)_2]$ was prepared

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by passage of Cl_2 gas through suspension of cis and trans isomers of $[PtCl_2(MeCN)_2]$[39,40] in MeCN for 15 min with vigorous stirring.

Reactions of $[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph, Ph) with dimethylglyoxime and reactions of $[PtCl_4(MeCN)_2]$ with the other dioximes were carried out as we previously reported[2] upon treatment of the platinum(IV) starting materials with the *vic*-dioximes in a molar ratio 1:2.5 in MeCN or $CHCl_3$ at 55−60 °C.

$[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]$ (1). The yield is 84% with needlelike bright yellow crystals from the reaction mixture; space group *C*2/*m* or *C*2, a = 13.817 Å, b = 8.055 Å, c = 11.226 Å, and β = 120.25°. Anal. Calcd for $C_{12}H_{22}N_6Cl_4O_4Pt$: C, 22.1; H, 3.4; N, 12.9; Cl, 21.8; Pt, 30.0. Found: C, 22.4; H, 3.4; N, 12.5; Cl, 22.0; Pt, 30.4. FAB^+-MS, *m*/*z*: 615, $[M - Cl]^+$. FAB^+-MS in glycerol matrix, *m*/*z*: 673, $[M + Na]^+$. This complex does not have a characteristic melting point. On heating, it decomposes above 200 °C. TLC on SiO_2, R_f = 0.61 (eluent $CHCl_3$:Me_2CO = 5:1, v/v). IR spectrum (selected bands), cm^{-1}: 3438 m ν(O−H), 3284 m-w ν(N−H), 1665 and 1622 s ν(C=N), 1199 m ν(C−O). ^1H NMR spectrum in acetone-d_6, δ: 2.04 and 2.30 (two s, 3*H* each, =C(Me)C(Me)), 2.73 (s + d, $^4J_{PtH}$ 3.9 Hz, 3*H*, =C(Me)O), 8.75 (s, br, NH), 11.50 (s, 1*H*, OH). $^{13}C\{^1H\}$ NMR spectrum in acetone-d_6, δ: 175.0 ($^2J_{PtC}$ 40.0 Hz, =*C*(Me)O), 164.7 (ON=*C*), 151.7 (=C), 17.8 (=C(*Me*)O), 11.7 and 9.3 (Me). ^{195}Pt NMR spectrum in acetone-d_6, δ: −150 (750 Hz).

Dissolution of **1** in dimethylformamide at room temperature and keeping the solution for 1 d resulted in precipitation of a small amount of yellow needlelike crystals of the bis(dimethylformamide) solvate $[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]\cdot 2Me_2NCHO$ (**1a**), whose structure was studied by X-ray single-crystal diffractometry (see below). Anal. Calcd for $C_{18}H_{36}N_8Cl_4O_6Pt$: C, 27.1; H, 4.6; N, 14.1. Found: C, 27.2; H, 4.7; N, 14.3. FAB^+-MS in glycerol matrix, *m*/*z*: 615, $[M - Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3440 m ν(O−H), 3293 m-w ν(N−H), 1667 vs, br and 1622 sh ν(C=N) and ν(C=O), 1200 m ν(C−O). ^1H NMR spectrum in DMSO-d_6, δ: 2.00 and 2.31 (two s, 3*H* each, =C(Me)C(Me)), 2.77 (s + d, $^4J_{PtH}$ 3.8 Hz, 3*H*, =C(Me)O), 2.73 and 2.89 (two s, 3*H* each, *Me*$_2$NCHO), 8.83 (s + d, 1*H*, $^2J_{PtH}$ 34.7 Hz, NH), 12.50 (s, 1*H*, Me_2NCHO). ^{195}Pt NMR spectrum in DMSO-d_6, δ: −78 (700 Hz).

$[PtCl_4(NH{=}C(CH_2Ph)ON{=}C(Me)C(Me){=}NOH)_2]$ (2). The yield is 88%. Anal. Calcd for $C_{24}H_{30}N_6Cl_4O_4Pt$: C, 35.9; H, 3.8; N, 10.5; Cl, 17.7; Pt, 24.3. Found: C, 35.6; H, 3.8; N, 10.3; Cl, 18.0; Pt, 23.9. FAB^+-MS, *m*/*z*: 733, $[M - 2Cl]^+$; 698, $[M - 3Cl]^+$; 662, $[M - 4Cl - H]^+$. This complex does not have a characteristic melting point. On heating, it decomposes above 200 °C. TLC on SiO_2, R_f = 0.67 (eluent $CHCl_3$). IR spectrum (selected bands), cm^{-1}: 3423 m ν(O−H), 3275 m-w ν(N−H), 1623 m-w ν(C=N), 1163 m ν(C−O). ^1H NMR spectrum in acetone-d_6, δ: 2.07 and 2.08 (two s, 3*H* each, =C(Me)C(Me)), 4.74 (s, 2 *H*, C*H*$_2$Ph), 7.37 (m, 3*H*) and 7.56 (m, 2*H*, CH$_2$*Ph*), 9.01 (s, br, 2H, OH, NH). $^{13}C\{^1H\}$ NMR spectrum in acetone-d_6, δ: 174.8 (=*C*(CH$_2$Ph)O), 165.8 (ON=*C*), 152.2 (=C), 133.9, 130.8, 129.5 and 128.4 (Ph), 37.7 (CH$_2$), 11.9 (Me), 9.5 (Me). ^{195}Pt NMR spectrum in acetone-d_6, δ: −164 (840 Hz).

$[PtCl_4(NH{=}C(Ph)ON{=}C(Me)C(Me){=}NOH)_2]$ (3). The yield is 83%. Anal. Calcd for $C_{22}H_{26}N_6Cl_4O_4Pt$: C, 34.1; H, 3.4; N, 10.8; Cl, 18.3; Pt, 25.2. Found: C, 33.8; H, 3.7; N, 10.7; Cl, 18.2; Pt, 25.1. FAB^+-MS, *m*/*z*: 739, $[M - Cl]^+$. This complex does not have a characteristic melting point. On heating, it decomposes above 200 °C. TLC on SiO_2, R_f = 0.58 (eluent $CHCl_3$:Me_2CO = 8:1, v/v). IR spectrum (selected bands), cm^{-1}: 3435 m ν(O−H), 3265 m-w ν(N−H), 1650 m-w and 1623 m-w ν(C=N), 1180 or 1143 m ν(C−O). ^1H NMR spectrum in acetone-d_6, δ: 2.04 and 2.30 (two s, 3*H* each, =C(Me)C(Me)), 7.47 (t, 6.8 Hz, 2*H*), 7.64 (t, 6.5 Hz, 1*H*) and 8.07 (d, 7.2 Hz, 2H) (Ph), 9.52 (s, br 1*H*, NH), OH not detected. $^{13}C\{^1H\}$ NMR spectrum in DMSO-d_6, δ: 172.2 (=*C*(Ph)O), 166.3 (ON=*C*), 153.0 (=C); 132.3, 129.5 and 127.9 (Ph, quarternary carbon was not observed), 9.3 (Me), 9.2 (Me). ^{195}Pt NMR spectrum in DMSO-d_6, δ: −78 (700 Hz).

$[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\}C{=}NOH)_2]$ (4). The yield is 82%. Anal. Calcd for $C_{16}H_{26}N_6Cl_4O_4Pt$: C, 27.3; H, 3.7; N, 12.0; Cl, 20.2; Pt, 27.7. Found: C, 27.6; H, 3.6; N, 11.7; Cl, 20.0; Pt, 27.4. FAB^+-MS, *m*/*z*: 667, $[M - Cl]^+$; 632, $[M - 2Cl]^+$. Mp: 156 °C (dec). TLC on SiO_2, R_f = 0.58 (eluent Me_2CO:$CHCl_3$ = 1:6, v/v). IR spectrum (selected bands), cm^{-1}: 3434 m, br ν(O−H), 3270 and 3224 m-w ν(N−H), 1661 vs and 1639 sh ν(C=N), 1151 m-w ν(C−O). ^1H NMR in DMSO-d_6, δ: 1.65 (m, 4*H*), 2.61 (m, 4*H*) (C_4H_8), 2.83 (s + d, $^4J_{PtH}$ 4.0 Hz, 3*H*, =C(Me)O), 8.98 (s + d, $^2J_{PtH}$ 23.3 Hz, 1*H*, NH), 12.18 (s, 1 *H*, OH). $^{13}C\{^1H\}$ NMR spectrum in DMSO-d_6, δ: 17.9 (=C(*Me*)O), 20.3, 21.3, 25.5, and 26.3 (C_4H_8), 153.9 (C=N), 164.1 (C=N), 173.3 (=*C*(Me)O). ^{195}Pt NMR spectrum in DMSO-d_6, δ: 57 (350 Hz).

$[PtCl_4(NH{=}C(Me)ON{=}C\{C_5H_{10}\}C{=}NOH)_2]$ (5). The yield is 80%. Anal. Calcd for $C_{18}H_{30}N_6Cl_4O_4Pt$: C, 29.6; H, 4.1; N, 11.5; Cl, 19.4; Pt, 30.6. Found: C, 30.0; H, 4.0; N, 11.3; Cl, 19.8; Pt, 27.0. FAB^+-MS, *m*/*z*: 576, $[M - L]^+$. Mp: 126−130 °C. TLC on SiO_2, R_f = 0.61(eluent Me_2CO:$CHCl_3$ = 1:2, v/v). IR spectrum (selected bands), cm^{-1}: 3420 m ν(O−H), 3260 m-w ν(N−H), 1652 s ν(C=N), 1140 m-w ν(C−O). ^1H NMR spectrum of both isomers in an approximate ratio 2:1 in DMSO-d_6, δ: 1.60 (m, 6*H*), 2.71 (m, 2*H*), 3.01 (m, 2*H*, C_5H_{10}), 2.71 (s, 3*H*, =C(Me)O), 8.60 (s + d, $^2J_{PtH}$ 32.3 Hz, NH of the trans isomer), 9.06 (s + d, $^2J_{PtH}$ 23.4 Hz, NH of the cis isomer), 11.85 (s, OH of the cis isomer), 11.94 (s, OH of the trans isomer). $^{13}C\{^1H\}$ NMR spectrum of both isomers in DMSO-d_6, δ: 18.4 and 18.5 (N=C(Me)O), 23.5, 26.3, 26.7, 28.5, and 28.8 (C_5H_{10}), 155.0 (C=N), 167.3 (C=N), 175.2 (=C(Me)O). ^{195}Pt NMR spectrum in DMSO-d_6, δ: for the cis isomer +76 (369 Hz), for the trans isomer −72 (700 Hz).

$[PtCl_4(NH{=}C(Me)ON{=}C\{C_6H_{12}\}C{=}NOH)_2]$ (6). The yield is 90%. Anal. Calcd for $C_{20}H_{34}N_6Cl_4O_4Pt$: C, 31.6; H, 4.5; N, 11.1; Cl, 18.7; Pt, 25.7. Found: C, 30.9; H, 3.9; N, 10.8; Cl, 18.4; Pt, 25.9. FAB^+-MS, *m*/*z*: 723, $[M - Cl]^+$; 689, $[M - 2Cl + H]^+$. Mp: 180 °C (dec). TLC on SiO_2, R_f = 0.63 (eluent $CHCl_3$). IR spectrum (selected bands), cm^{-1}: 3450 ν(O−H), 3285 m-w ν(N−H), 1660 and 1643 m ν(C=N), 1190 m ν(C−O). ^1H NMR spectrum in DMSO-d_6, δ: 1.49 (m, 4*H*), 1.62 (m, 2*H*), 1.71 (m, 2*H*), 2.68 (m, 2*H*) and 2.88 (m, 2*H*) (C_8H_{12}), 2.73 (s, 3*H*, CH_3), 8.62 (s + d, $^2J_{PtH}$ 35 Hz, 1*H*, NH), OH was not detected. $^{13}C\{^1H\}$ NMR spectrum in DMSO-d_6, δ: 17.9 (CH_3), 24.6 (CH_2), 24.9 (CH_2), 25.2 (CH_2), 25.5 (CH_2), 25.8 (CH_2), 27.6 (CH_2), 154.0 (C=N), 168.8 (C=N), 174.5 (=*C*(Me)O). ^{195}Pt NMR spectrum in DMSO-d_6, δ: −78 (700 Hz).

Reaction of $[PtCl_4(MeCN)(Me_2SO)]$ with $HON{=}CMe_2$, $HON{=}C(C_4H_8)$, $HON{=}C(C_5H_{10})$, HON=C(H)Ph, and $HON{=}C(H)C_6H_4$-(OH) proceeds as described above upon treatment of the platinum(IV) starting materials with the oximes in a molar ratio 1:1.3 in MeCN.

$[PtCl_4(NH{=}C(Me)ON{=}CMe_2)(Me_2SO)]$ (7). The yield is 81%. Anal. Calcd for $C_7H_{16}N_2Cl_4O_2PtS$: C, 15.9; H, 3.1; N, 5.3; Cl, 26.8; Pt, 36.9. Found: C, 15.6; H, 3.2; N, 5.2; Cl, 26.7; Pt, 36.9. FAB^+-MS, *m*/*z*: 495, $[M - Cl, +2H]^+$; 456, $[M - 2HCl]^+$; 421, $[M - 2HCl, -Cl]^+$. Mp: 122 °C. TLC on SiO_2, R_f = 0.42 and 0.60 (eluent acetone:$CHCl_3$ 1:12). IR spectrum (selected bands), cm^{-1}: 3011 and 2921 m ν(N−H), 1664 s and 1641 vs ν(C=N), 1169 s and/or 1188 s ν(S=O). ^1H NMR spectrum for cis and trans isomers in an approximate ratio 2:1 in $CDCl_3$, δ: for the cis isomer 2.07 and 2.08 (s, 3*H* each, CMe_2), 2.69 (s + d, $^4J_{PtH}$ 3.6 Hz, 3*H*, =C(Me)O), 3.70 (s + d, $^3J_{PtH}$ 15.0 Hz, 6*H*, Me_2SO), 8.38 (s, br, NH); for the trans isomer 2.08 and 2.09 (s, 3*H* each, CMe_2), 2.68 (s + d, $^3J_{PtH}$ 3.6 Hz, 3*H*, =C(Me)O), 3.72 (s + d, $^3J_{PtH}$ 13.6 Hz, 6*H*, Me_2SO), 8.58 (s, br, NH). $^{13}C\{^1H\}$ NMR spectrum for both isomers in $CDCl_3$, δ: 18.3 (s + d, $^3J_{PtC}$ 6.7 Hz, N=C(*Me*)O), 17.5 and 21.9 (C*Me*$_2$), 40.6 ($^2J_{PtC}$ 28.9 Hz, Me_2SO of the cis isomer) and 42.0 ($^2J_{PtC}$ 32.7 Hz, Me_2SO of the trans isomer), 166.4 (*C*=NMe_2), 174.5 (HN=C). ^{195}Pt NMR spectrum in DMSO-d_6, δ: for the cis isomer −966 (t, $^1J_{Pt^{14}N}$ 260 Hz) and for the trans isomer −1082 (400 Hz).

$[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\})(Me_2SO)]$ (8). The yield is 74%. Anal. Calcd for $C_9H_{18}N_2Cl_4O_2PtS$: C, 19.5; H, 3.3; N, 5.1; Cl, 25.5; Pt, 35.1. Found: C, 19.3; H, 3.3; N, 5.4; Cl, 25.2; Pt, 34.9. FAB^+-MS, *m*/*z*: 507, $[M - 2Cl + Na]^+$. Mp: 104 °C. TLC on SiO_2, R_f = 0.60 and 0.71 (eluent acetone:$CHCl_3$ = 1:8, v/v). IR spectrum (selected bands), cm^{-1}: 3008 w, 2968 w and 2918 w-m ν(N−H), 1639 vs ν(C=N), 1180 s ν(S=O). ^1H NMR spectrum of both isomers in an approximate ratio 1:1 in $CDCl_3$, δ: 2.72 and 2.73 (s, 3*H* each, =C(Me)O), 1.90 (m, 8*H*) and 2.64 (m, 8*H*)(C_4H_8), 3.76 (s + d, $^3J_{PtH}$ 14.4 Hz, 6*H*, Me_2SO), 3.78 (s + d, $^3J_{PtH}$ 13.3 Hz, 6*H*, Me_2SO), 8.30 (s, br, 1*H*, NH), 8.58 (s, br, 1*H*, NH). $^{13}C\{^1H\}$ NMR spectrum of both

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isomers in $CDCl_3$, δ: 18.4 (N=C(*Me*)O), 24.4, 25.0, 30.1, and 31.7 (C_4H_8), 40.5 ($^2J_{PtC}$ 28 Hz) and 41.8 ($^2J_{PtC}$ 32 Hz)(Me_2SO), 174.8 (HN=C), and 178.0 (*C*=N(C_4H_8)). ^{195}Pt NMR spectrum in DMSO-d_6, δ: for the cis isomer −970 (t, $^1J_{Pt^{14}N}$ 240 Hz) and for the trans isomer −1082 (400 Hz).

[$PtCl_4$(NH=C(Me)ON=C{C_5H_{10}})(Me_2*S*O)] (9). The yield is 76%. Anal. Calcd for $C_{10}H_{20}N_2Cl_4O_2PtS$: C, 21.1; H, 3.5; N, 4.9; Cl, 24.9; Pt, 34.3. Found: C, 21.2; H, 3.7; N, 5.2; Cl, 25.2; Pt, 34.6. FAB$^+$-MS, *m*/*z*: 533, [M − Cl]$^+$; 498, [M − 2Cl]$^+$; 463, [M − 3Cl]$^+$. Mp: 112 °C. TLC on SiO_2, R_f = 0.62 and 0.71 (eluent acetone:$CHCl_3$ = 1:8, v/v). IR spectrum (selected bands), cm^{-1}: 3007 w, 2921 m, and 2858 m ν(N−H), 1657 s and 1633 vs ν(C=N), 1184 s ν(S=O). ^{1}H NMR spectrum of both isomers in an approximate ratio 1:1 in $CDCl_3$, δ: 2.72 (s, 6*H*, =C(Me)O), 1.65 (m, 4*H*), 1.72 (m, 8*H*), 2.37 (m, 4*H*) and 2.57 (m, 4*H*) (C_5H_{10}), 3.69 (s, 6*H*, Me_2SO; value of J_{PtH} was not determined due to overlapping of the signals), 3.71 (s, 6*H*, Me_2SO; value of J_{PtH} was not determined due to overlapping of the signals), 8.38 (s, br, 1*H*, NH), 8.60 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR spectrum of both isomers in $CDCl_3$, δ: 18.4 (N=C(*Me*)O), 25.0, 25.7, 26.7, 27.4 and 31.9 (C_5H_{10}), 40.5 ($^2J_{PtC}$ 30 Hz) and 41.9 ($^2J_{PtC}$ 28 Hz)(Me_2SO), 169.0 (*C*=N(C_5H_{10})), 174.6 (HN=C). ^{195}Pt NMR spectrum in DMSO-d_6, δ: for the cis isomer −967 (400 Hz) and for the trans isomer −1080 (t, $^1J_{Pt^{14}N}$ 200 Hz).

[$PtCl_4$(NH=C(Me)ON=C(H)Ph)(Me_2*S*O)] (10). The yield is 76%. Anal. Calcd for $C_{11}H_{16}N_2Cl_4O_2PtS$: C, 22.9; H, 2.8; N, 4.9; Cl, 24.6; Pt, 33.8. Found: C, 22.5; H, 3.1; N, 4.8; Cl, 24.5; Pt, 33.5. FAB$^+$-MS, *m*/*z*: 529, [M − 2Cl + Na]$^+$. Mp: 133 °C. TLC on SiO_2, R_f = 0.66 (eluent acetone:$CHCl_3$ = 1:1, v/v). IR spectrum (selected bands), cm^{-1}: 3005 w and 2918 w-m ν(N−H), 1665 s ν(C=N), 1623 m-s ν(C=C), 1171 s ν(S=O), 764 m-s δ(C−H). ^{1}H NMR spectrum in $CDCl_3$, δ: 2.83 (s + d, $^4J_{PtH}$ 3.7 Hz, 3*H*, =C(Me)O), 3.78 (s + d, $^3J_{PtH}$ 14.5 Hz, 6*H*, Me_2SO), 7.52 (m, 2*H*), 7.59 (m, 1*H*), and 7.76 (m, 2*H*) (Ph), 8.58 (s, 1*H*, =CH), 6.00 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, δ: 18.2 (N=C(*Me*)O), 40.4 ($^2J_{PtC}$ 29 Hz, Me_2SO), 128.8, 128.9, 129.4 and 133.1 (Ph), 157.3 (=CH), 171.4 (HN=C). ^{195}Pt NMR spectrum in DMSO-d_6, δ: −978 (t, $^1J_{Pt^{14}N}$ 240 Hz).

[$PtCl_4$(NH=C(Me)ON=C(H)C_6H_4(OH))(Me_2*S*O)] (11). The yield is 85%. Anal. Calcd for $C_{11}H_{16}N_2Cl_4O_3PtS$: C, 22.3; H, 2.7; Cl, 23.9; N, 4.7; Pt, 32.9. Found: C, 22.0; H, 2.6; Cl, 23.4; N, 4.5; Pt, 33.1. FAB$^+$-MS, *m*/*z*: 545, [M − 2Cl + Na]$^+$. The complex has no characteristic melting point. On heating it decomposes above 170 °C. TLC on SiO_2, R_f = 0.43 (eluent acetone:$CHCl_3$ = 1:6). IR spectrum (selected bands), cm^{-1}: 3463 m ν(O−H), 3015 w and 2912 w ν(N−H), 1661 vs ν(C=N), 1619 s ν(C=C), 1165 vs ν(S=O), 772 m-s δ(C−H). ^{1}H NMR spectrum in acetone-d_6, δ: 2.76 (s + d, $^4J_{PtH}$ 3.8 Hz, 3*H*, =C(Me)O), 3.80 (s + d, $^3J_{PtH}$ 15.4 Hz, 6*H*, Me_2SO), 6.97 (d, 7.5 Hz, 1*H*), 7.03 (t, 8.4 Hz, 1*H*), 7.46 (ddd, 8.8 Hz, 7.3 Hz, 1.6 Hz, 1*H*), 7.76 (dd, 8.1 Hz, 1.9 Hz, 1*H*)(C_6H_4OH), 9.04 (s, 1*H*, =CH), 8.47 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR spectrum in acetone-d_6, δ: 18.3 (N=C(*Me*)O), 44.5 ($^2J_{PtC}$ 28 Hz, Me_2SO), 117.4, 121.1, 129.0, 132.6, 135.5, and 155.5 (C_6H_4OH), 155.8 (=CH), 175.4 (HN=C). ^{195}Pt NMR spectrum in DMSO-d_6, δ: −879 (t, $^1J_{Pt^{14}N}$ 280 Hz).

Reaction of [$PtCl_4$(MeCN)(Me_2SO)] with Dioximes. The solid oxime (0.9 mmol) is added to a solution of [$PtCl_4$(MeCN)(Me_2SO)] (0.1 g, 0.36 mmol) in acetonitrile (7 mL) on stirring at 50−60 °C. After completion of homogenization (ca. 1−2 min) the solution became darker. In the case of cyclohexanedione dioxime a green precipitate of [Pt($C_6H_9N_2O_2$)$_2$] started to release. The precipitate is filtered off, and the filtrate is left to stand for 1 d at room temperature whereafter released dark-orange crystals of [$PtCl_2$($C_6H_9N_2O_2$)$_2$] (**13**) are collected on a filter. In the case of dimethylglyoxime, the compounds of platinum(II) and platinum(IV), e.g. [Pt($C_4H_7N_2O_2$)$_2$] and [$PtCl_2$($C_4H_7N_2O_2$)$_2$] (**12**), precipitated together after approximately 1 week from the mixing the reagents. These two precipitates were separated mechanically. In the two other cases (cycloheptane and cyclooctanedione dioximes) formation of [Pt(dioximato)$_2$] was not observed and only the platinum(IV) compounds [$PtCl_2$(dioximato)$_2$] (**14**, **15**) were isolated from the reaction mixtures.

Reaction of [$PtCl_4$(Me_2SO)$_2$] with Dioximes. The oxime (0.63 mmol) is added to a solution of [$PtCl_4$(Me_2SO)$_2$] (0.15 g, 0.30 mmol) in acetonitrile (7−10 mL) at room temperature, and then the mixture is heated at 50−60 °C for ca. 5 min on stirring until homogenization is completed. The solutions formed are cooled to 20−25 °C and left to stand without stirring. In the case of dimethylglyoxime a product precipitates after 5 h, while in the other cases release of products was observed after ca. 30 min. The precipitate is collected on a filter shortly after appearance, washed with three 2-mL portions of diethyl ether, and dried in air at 20−25 °C. Keeping the precipitates in the suspension results in contamination of the products with the platinum(II) complexes [Pt(dioximato)$_2$]. Yields of [$PtCl_2$(dioximato)$_2$] are ca. 50%, based on Pt.

[$PtCl_2$($C_4H_7N_2O_2$)$_2$] (12). Anal. Calcd for $C_8H_{14}N_4Cl_2O_4Pt$: C, 19.4; H, 2.8; N, 11.3; Cl, 14.3; Pt, 39.3. Found: C, 18.9; H, 2.6; N, 10.8; Cl, 14.0; Pt, 39.3. FAB$^+$-MS, *m*/*z*: 425, [M − 2Cl]$^+$. This compound has no characteristic melting point. On heating, it decomposes above ca. 240 °C. TLC on SiO_2, R_f = 0.68 (eluent Me_2CO:$CHCl_3$ = 1:1, v/v). IR spectrum (selected bands), cm^{-1}: 3327 s ν(O−H), 1594 w ν(C=N). ^{1}H NMR in DMSO-d_6, δ: 2.44 (s).

[$PtCl_2$($C_6H_9N_2O_2$)$_2$] (13). Anal. Calcd for $C_{12}H_{18}N_4Cl_2O_4Pt$: C, 26.3; H, 3.3; N, 10.2; Cl, 12.9; Pt, 35.6. Found: C, 26.4; H, 3.6; N, 10.3; Cl, 12.6; Pt, 35.6. FAB$^+$-MS, *m*/*z*: 477, [M − 2Cl]$^+$. Mp: 185 °C. TLC on SiO_2, R_f = 0.56 (eluent Me_2CO:$CHCl_3$ = 3:2, v/v). IR spectrum (selected bands), cm^{-1}: 3433 vs, br ν(O−H), 1655 m-w ν(C=N). ^{1}H NMR in DMSO-d_6, δ: 1.64 (m, 4 *H*), 2.83 (m, 4 *H*).

[$PtCl_2$($C_7H_{11}N_2O_2$)$_2$] (14). Anal. Calcd for $C_{14}H_{22}N_4Cl_2O_4Pt$: C, 29.1; H, 3.9; N, 9.7; Cl, 12.3; Pt, 33.9. Found: C, 29.3; H, 3.7; N, 9.4; Cl, 12.4; Pt, 34.0. FAB$^+$-MS, *m*/*z*: 506, [M − 2Cl]$^+$. Mp: 200 °C (dec). TLC on SiO_2, R_f = 0.55 (eluent $CHCl_3$). IR spectrum (selected bands), cm^{-1}: 3437 vs, br ν(O−H), 1652 m-w ν(C=N). ^{1}H NMR in DMSO-d_6, δ: 1.58 (m, 4 *H*), 1.74 (m, 2 *H*), 3.02 (m, 4 *H*).

[$PtCl_2$($C_8H_{13}N_2O_2$)$_2$] (15). Anal. Calcd for $C_{16}H_{26}N_4Cl_2O_4Pt$: C, 31.8; H, 4.3; N, 9.3; Cl, 11.7; Pt, 32.3. Found: C, 32.1; H, 4.0; N, 9.7; Cl, 12.3; Pt, 32.0. FAB$^+$-MS, in NBA matrix, *m*/*z*: 533, [M − 2Cl]$^+$. Mp: 230 °C. IR spectrum (selected bands), cm^{-1}: 3442 vs, br ν(O−H), 1655 m-w ν(C=N). ^{1}H NMR in DMSO-d_6, δ: 1.47 (m, 4*H*), 1.64 (m, 4*H*), and 2.96 (m, 4*H*).

X-ray Structure Determinations of [$PtCl_4$(NH=C(Me)ON=C(Me)C(Me)=NOH)$_2$]·2DMF (1a) and [$PtCl_2$($C_8H_{13}N_2O_2$)$_2$] (15). Yellow needlelike crystals of **1a** were grown from DMF (see above) while yellow prisms of **15** were obtained directly from the reaction mixtures. Diffraction data were collected on an Enraf-Nonius CAD 4 diffractometer (Mo Kα radiation, β-filter). Cell parameters for the complexes were obtained from 24 centered reflections with θ between 10 and 13° for both complexes. Data collection has been done with 2θ between 2.3 and 25°. Range of *hkl*: h = 0 to 8, k = −9 to 9, l = −16 to 16 for **1a**, and h = −8 to 9, k = 0 to 9, l = −10 to 11 for **15**. Standard reflections were measured every 60 min and showed practically no change with time (±1%). Diffractometer data were processed by the program PROFIT[41] with profile analysis of reflections. The structures were solved by means of Fourier syntheses based upon the Pt-atom coordinates obtained from the Patterson synthesis using the SHELXTL package.[42] After that, all reflections with $I \le 2\sigma(I)$ were excluded from calculations. Refinement was done by full-matrix least squares based on F^2 using the SHELXL-97 package.[43] All non-H atoms were treated anisotropically. An extinction correction has been applied. Lorenz, polarization, and absorption correction were made.[44] Crystal size: 0.42 × 0.34 × 0.09 mm for **1a** and 0.33 × 0.32 × 0.13 mm for **15**. T_{max} and T_{min} are 0.674 and 0.238 for **1a** and 0.420 and 0.162 for **15**. Scattering factors are from ref 45. Crystal data are given in Table 1, and bond distances and angles are in Tables 2 and 5.

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Table 1. Crystallographic Data for $[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]\cdot 2DMF$ (**1a**), $[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\}C{=}NOH)_2]$ (**4**), $[PtCl_2(C_7H_{11}N_2O_2)_2]$ (**14**), and $[PtCl_2(C_8H_{13}N_2O_2)_2]$ (**15**)

	1a	**4**	**14**	**15**
empirical formula	$C_{18}H_{36}N_8Cl_4O_6Pt$	$C_{16}H_{22}N_6Cl_4OPt$	$C_{14}H_{22}N_4Cl_2O_4Pt$	$C_{16}H_{26}N_4Cl_2O_4Pt$
fw	797.44	699.28	576.34	604.40
temp, °C	20(2)	20(2)	20(2)	20(2)
λ, Å	0.710 73	0.710 69	0.710 69	0.710 73
space group	$P1$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P1$ (No. 2)
a, Å	6.9010(10)	10.290	8.163(3)	7.670(2)
b, Å	8.303(2)	18.153	7.823(3)	8.230(2)
c, Å	14.177(3)	13.059	14.51(4)	9.682(2)
α, deg	101.02(3)	90	90	65.14(3)
β, deg	99.35(3)	94.46	100.04(3)	86.18(3)
γ, deg	96.68(3)	90	90	65.12(3)
V, Å^3	777.6(3)	2431.96	912(3)	498.5(2)
Z	1	4	2	1
ρ_{calcd}, g/cm^3	1.703	1.915	2.098	2.013
μ(Mo Kα), cm^{-1}	48.99	65.42	80.08	73.3
R_1[a]	0.0263	0.058	0.0412	0.0264
wR_2[b]	0.066	0.078	0.1117	0.0747

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]\cdot 2DMF$ (**1a**)[a]

Pt−N(1)	2.013(3)	C(1)−C(6)	1.484(7)
Pt−Cl(1)	2.3098(13)	C(2)−C(3)	1.469(7)
Pt−Cl(2)	2.3161(13)	C(2)−C(4)	1.496(7)
O(1)−C(1)	1.347(5)	C(3)−C(5)	1.498(8)
O(1)−N(2)	1.426(5)	O(3)−C(7)	1.215(8)
O(2)−N(3)	1.385(6)	N(4)−C(7)	1.301(8)
N(1)−C(1)	1.261(6)	N(4)−C(9)	1.432(8)
N(2)−C(2)	1.278(6)	N(4)−C(8)	1.448(8)
N(3)−C(3)	1.284(6)		

N(1)−Pt−Cl(1)	94.34(11)	N(1)−C(1)−C(6)	127.2(4)
N(1)−Pt−Cl(2)*	93.80(11)	O(1)−C(1)−C(6)	110.6(4)
Cl(1)−Pt−Cl(2)*	90.52(6)	N(2)−C(2)−C(3)	113.3(4)
Cl(1)−Pt−Cl(2)	89.48(6)	N(2)−C(2)−C(4)	124.9(4)
C(1)−O(1)−N(2)	111.7(3)	C(3)−C(2)−C(4)	121.7(4)
C(1)−N(1)−Pt	136.0(3)	N(3)−C(3)-C(2)	114.9(5)
C(2)−N(2)−O(1)	110.9(4)	N(3)−C(3)−C(5)	125.2(5)
C(3)−N(3)−O(2)	111.9(5)	C(2)−C(3)−C(5)	119.9(4)
N(1)−C(1)−O(1)	122.2(4)		

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

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\}C{=}NOH)_2]$ (**4**)

Pt−Cl(2)	2.307(7)	O(29)−N(21)	1.41(3)
Pt−Cl(3)	2.312(6)	N(7)−C(16)	1.30(3)
Pt−Cl(4)	2.315(6)	N(18)−C(14)	1.28(2)
Pt−Cl(5)	2.332(6)	N(20)−C(23)	1.27(3)
Pt−N(7)	2.048(17)	N(21)−C(42)	1.30(4)
Pt−N(55)	2.029(17)	N(26)−C(9)	1.25(4)
O(11)−N(18)	1.47(2)	N(55)−C(13)	1.27(3)
O(11)−C(13)	1.36(3)	C(9)−C(23)	1.51(3)
O(12)−N(20)	1.45(2)	C(13)−C(25)	1.50(3)
O(12)−C(16)	1.35(3)	C(14)−C(42)	1.45(3)
O(17)−N(26)	1.43(2)	C(16)−C(34)	1.49(3)

Cl(2)−Pt−Cl(3)	90.3(2)	O(12)−N(20)−C(23)	110.5(15)
Cl(2)−Pt−Cl(4)	91.0(2)	O(29)−N(21)−C(42)	116(2)
Cl(2)−Pt−Cl(5)	89.7(2)	O(17)−N(26)−C(9)	112.7(19)
Cl(2)−Pt−N(7)	92.0(5)	Pt−N(55)−C(13)	137.1(16)
Cl(2)−Pt−N(55)	174.2(6)	N(26)−C(9)−C(23)	113(2)
Cl(3)−Pt−Cl(4)	177.6(2)	N(26)−C(9)−C(40)	128(2)
Cl(3)−Pt−Cl(5)	90.3(2)	N(55)−C(13)−C(25)	125.0(19)
Cl(3)−Pt−N(7)	93.7(5)	N(18)−C(14)−C(37)	124.0(19)
Cl(3)−Pt−N(55)	94.1(5)	N(18)−C(14)−C(42)	116.6(19)
Cl(4)−Pt−Cl(5)	91.7(2)	N(18)−C(14)−C(42)	116.6(19)
Cl(4)−Pt−N(7)	84.3(5)	O(12)−C(16)−N(7)	120.5(17)
Cl(4)−Pt−N(55)	84.5(5)	O(12)−C(16)−C(34)	114.5(19)
Cl(5)−Pt−N(7)	175.7(5)	N(7)−C(16)−C(34)	125(2)
Cl(5)−Pt−N(55)	94.1(5)	N(20)−C(23)−C(9)	113(2)
N(7)−Pt−N(55)	84.0(7)	N(20)−C(23)−C(22)	128(2)
N(18)−O(11)−C(13)	109.1(13)	N(21)−C(42)−C(14)	117(2)
N(20)−O(12)−C(16)	111.8(15)	N(21)−C(42)−C(50)	119(2)
Pt−N(7)−C(16)	138.4(15)	O(11)−C(13)−N(55)	125.2(18)
O(11)−N(18)−C(14)	106.8(16)	O(11)−C(13)−C(25)	109.8(17)

X-ray Structure Determination of $[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\}C{=}NOH)_2]$ (4) and $[PtCl_2(C_7H_{11}N_2O_2)_2]$ (14). Brownish-yellow prismatic crystals of **4** and **14** were obtained directly from the reaction mixtures and before the data collection were studied in the Weissenberg camera. Diffraction data were collected on a Syntex $P2_1$ diffractometer (Mo Kα radiation, graphite monochromator, ω-method). Cell parameters for the complexes were obtained from 15 centered reflections with θ between 10 and 20°. Data collection has been done with 2θ between 2 and 60° for **4** and 2 and 85° for **14**. Range of hkl: $h = 0$ to 13, $k = 0$ to 25, $l = -18$ to 18 for **4**, and $h = 0$ to 16, $k = 0$ to 15, $l = -29$ to 28 for **14**. Standard reflections were measured every 50 reflections and showed practically no change with time (±1%). The structures were solved by means of Patterson method using the CSD-universal program package.[44] After that, all reflections with $I < 3\sigma(I)$ were excluded from calculations. Lorenz, polarization, and absorption correction were made.[44] Crystal sizes: 0.1 × 0.1 × 0.2 mm for **4**, and 0.15 × 0.2 × 0.1 mm for **14**. T_{max} and T_{min} are 1.328 and

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[PtCl_2(C_7H_{11}N_2O_2)_2]$ (**14**)[a]

Pt−Cl	2.312(7)	N(1)−C(2)	1.318(7)
Pt−N(1)	1.998(7)	N(2)−C(1)	1.300(7)
Pt−N(2)	2.000(7)	C(1)−C(2)	1.470(9)
O(1)−N(1)	1.321(8)	C(1)−C(3)	1.487(8)
O(2)−N(2)	1.349(8)	C(2)−C(7)	1.491(9)

Cl−Pt−N(1)	89.77(17)	Pt−N(1)−O(1)	118.7(3)
Cl−Pt−N(2)	88.19(17)	Pt−N(1)−C(2)	116.6(4)
Cl−Pt−N(1)*	90.23(17)	O(1)−N(1)−C(2)	124.6(5)
Cl−Pt−N	91.81(17)	Pt−N(2)−O(2)	120.1(3)
N(1)−Pt−N(2)	78.50(19)	Pt−N(2)−C(1)	117.1(4)
Cl−Pt−N	90.23(17)	O(2)−N(2)−C(1)	122.7(4)
N(1)−Pt−N	101.50(19)	N(2)−C(1)−C(2)	113.9(4)
Cl−Pt−N(2)	91.81(17)	N(2)−C(1)−C(3)	123.1(5)
N(1)*−Pt−N(2)	101.50(19)	C(2)−C(1)−C(3)	123.0(4)
Cl−Pt−N(1)*	89.77(17)	N(1)−C(2)−C(1)	113.7(4)
Cl−Pt−N	88.19(17)	N(1)−C(2)−C(7)	123.4(5)
N(1)*−Pt−N	78.50(19)	C(1)−C(2)−C(7)	122.9(4)

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

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[PtCl_2(C_8H_{13}N_2O_2)_2]$ (**15**)[a]

Pt−N(2)	1.989(5)	N(1)−C(1)	1.308(9)
Pt−N(1)	2.002(5)	N(2)−C(8)	1.293(8)
Pt−Cl	2.3067(19)	C(1)−C(8)	1.456(9)
O(1)−N(1)	1.296(7)	C(1)−C(2)	1.504(8)
O(2)−N(2)	1.357(7)	C(7)−C(8)	1.498(9)

N(2)−Pt−N(1)*	101.4(2)	N(1)−C(1)−C(2)	121.8(6)
N(2)−Pt−N(1)	78.6(2)	C(8)−C(1)−C(2)	123.9(6)
N(2)−Pt−Cl	90.65(17)	C(8)−N(2)−Pt	116.9(4)
N(1)*−Pt−Cl	89.35(18)	O(2)−N(2)−Pt	122.2(4)
O(1)−N(1)−C(1)	125.5(5)	N(1)−C(1)−C(8)	114.3(5)
O(1)−N(1)−Pt	118.6(4)	N(2)−C(8)−C(1)	114.3(5)
C(1)−N(1)−Pt	115.9(4)	N(2)−C(8)−C(7)	122.8(6)
C(8)−N(2)−O(2)	120.9(5)	C(1)−C(8)−C(7)	122.7(6)

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

0.883 for **4** and 1.018 and 0.990 for **14**. Atomic scattering factors are from ref 45. Crystal data are given in Table 1, and bond distances and angles, in Tables 3 and 4.

Calculations. The full geometry optimization of the structures was carried out in Cartesian coordinate using the quasi-Newton−Raphson gradient method and the restricted Hartree−Fock approximation with the help of the GAMESS-97 package.[46] Symmetry operations were not applied. As quantum-chemical calculations of compounds with heavy 5d and 6d elements should use a relativistic quantum mechanic approach, a quasi-relativistic pseudopotential for 60 core electrons and the contracted basis set (8s7p6d)/[6s5p3d][47] for the platinum atom along with the analogous pseudopotentials and basis sets (4s4p)/[2s2p] (C, N) and (4s5p)/[2s3p] (O)[48] for other non-hydrogen atoms have been used. The standard basis set of Gauss functions 6-31G[49] was selected for hydrogen atoms.

Results and Discussion

Synthetic Experiments and Characterization of Products. The experimental conditions for conducting the reaction between the *vic*-dioximes and *trans*-$[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph, Ph, dioxime = dimethylglyoxime; R = Me, dioxime = cyclohexa-, cyclohepta-, and cyclooctanedione dioximes) are similar to the earlier described ones for the reaction between *trans*-$[PtCl_4(RCN)_2]$ with so-called "simple" oximes.[2] Elemental analyses (C, H, N, Cl, Pt) and FAB^+ mass spectrometry data (see Experimental Section) of products of the reaction suggest *addition* of two molecules of the dioxime/one molecule of the starting Pt(IV) material. IR spectra of the products show no bands due to ν(C≡N) vibrations (in the starting *trans*-$[PtCl_4(RCN)_2]$ bands at 2354 cm^{-1} for R = Me, 2337 cm^{-1} for R = CH_2Ph, and 2316 cm^{-1} for R = Ph) but display ν(C═N) bands (ca. 1665−1620 cm^{-1}) along with rather weak bands in ranges of 3225−3285 and 1140−1199 cm^{-1} which were attributed to ν(N−H) and ν(C−O) stretching vibrations,[50,51] respectively. Concurrently, in all compounds bands due to ν(O−H) stretch which emerge in range 3420−3450 cm^{-1} were detected.

In ^1H and $^{13}C\{^1H\}$ NMR, the iminoacylated ligands show characteristic signals of the amidine carbon (average 174 ppm), as well as for the methyl group (average 1.7 ppm in ^1H and average 18 ppm in $^{13}C\{^1H\}$ NMR). These mean values agree well with those found for the previously described addition products of the "simple" oximes.[2] The two dioxime C═N groups appear at different chemical shifts (average 165 ppm and average 154 ppm), thus indicating that only one of the oxime groups was added to the nitrile. A difference in chemical shifts was also observed for the alkyl substituents on the dioxime part, which appear as individual signals due to the loss of symmetry. For discussion of NMR spectroscopy data relevant to cis−trans isomerization of the iminoacylated complexes, see below.

Reactions of *trans*-$[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph or Ph) with Dimethylglyoxime and Cycloheptane- and Cyclooctanedione Dioximes. The reactions proceed in good yield and give $[PtCl_4(NH{=}C(R)ON{=}C(Me)C(Me){=}NOH)_2]$ (**1**−**3**). In the case of $[PtCl_4(MeCN)_2]$, the product **1** releases from the reaction mixture as crystals which were subject to X-ray structure determination. Unfortunately, a strong disorder of the newly formed ligand prevented complete structure solution. However, it was clear that these ligands are in trans positions to each other. Recrystallization of thus prepared *trans*-**1** from dimethylformamide resulted in precipitation of the bis-solvate *trans*-$[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]\cdot 2DMF$ (**1a**), whose structure was successfully determined by X-ray single-crystal diffraction (Figure 2, Tables 1 and 2).

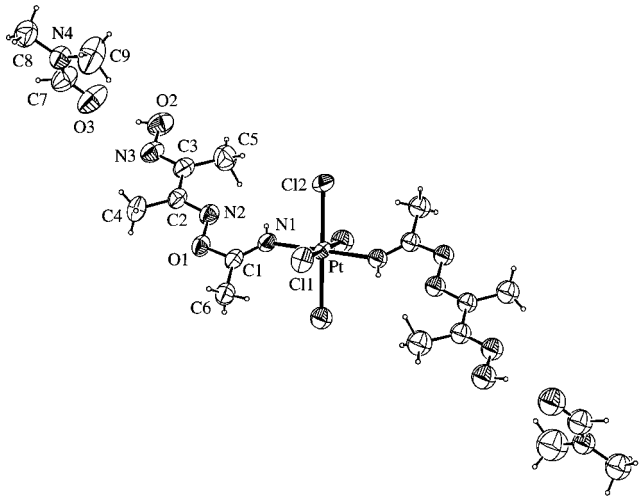

Figure 2. ORTEP drawing of *trans*-$[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]\cdot 2DMF$ (**1a**) with atomic numbering scheme.

The coordination polyhedron of the complex is a slightly distorted octahedron and the Pt atom is in the center of symmetry. The two iminoacylated ligands are in mutual trans positions, and their oxime parts are in anti conformation. Two OH groups are involved in strong[8,52,53] intermolecular hydrogen bonding [OH···O distance is 1.877(7) Å, O···O is 2.664(6) Å, and O−H···O angle is 161.25°] with two dimethylformamide molecules. In the iminoacylated ligands, values of the two C═N bonds are almost identical and correspond to the mean values of the C═N double bonds.[54,55] All other bonds and angles are normal and agree well with iminoacylated oxime[2] and iminoacylated diethylhydroxylamine platinum(IV)[3] compounds previously characterized by some of us.

When the addition was performed starting from a mixture of *cis*- and *trans*-$[PtCl_4(MeCN)_2]$, formation of the two geometrical isomers was observed and their interconversion was monitored by ^1H, 2D [^1H,^{15}N] HMQC, and ^{195}Pt NMR spectroscopy in DMSO-d_6 solutions. Complex *cis*-**1** (^1H NMR spectrum, δ, 2.01 and 2.28 (two s, 3*H* each, ═C(Me)C(Me)), 2.68 (s, $^4J_{PtH}$ was not resolved, 3*H*, ═C(Me)O), 9.19 (s + d, $^2J_{PtH}$ 23.7 Hz, NH), 12.43 (s, 1*H*, OH); 2D [^1H,^{15}N] HMQC NMR spectrum, δ, 104.5 ($^1J_{PtN}$ was not resolved); ^{195}Pt NMR spectrum, δ, 63 (320 Hz)) in DMSO-d_6 solution at 20−25 °C for 3 d converts completely to the trans isomeric form (^1H NMR spectrum, δ, 2.00 and 2.31 (two s, 3*H* each, ═C(Me)C(Me)), 2.78 (s, $^4J_{PtH}$ was not resolved, 3*H*, ═C(Me)O), 8.87 (s + d, $^2J_{PtH}$ 33.2 Hz, NH), 12.52 (s, 1*H*, OH); 2D [^1H,^{15}N] HMQC NMR spectrum,

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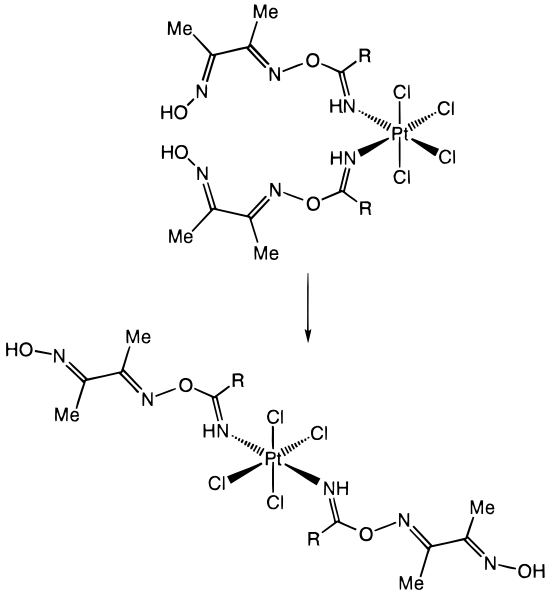
Scheme 2. Cis−Trans Isomerization of $[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]$ (**1**)



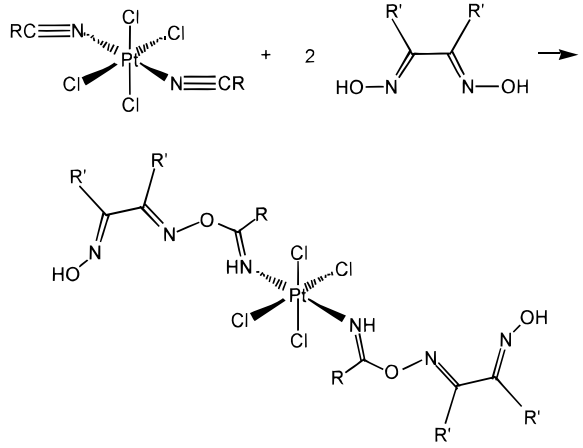
δ, 85.2 ($^1J_{PtN}$ 363 Hz); ^{195}Pt NMR spectrum, δ, −87 (550 Hz)). Indeed, the larger value of $^2J_{PtH}$ for the N*H*=C hydrogen and the value of ^{195}Pt chemical shift of the latter complex are in complete accord with the values found for the previously described *trans*-Pt(IV) complexes containing iminoacylated ligands.[2] In contrast, the corresponding NMR data of the former isomer are similar to values found for the structurally characterized *cis*-$[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\}C{=}NOH)_2]$ (**4**) (see below). The fact that the ^{195}Pt NMR signal of the cis complex appears downfield vs the corresponding trans isomer also agrees well with the observations made for cis and trans isomeric couple $[PtCl_4(Me_2C{=}NOH)_2]$.[10] The ^{15}N chemical shifts follow a similar trend, and the cis isomer appears downfield vs the trans one. To the best of our knowledge, detection of ^{15}N resonances for any platinum(IV) isomeric compounds is the first observation of this kind.

On the basis of all the above listed data we suggest that the isomerization is described by Scheme 2, where the cis form is, similar to the complex *cis*-**4** (see below), conditionally presented in syn configuration of the oxime parts.

Cyclooctanedione dioxime reacts with *trans*-$[PtCl_4(MeCN)_2]$ similar to dimethylglyoxime (Scheme 3), and only the trans isomer (*trans*-**6**) was isolated. Indeed, the amidine NH group in the ^{1}H NMR spectrum shows a typical large $^2J_{PtH}$ (35 Hz) and a ^{195}Pt chemical shift of −78 ppm that agree well with those found for *trans*-**1** or previously described[2] *trans*-imioacylated complexes.

Treatment of *trans*-$[PtCl_4(MeCN)_2]$ with cycloheptanedione dioxime gave a mixture of *cis*-**5** and *trans*-**5**, but their interconversion was not monitored due to decomposition of the addition product in DMSO-d_6 (the compound is not sufficiently soluble in other most common solvents for NMR studies). Although the ^{1}H and $^{13}C\{^1H\}$ chemical shifts for the cis and trans isomers are very similar, the signal of the NH group allows for assignment. In complete accordance with the reaction of dimethylglyoxime, the cis isomer exhibits a higher chemical shift for the NH hydrogen, and the coupling constant $^2J_{PtH}$ is smaller (23.4 Hz) than for the corresponding trans isomer ($^2J_{PtH}$ 32.3 Hz). In ^{195}Pt NMR, the signal of the trans compound (−72 ppm) lies in a similar range as for the previously described "simple" oxime addition products,[2] whereas the cis compounds

Scheme 3. Iminoacylation of Dimethylglyoxime and Cyclooctanedione Dioxime To Give **1** and **6**, Respectively



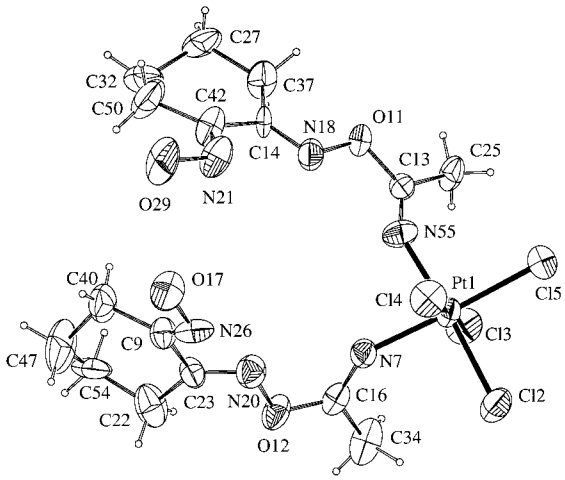


Figure 3. ORTEP drawing of *cis*-$[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\}C{=}NOH)_2]$ (**4**) with atomic numbering scheme.

appears at +76 ppm, i.e. about 150 ppm downfield of the corresponding trans isomer.

Surprisingly, in the reaction with cyclohexanedione dioxime merely the cis isomer (*cis*-**4**) was isolated and identified (see below). Reasons for the formation of the different isomers in the reaction with the structurally similar dioximes are not yet clear and probably deserve a separate study.

Reaction of *trans*-$[PtCl_4(MeCN)_2]$ and Cyclohexanedione Dioxime. Although the reaction with cyclohexanedione dioxime visually proceeds analogously to those described for the other dioximes, we were able to isolate and completely characterize by physicochemical methods and by X-ray crystallography only the cis isomer, i.e. *cis*-$[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\}C{=}NOH)_2]$ (**4**). The ^{1}H NMR spectrum shows one amidine NH signal with $^2J_{PtH}$ of 23 Hz, whereas the ^{195}Pt signal appears at 57 ppm. These values are in good agreement with those observed for the complexes *cis*-**1** and *cis*-**5**. Unfortunately, the compound is not enough stable in DMSO-d_6 and not sufficiently soluble in other solvents to study whether the isomerization occurs.

The structure of **4** consists of an octahedrally coordinated platinum(IV) center in which the two cis positions are filled with newly formed iminoacylated cyclohexadioxime ligands (Figure 3, Tables 1 and 3).

The Pt−Cl bond lengths [2.307(7)−2.332(6) Å] are of normal

values.[56−58] All six C═N bonds [1.25(4)−1.30(3) Å] and the four N−O bonds [1.41(3)−1.47(2) Å] are equal within 3σ, and these distances agree with the mean values of the C═N and the N−O bonds, correspondingly.[2,3,54,55] Apparently, the most interesting feature of *cis*-**4** is the existence of a potentially multidentate Pt(IV)-based metallaligand that consists of the platinum atom and the two adjacent iminoacylated species. Within the NH═C(Me)ON═C{C_4H_8}C═NOH ligands, the imino hydrogens [*H*N(55) and *H*N(7)] are involved in intramolecular hydrogen bonding with the neighboring nitrogens N(18) and N(20), respectively. Distances N(55)···N(18) (2.596 Å) and N(7)···N(20) (2.559 Å) are similar to those in the previously reported structures of *trans*-[$PtCl_4$(NH═C(Me)ONCR_1R_2)$_2$] and *trans*-[$PtCl_4$(NH═C(Me)ONEt_2)$_2$] (2.59−2.60 Å[2,3]), where the same type of H-bond was unambiguously detected. Although we were unable to refine hydrogen atoms on the OH groups, a relatively short O(29)···O(17) distance (3.12 Å) indicates this type of bonding. Appearance of a broad signal of O−H stretching frequencies in the IR spectra of the addition products which emerges in a range 3420−3450 cm^{-1} also suggests a hydrogen bond, albeit weak.[50,51]

Geometrical Isomerism and Isomerization. For better understanding of the geometrical isomerism for the platinum(IV) iminoacylated complexes we have calculated the equilibrium geometry and the relative stability for the molecules and fragments with structures similar to *cis*-**4** but without a possibility to form intramolecular hydrogen bonds of the above-mentioned type. Thus, the influence of the H-bond on the stability of the cis conformation was excluded. For the calculations, we addressed *cis*- and *trans*-[$PtCl_4$(NH═C(Me)ON═CMe_2)$_2$]. The X-ray structure of the latter isomer (**I**) (Figure 4) was reported earlier by some of us,[2] and these data were taken as the starting geometry for the model simplified trans structure (**II**) and as initial geometry parameters of oxime ligands for the model cis isomer (**III**), where the methyl groups were displaced by hydrogen atoms for simplicity reasons. Since X-ray data for *cis*-[$PtCl_4$(NH═C(Me)ON═CMe_2)$_2$] are unavailable, several initial conformations of **III**, which differ by the orientation of the oxime ligands relative to the Pt−N bond, have been used.

To justify the chosen model structures, the full geometry optimization of **I** has also been carried out. The calculated geometry parameters for the simplified model structure and the real one appeared to be very similar, e.g. the maximum difference for bond lengths is 0.017 Å, whereas the maximum deviation of bond angles is 8.7° for Pt−N−C and not more than 4.6° for the other ones. The significant difference for the Pt−N−C angles is probably due to the steric hindrance of the methyl group. Taking into account well-coherent calculated geometrical parameters for both **I** and **II**, the geometry optimization of the cis conformation (**III**) was performed only for the simplified model molecule.

The general calculated conformation of **I** and **II** corresponds well to the X-ray structure of *trans*-[$PtCl_4$(NH═C(Me)ON═CMe_2)$_2$], even taking into account orientations of the methyl groups. Calculated bond lengths and angles are also in good agreement with the experimental parameters, except for the Pt−Cl bonds, e.g. the maximum bond length difference consists

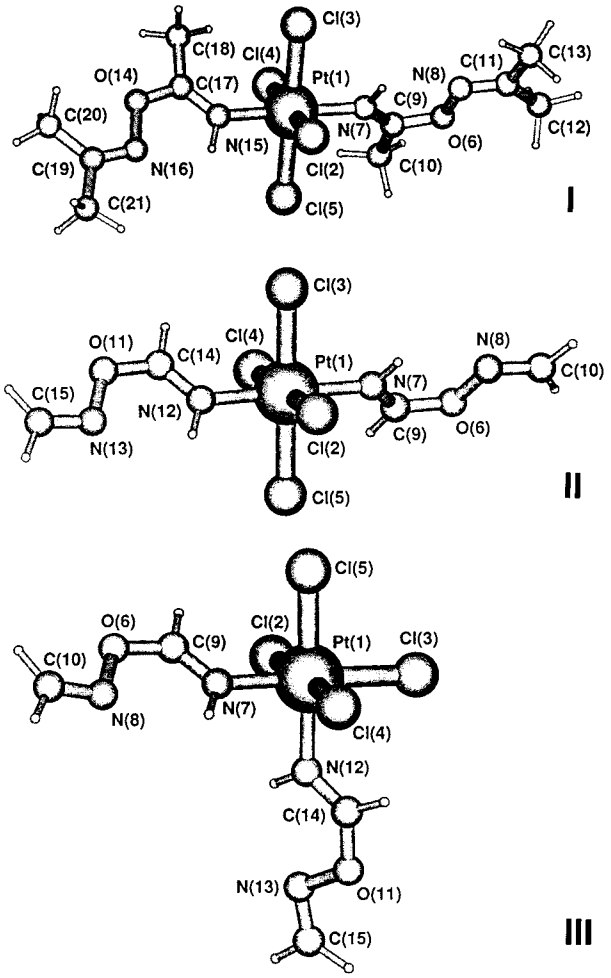


Figure 4. Models used for calculations.

0.089 Å for the Pt−Cl bonds and is not higher than 0.025 Å for other bonds of both **I** and **II**. The maximum difference for bond angles is 8.9° for **II** (the Pt−N−C angle) and 2.2° for **I** (the O−N−C angle). The intramolecular N−H···N hydrogen bond that stabilizes the general conformation of oxime ligands can be suggested on the basis of interatomic distances (the calculated distances for N(7)···N(8), N(7)−H, and N(7)H··· N(8) are 2.63, 1.00, and 2.15 Å, respectively, and the angle N−H···N is 107.7° for **I**; they are 2.69, 1.00, and 2.32 Å and 100.7° for **II**, correspondingly). However their calculated parameters differ from the experimental ones (the corresponding values are 2.605, 0.74, and 2.20 Å and 115°). It is well-known that X-ray diffraction often gives shorter distances for E−H bonds than distances determined by neutron diffraction because the location of the hydrogen atoms electron cloud is different from the positions of the hydrogen nucleus,[8,59] and this might be the reason of the disagreement between experimental and calculated parameters of the H-bonds.

Three equilibrium structures with very similar energies (the most stable of these structures is marked as **III**), differing only by the conformations of the oxime ligands, have been obtained for the cis isomer. The torsion angles NPtNC for these structures are −51.0 and −51.5°, 52.9 and −53.6°, and 51.5 and 51.0°. Other geometrical parameters exluding the angles N−Pt−Cl and Cl−Pt−Cl are almost the same for these conformations and very similar to the corresponding parameters of **II**. The most noticeable difference was observed for the Pt−N bonds (2.035

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Å for **II** and 2.058 Å for **III**) and for the Pt−Cl bonds which are in the trans position to the oxime ligands (2.389 Å for **II** and 2.371 Å for **III**), probably reflecting the higher ground-state trans influence of chloride compared with the iminoacylated oxime ligand. The conformation of the oxime ligands is also stabilized by intramolecular hydrogen bonds [N(7)···N(8), N(7)−H, and N(7)H···N(8) of 2.70, 1.00, and 2.32 Å and N−H···N of 101.0°].

The energy difference between the trans conformation and the most stable of three calculated cis conformation is 7.96 kcal/mol (the full energy is −274.273 34 hartree for the structure **II** and −274.260 66 hartree for the structure **III**).

Thus, the calculations showed that for the iminoacylated dioxime complexes of platinum(IV) which do not contain intramolecular hydrogen bonds between two oxime ligands, the trans isomers are more stable than cis isomers. Derivatization by introducing substituents that can form intramolecular hydrogen bonds of such type leads to increase of the relative stability of the cis isomer. These facts are indirect arguments in favor of the additional stabilization of cis isomer of **4** by the H-bond between the two peripherical OH groups.

The calculations agree well with experimental observations. Indeed, when "simple" oximes reacted with *trans*-[$PtCl_4(MeCN)_2$] the iminoacylation always led to complexes of the trans configuration.[2] Moreover, on the basis of massive experimental data, it was declared as a general statement that namely the trans form is the more stable one for metal complexes (including platinum(IV) compounds[60−65]) in high oxidation states.[66] Formation of relatively stable cis isomer in the case of complexes with iminoacylated *vic*-dioximes is probably due to the hydrogen bond between the two OH groups that "sew" the two iminoacyl arms.

Formation of the Substitution Products [$PtCl_2$(dioximato)$_2$] (13−15) in the Course of the Iminoacylation and X-ray Structures of [$PtCl_2(C_7H_{11}N_2O_2)_2$] (14) and [$PtCl_2(C_8H_{13}N_2O_2)_2$] (15). In the course of the iminoacylation we also isolated the products which formed due to a substitution process, e.g. compounds [$PtCl_2$(dioximato)$_2$] (**13**−**15**) (where dioximato = monodeprotonated cyclohexa-, cyclohepta-, or cyclooctanedione dioxime); the complex of this type was not observed in the case of dimethylglyoxime. In fact, the substitution products are formed in such a low yields that we succeded only in mechanical separation of their crystals from crystals of the addition products exhibiting different shape. However, the amount of the materials thus obtained was sufficient for their characterization by both analytical and spectroscopic methods. Structures of the two compounds, [$PtCl_2(C_7H_{11}N_2O_2)_2$] (**14**) and [$PtCl_2(C_8H_{13}N_2O_2)_2$] (**15**), were determined by X-ray single-crystal diffraction. The coordination polyhedron of both complexes is a slightly distorted octahedron (Figures 5 and 6, Tables 1, 4, and 5).

Dioximato ligands in the structures are in trans configuration. The values of the Pt−Cl bond distances [2.312(7) in **14** and 2.307(2) Å in **15**] agree well with those of previously characterized platinum(IV) chloride compounds,[56−58] and the Pt−N and N=C distances are of normal values.[54,55] In **15**, where hydrogen atoms on the OH groups were found from difference syntheses and were refined, it is clearly seen that the oxime and oximato parts of the ligands form six-membered rings involving intramolecular hydrogen bonds [O(1)···O(2*), 2.681(9) Å; O(1)···H−O(2*), 142(13)°]. As expected for the negative charge assisted hydrogen bonding,[52] these distances are in the range of strong hydrogen bonds.[8,67,68] Since the structure of **15** contains both the oxime and oximato parts of the chelating ligands, the N−O(oximato) distance [1.296(7) Å] is reasonably shorter than the N−O(oxime) one [1.357(7) Å]. The same trend in the N−O bond lengths was observed in **14** although H-atoms on the OH groups were not located. Despite the traditional coordination mode of the oxime ligands, these two complexes are the first example of structurally characterized derivatives of platinum(IV) with *vic*-dioximes. Previously only complexes of both platinum(II)[69−80] and platinum(III)[81,82] that contain dioximes were subject of crystallographic studies.

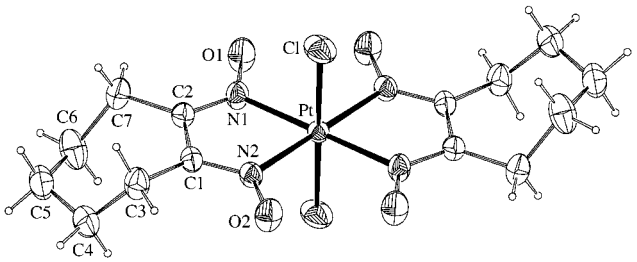

Figure 5. ORTEP drawing of [$PtCl_2(C_7H_{11}N_2O_2)_2$] (**14**) with atomic numbering scheme.

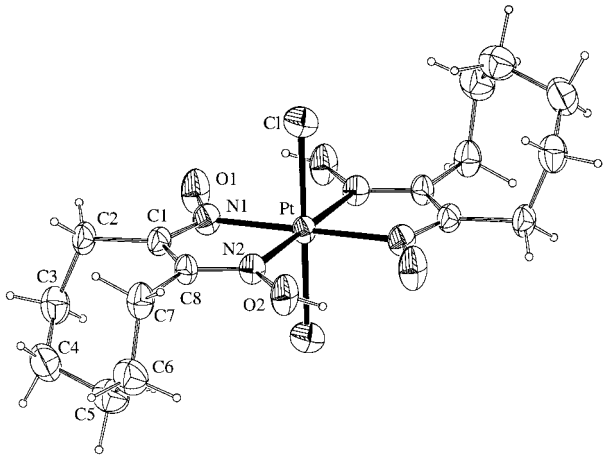

Figure 6. ORTEP drawing of [$PtCl_2(C_8H_{13}N_2O_2)_2$] (**15**) with atomic numbering scheme.

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The complexes **13**−**15** and $[PtCl_2(C_4H_7N_2O_2)_2]$ (**12**) ($C_4H_7N_2O_2$ is the monodeprotonated dimethylglyoxime) were also obtained in a reasonable yield on treatment of either $[PtCl_4(Me_2SO)_2]$ or $[PtCl_4(MeCN)(Me_2SO)]$ with 2 equiv of the dioxime. However, in these two cases the substitution was accompanied by reduction of the central ion—probably by the released dimethyl sulfoxide[83−87]—and this led to contamination of **12**−**15** with the well-known platinum(II) complexes [Pt(dioximato)$_2$].[88,89]

Reactions of $[PtCl_4(MeCN)(Me_2SO)]$ with "Simple" Oximes. For comparative reasons, it is worthwhile to mention that the reaction between $[PtCl_4(MeCN)(Me_2SO)]$ and the *vic*-dioximes proceeds in a different direction than that, which was also investigated in this study, for this complex and "simple" oximes (Me_2C═NOH, $\{C_4H_8\}$C═NOH, $\{C_5H_{10}\}$C═NOH, PhC(H)═NOH) and even salicylaldoxime, (OH)C_6H_4C(H)═NOH (for the relevant reaction see Scheme 1). In the latter case the addition of the oximes to the ligated acetonitrile was observed, leading to the iminoacylated species $[PtCl_4(NH{=}C(Me)ON{=}CRR')(Me_2SO)]$ (**7**−**11**) (RR′ = Me_2, $\{C_4H_8\}$, $\{C_5H_{10}\}$, Ph(H), (OH)C_6H_4(H)) which exist as a mixture of cis and trans isomers. The iminoacylated ligands display a similar ^{1}H and $^{13}C\{^1H\}$ spectra for both isomers. However, the presence of two compounds is shown by their distinct NH proton resonances (average 8.4 ppm for the cis isomers vs average 8.6 ppm for the trans isomers).

In contrast to the iminoacylated ligand, the coordinated dimethyl sulfoxide appears as two distinct signals in ^{1}H as well as in $^{13}C\{^1H\}$, both showing coupling to platinum ($^3J_{PtH}$ and $^2J_{PtC}$). This observation suggests that in both complexes the Me_2SO is coordinated via its sulfur. According to the previously described starting material,[37] the signals with lower proton chemical shift and larger J_{PtH} (typically ca.15.0 Hz for cis isomers vs ca.13.5 Hz for trans ones) and smaller carbon chemical shift and smaller J_{PtC} (typically ca. 28 Hz for cis isomers vs ca. 32 Hz for trans ones) are assigned to the cis isomer.

In ^{195}Pt NMR, both isomers show clearly separate signals, i.e. the cis isomer appearing at ca. −970 ppm whereas the trans isomer resonates at around −1080 ppm. It is worthwhile to mention that for most compounds the coupling between platinum and ^{14}N could be resolved, thus leading to a triplet structure of the platinum signal with a typical $^1J_{Pt^{14}N}$ of 200 to 260 Hz.

Concluding Remarks

To the best of our knowledge, all known metallaligands were previously prepared by direct addition of *ligands* to metal-containing precursors. In our case, the dioxime part of the metallaligand was created in the course of the addition of *reagents* to coordinated organonitriles which are activated by the metal center. It is also noteworthy to mention that, despite the variety of products that might be expected to be formed in these reactions—in view of the usability of dioximes as ligands—our system presents a remarkable selectivity toward the nucleophilic addition of one oxime moiety of each dioxime to each of the nitrile ligands to form an unusual arrangement of two iminoacyl ligands that interact, by hydrogen bond, through their terminal unreacted oxime groups which, thus, are not simple spectators and play a significant role in the stabilization of the unexpected final product. Hence, within the various factors that drive the observed reaction, the relevance of the hydrogen bond appeared to be evident. This ability of hydrogen bonding to stabilize unusual structures derived from dioxime reactions should be explored further. Moreover, our reaction might be useful for the preparation of a broad spectrum of Pt(IV)-based metallaligands since a variety of dioximes and other bidentate ligands that contain the N−OH moiety are either comercially available or well described in the literature.

We hope that the results reported in this article contribute to the chemistry of *vic*-dioximes considerably, and we will continue these investigations in depth. Further synthetic studies are now in progress to establish, on one hand, a potential of the discovered type of metallaligands for further complexing and, on the other hand, to extend the iminoacylation reactions to other high-valent metal complexes including, in particular, rhodium(III)[90] and rhenium(IV)[91] compounds.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $[PtCl_4(NH{=}C(Me)ON{=}C(Me)C(Me){=}NOH)_2]\cdot 2DMF$ (**1a**), $[PtCl_4(NH{=}C(Me)ON{=}C\{C_4H_8\}C{=}NOH)_2]$ (**4**), $[PtCl_2(C_7H_{11}N_2O_2)_2]$ (**14**), and $[PtCl_2(C_8H_{13}N_2O_2)_2]$ (**15**). This material is available free of charge via the Internet at http://pubs.acs.org.

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