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Oxidation of Pt-bound *Bis*-hydroxylamine as a Novel Route to Unexplored Dinitrosoalkane Ligated Species

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The reaction of $K_2[PtCl_4]$ and $HO(H)NCMe_2CMe_2N(H)OH \cdot H_2SO_4$ (**BHA**$\cdot H_2SO_4$; **2**) in a molar ratio 1:2 at 20−25 °C in water affords a mixture of $[Pt(BHA)_2][PtCl_4]$ (**5**) and $[Pt(BHA\text{-}H)_2]$ (**6**) (**BHA-H** = anionic monodeprotonated form of **BHA**) which, upon heating at 80−85 °C for 12 h or on prolonged keeping at 20−25 °C for 2 weeks, is subject to a slow transformation giving $[PtCl_2(BHA)]$ (**7**). The latter compound is also obtained from the reaction between $K[PtCl_3(Me_2\underline{S}O)]$ and **2**. The chlorination of $[PtCl_2(BHA)]$ (**7**) in freshly distilled dry *chloroform* leads to the selective oxidation of one N(H)OH group yielding $[PtCl_2\{HO(H)\underline{N}CMe_2CMe_2\underline{N}{=}O\}]$ (**13**), while the chlorination in *water* produces the complex $[PtCl_2(O{=}\underline{N}CMe_2CMe_2\underline{N}{=}O)]$ (**14**) bearing the unexplored dinitrosoalkane species. Treatment of **14** with 2 equiv of 1,2-bis-(diphenylphosphino)ethane (dppe) in CH_2Cl_2 results in the liberation of the dinitrosoalkane ligand followed by its fast cyclization giving the α-dinitrone (3,3,4,4-tetramethyl-1,2-diazete-1,2-dioxide) in solution and the solid $[Pt(dppe)_2](Cl)_2$. The Pt^{II} complexes with hydroxylamino$^{\cap}$oximes $[PtCl_2\{HO(H)\underline{N}C(Me)_2C(R){=}\underline{N}OH\}]$ (R = Me **8**; R = Ph **9**) upon their oxidation with Cl_2 in $CHCl_3$ afford the nitrosoalkane derivatives $[PtCl_2\{O{=}\underline{N}CMe_2C(R){=}\underline{N}OH\}]$ (R = Me **16**; Ph **17**), respectively, while the corresponding chlorination of the *bis*-chelates $[Pt\{HO(H)\underline{N}CMe_2C(R){=}\underline{N}OH\}_2]$ (R = Me **10**; Ph **11**) gives $[Pt\{O{=}\underline{N}CMe_2C(R){=}\underline{N}O\}_2]$ (R = Me **18**; Ph **19**). The formulation of **5**−**19** is based on C, H, and N microanalyses, IR, 1D (^1H, $^{13}C\{^1H\}$, ^{195}Pt) and 2D (^1H,^1H-COSY,^1H,^{13}C-HSQC) NMR spectroscopies, and X-ray diffraction for five complexes (**5**, **7**, and **12**−**14**).

Introduction

The general chemistry of *C*-nitroso species, in particular, nitrosoalkanes (for comprehensive reviews see refs 1,2) became a subject of rapt attention after the recent discovery of the important role of these compounds in various biochemical metabolic processes. In addition, these species are intriguing ligands in coordination chemistry giving metal-containing systems which exhibit a variety of unusual reactivity modes.[3,4]

In comparison with *mono*nitrosoalkanes, the family of *di*nitrosoalkanes (for a recent review see ref 2), especially those with two nitroso groups in *vicinal* or *geminal* position, includes only a small number of representatives.[2] This is explained, on one hand, by the high reactivity of free dinitrosoalkanes determining their short lifetime and involvement in secondary reactions right after the generation. On the other hand, methods for preparation of the dinitrosoalkanes are still undeveloped.

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To our knowledge, the coordination chemistry of dinitrosoalkanes is at the very early stage of its growth, and metal dinitrosoalkane derivatives are so far represented exclusively by the series of cobalt(I) complexes of type $[Co(\eta^5\text{-}Cp)(O{=}\underline{N}CR^1R^2CR^3R^4\underline{N}{=}O)]$ (R^1, R,^{2} R^3, R^4 = H, Me, Et, Ph, C_3H_8) and the dimer $[\{Co(\eta^5\text{-}Cp)\}_2(C_7H_8(N{=}O)_4)]$, and the ruthenium(II/III) $[Ru(O{=}\underline{N}CMe_2CMe_2\underline{N}{=}O)(bpy)_2]^{2+/3+}$(bpy = 2,2′-bipyridine) species. The cobalt complexes were generated via a multicomponent reaction of $[Co(\eta^5\text{-}Cp)(CO)_2]$ with a Diels−Alder adduct of cyclopentadiene and the dimethyl ester of acetylenedicarboxylic acid in the presence of NO,[5] or via the addition of alkenes to $[Co(\eta^5\text{-}Cp)(NO)]_2$.[5] The ruthenium complex originated from the oxidation of $[Ru(bpy)_2(NH_2CMe_2CMe_2NH_2)]^{2+}$ by $Ce(NO_3)_6^{2-}$ in CF_3CO_2H.[6] The years passed since the preparation of these complexes did not bring any further dinitrosoalkane metal compounds that give a collateral evidence that the observed synthetic routes to the dinitroso systems are more specific than general.

In view of our ongoing interest on the coordination chemistry of compounds with N−O and N=O bonds as ligands (including nitrosoalkanes),[7–10] nucleophiles,[11] promoters[12] or dipoles,[13] we endeavored to discover a novel route to dinitrosoalkane metal derivatives. The hypothesis of this work was to employ for the study the metal-bound *bis*-hydroxylamine ligand (**1** in Figure 1; an efficient synthesis of **1** was developed by one of us[14]) and to conduct its intramolecular oxidation to achieve the dinitrosoalkane chelates. This starting idea was supported by the following previous works: (i) some metal-free *C*-nitroso compounds (albeit aromatic rather than aliphatic) have been synthesized by oxidation of *N*-substituted hydroxylamines by ferric chloride,[15] pyridinium chlorochromate,[16] or ^{t}Bu hypochlorite;[15] (ii) 1,2-hydroxylamino-2,3,5,6-tetrachlorobenzene was selectively oxidized to 1,2-nitroso-2,3,5,6-tetrachlorobenzene.[2]

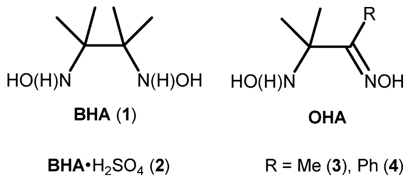

Figure 1. *Bis*-hydroxylamine and hydroxylamino∩oximes employed for this study.

As a metal center for this study we addressed platinum(II) insofar as it gives kinetically inert metal complexes, and this property allows the trapping of species which are *unstable* or even *elusive* in the free state. In addition, it is our experience that Pt^{II} centers strongly stabilize ligated nitrosoalkanes.[8,9]

The scenario for this work was the following. First, to synthesize novel (*bis*-hydroxylamino)Pt^{II} complexes. Second, to attempt the stepwise selective oxidation of the prepared species to achieve mixed hydroxylamino/nitrosolkane systems and then the dinitroso ligand. Third, to liberate the dinitrosoalkane ligand and to study its stability in the free state and/or its conversions. Fourth, to compare the oxidation of the (*bis*-hydroxylamino)Pt^{II} complexes with that of (hydroxylamino∩oximes)Pt^{II} compounds; the latter are based on the ligands **3** and **4** depicted in Figure 1. Details of the obtained results are elaborated in this article.

Results and Discussions

Synthesis and Characterization of $\{HO(H)\underline{N}{-}C^{\cap}C{-}\underline{N}(H)\text{-}OH\}Pt^{II}$-Type Chelates. The complexation of various hydroxylamines to Pt^{II} and Pt^{IV} centers is well-known, and species with unsubstituted,[17] *N*-substituted,[18] and *N,N*-disubstituted hydroxylamines[19] were described in the literature. In spite of the reported variety of *monodentate* Pt-bound hydroxylamine ligands, platinum(II) complexes with *N,N*-bidentate ligands having *two hydroxylamine binding sites* have never been reported in the past. Moreover, up to date the only documented example of metal complexes bearing

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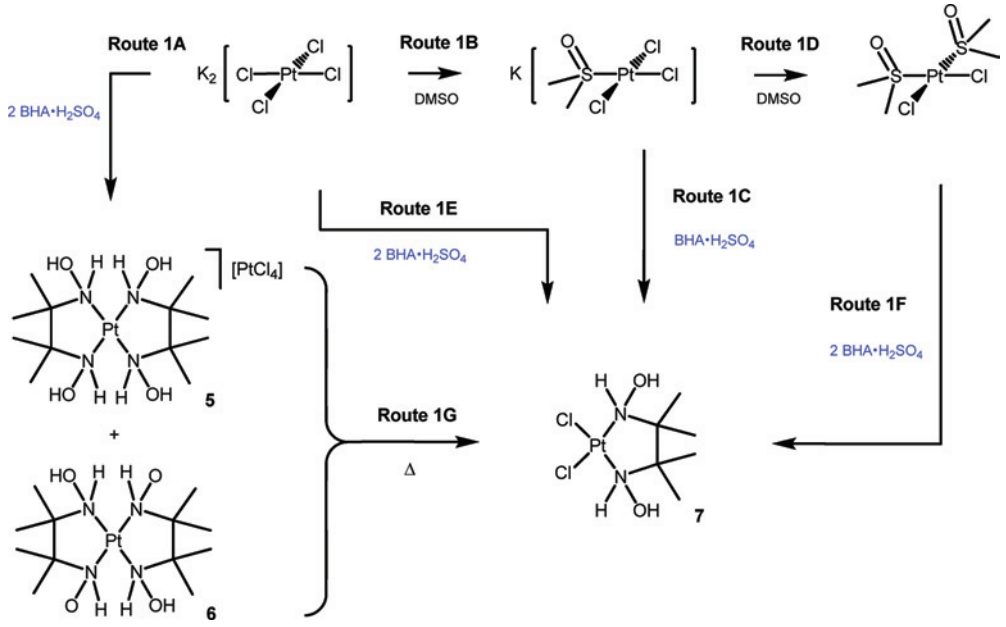
Scheme 1



the bifunctional hydroxylamine concerns the nickel(II) chelate [NiCl(BHA-H)(BHA)][20] (**BHA** is **1**, IUPAC name[21] is N^2,N^3-dihydroxy-2,3-dimethylbutane-2,3-diamine; **BHA-H** is anionic monodeprotonated form of **BHA**), synthesized by one of us.[14]

We have now found that the reaction of $K_2[PtCl_4]$ and **BHA**·H_2SO_4 (**2**) in a molar ratio 1:2 at 20−25 °C in water affords a mixture of the red crystalline solid $[Pt(BHA)_2]$-$[PtCl_4]$ (**5**) and the colorless amorphous $[Pt(BHA\text{-}H)_2]$ (**6**), (Scheme 1, **Route 1A**), from which **5** was separated in 37% yield. When the synthesis is performed in D_2O, the monitoring of the filtrate using 2D ^{1}H,^{1}H-COSY, and ^{1}H,^{13}C-HSQC NMR correlation experiments, allowed the identification of dissolved **5** and **6** along with $[PtCl_2(BHA)]$ (**7**). Our attempts to isolate some additional amounts of **5** from the filtrate were unsuccessful insofar as it is strongly contaminated with other products because of similar and rather high water solubilities of the components of the mixture.

The (BHA)Pt^{II} complexes were also obtained starting from the sulfoxide precursor $K[PtCl_3(Me_2\underline{S}O)]$[22] (prepared via **Route 1B**). Thus, reaction of equimolar amounts of $K[PtCl_3(Me_2\underline{S}O)]$ and **BHA**·H_2SO_4 furnishes the solid $[PtCl_2(BHA)]$ (**7**) isolated in 45% yield (**Route 1C**). The latter compound was also prepared from $K_2[PtCl_4]$ or *cis*-$[PtCl_2(Me_2\underline{S}O)_2]$ and 2 equiv **BHA**·H_2SO_4 but in lower yields (28 and 22%, respectively, **Routes 1E** and **1F**). However, in both latter cases the process is not selective and affords **7** strongly contaminated with other products (in particular with **5** and **6**) and, in the case of **Route 1F**, also with *cis*-$[PtCl_2(Me_2S)_2]$ (crystals of this sulfide complex released from the reaction mixture were subject to X-ray diffraction and the structure solution indicated a good agreement with the known structure of *cis*-$[PtCl_2(Me_2S)_2]$,[23] see Supplementary Information). The *bis*-sulfide complex derives from the known deoxygenation of the sulfoxide precursor by hydroxylamine.[24]

The mixture of **5** and **6** (obtained via **Route 1A**), upon heating at 80−85 °C for 12 h or on prolonged keeping at 20−25 °C for 2 weeks, is subject to a slow transformation giving **7** (**Route 1G**). The reaction of $K_2[PtCl_4]$ and the free base N^2,N^3-dihydroxy-2,3-dimethylbutane-2,3-diamine (**BHA**, **1**) in various molar ratios ranging from 1:1 to 1:2 in water does not achieve **5**−**7** but results in the formation of a mixture of yet unidentified products, including platinum black (which originates form the reduction of Pt-containing species), while the corresponding reaction of $K[PtCl_3$-$(Me_2\underline{S}O)]$ or *cis*-$[PtCl_2(Me_2\underline{S}O)_2]$ with **BHA** also in aqueous

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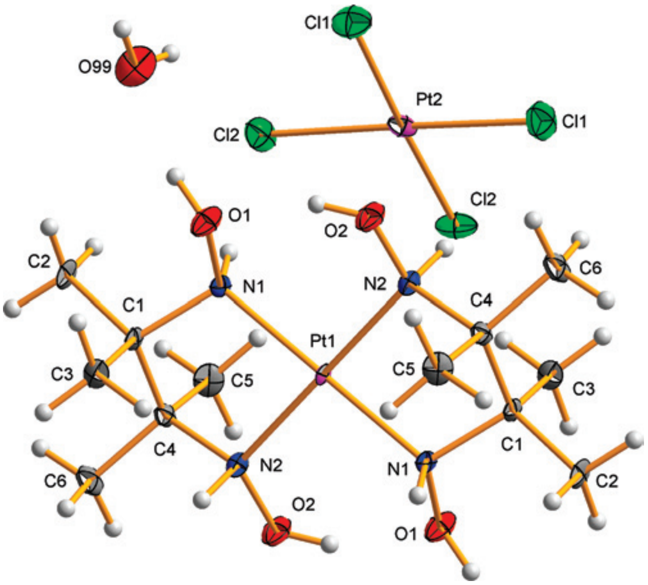

Figure 2. Thermal ellipsoid view of **5** with atomic numbering scheme (hydrogen labels are not shown for simplicity). Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.038(5), Pt(1)−N(2) 2.042(5), Pt(2)−Cl(1) 2.2833(17), Pt(2)−Cl(2) 2.2912(16), O(1)−N(1) 1.431(6), O(2)−N(2) 1.428(6), N(2)−Pt(1)−N(1) 82.5(2), N(2)#1-Pt(1)−N(1)#1 82.5(2). Symmetry transformations used to generate equivalent atoms: #1 = $-x + 3/2$, $-y + 1/2$, $-z + 1$.

media affords *cis*-[$PtCl_2(Me_2S)_2$][23] via the deoxygenation of the coordinated dimethyl sulfoxide by the N(H)OH centers of **BHA**.[24]

The formulation of complexes **5** and **7** was supported by satisfactory C, H, and N microanalyses. The complexes were also characterized by IR and 1D ^1H, $^{13}C\{^1H\}$, ^{195}Pt, and 2D ^1H,^1H-COSY,^1H,^{13}C-HSQC NMR spectroscopies, and X-ray crystallography.

The IR spectra of **5** and **7** exhibit two strong bands in the range of 3220−2990 cm^{-1} due to the ν(N−H) and ν(O−H) stretching vibrations of the hydroxylamine moieties. The ^1H NMR spectrum of **7** displays two broad singlets from the NH and OH protons of the hydroxylamine HO(H)N groups at about 7.7 and 9.5 ppm, respectively. In the $^{13}C\{^1H\}$ spectra of **5** in D_2O and **7** in DMSO-d_6, the CN carbon resonates in the expected field at about 72−77 ppm.[25] The ^{195}Pt NMR spectra of **5** in D_2O and **7** in DMSO-d_6, display one peak between −2450 and −2500 ppm in the typical range for Pt^{II} species.[26] In the ^{195}Pt NMR spectrum of **5** in D_2O, one more signal due to the anion $[PtCl_4]^{2-}$ emerging at −1713 ppm was detected.

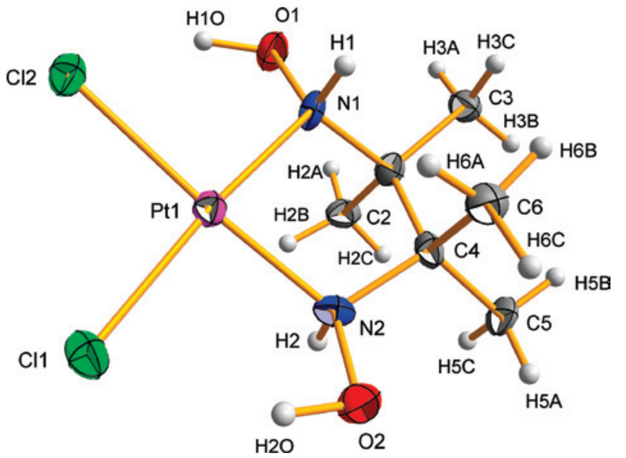

Figure 3. Thermal ellipsoid view of complex **7** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.027(9), Pt(1)−N(2) 2.027(9), Pt(1)−Cl(1) 2.311(3), Pt(1)−Cl(2) 2.310(3), O(1)−N(1) 1.423(11), O(2)−N(2) 1.436(11), N(1)−Pt(1)−N(2) 83.0(3), N(2)−Pt(1)−Cl(1) 91.9(3).

The structures of **5** and **7** have been determined by X-ray diffraction (Figures 2 and 3). In **5**, the coordination polyhedra of both platinum centers are slightly distorted squares. In the cation, two neutral **BHA** ligands are coordinated by both hydroxylamino N atoms forming two five-membered chelating rings (similar to those observed in the related PtN_4 chelates,[27,28] for example, [Pt{HO$\underline{N}$C(Me)C(Me)$\underline{N}$O}$_2$][27]), and the 2+ charge on the cation is compensated by the charge on the anion $[PtCl_4]^{2-}$. The bond lengths Pt(1)−N(1) 2.038(5) and Pt(1)−N(2) 2.042(5) Å are normal while O(1)−N(1) 1.431(6) and O(2)−N(2) 1.428(6) Å are equal within 3σ and belong to typical single O−N bonds.[29] The N(2)−Pt(1)−N(1) angle is 82.46(18)°, and this value compares well with those previously observed in the nickel chelate [NiCl(BHA)(BHA-H)] [84.0(3)−84.7(3)°].[20] Examination of the distances and angles between the hydroxylamine OH proton (H2O) of one chelated ligand and the hydroxylamine oxygen (O1) of another chelated ligand indicates the existence of two symmetric intramolecular hydrogen bonds between two chelated groups, stabilizing the structure of **5**, with the following observed distances and angles: O(2)−H(2O) 0.83, O(2)−H(2O)···O(1) 1.88 Å, O(2)−H(2O)···O(1) 155.1°. A similar type of intramolecular H-bonding was also observed in relevant *bis*-chelate complexes with MN_4 square-planar coordination environment, namely, in [Pt{HO$\underline{N}$C(Me)-C(Me)$\underline{N}$O}$_2$], [Pd{HO$\underline{N}$(1,2-C_6H_4)$\underline{N}$O}$_2$], and [Ni{HO$\underline{N}$C(=O)C(=O)$\underline{N}$O}$_2$]; the hydrogen bonding distance is 1.62−1.92 Å,[27] 1.51−1.77 Å,[30] and 1.65 Å,[31] respectively.

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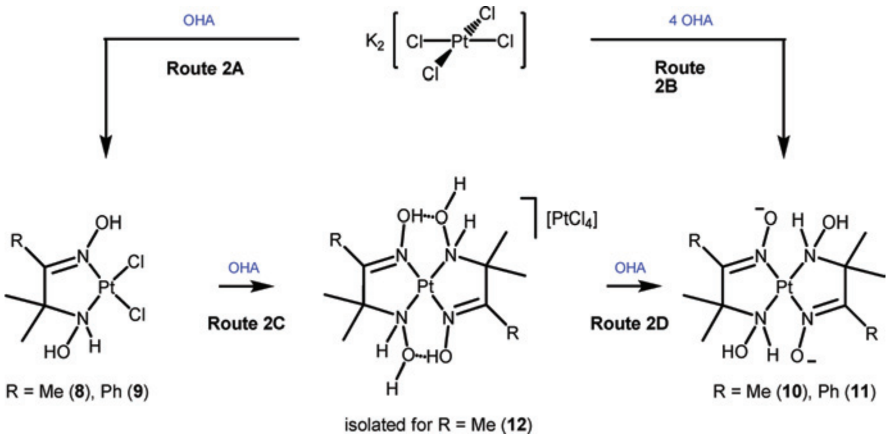
Scheme 2



Complex **7**, [PtCl$_2$(BHA)], is the first crystallographic evidence for *monochelate* metal complexes with two bonded hydroxylamine sites. In **7**, the coordination polyhedron of the metal center is a slightly distorted square, and the neutral **BHA** ligand is coordinated by both hydroxylamino N atoms giving a five-membered metallacycle. The Pt(1)−N(1) 2.027(9) and Pt(1)−N(2) 2.027(9) Å bond lengths are equal within 3σ, and O(1)−N(1) 1.423(11) and O(2)−N(2) 1.436(11) Å are typical single O−N bonds.[29] The N(1)−Pt(1)−N(2) angle is 83.0(3)°, and this value agrees well with those previously observed in the related *N*,*N*-coordinated five-membered Pt-chelates of the type [PtCl$_2$L] (see above).

Synthesis and Characterization of {HO(H)$\underline{\text{N}}$−C$^\cap$C=$\underline{\text{N}}$OH}-Pt^{II}-Type Chelates. The (hydroxylamino$^\cap$oxime)Pt^{II} chelates [PtCl$_2$(OHA)] (R = Me **8**, Ph **9**) and [Pt(OHA-H)$_2$] (R = Me **10**, Ph **11**; Scheme 2), where **OHA** = HO(H)-NCMe$_2$C(R)=NOH, and **OHA-H** = $^-$O(H)NCMe$_2$C(R)=NOH (Figure 1), have previously been synthesized by treatment of K$_2$[PtCl$_4$] with HO(H)NCMe$_2$C(Me)=NOH (**3**) or HO(H)NCMe$_2$C(Ph)=NOH (**4**) in 1:1 (**Route 2A**, Scheme 2) or 1:4 (**Route 2B**, Scheme 2) molar ratios, correspondingly, in an ethanol/water solution, but the then obtained species **8**−**11** were characterized only by microanalysis and no other physicochemical data were presented.[32] For the preparation of **8**−**11** we have now employed a modification of a method described in ref 32, and our synthetic procedure is given in the Experimental Section. We also characterized complexes **8**−**11** by IR, and ^{1}H, ^{13}C, ^{195}Pt NMR spectroscopies.

The monitoring of the filtrate from reactions **2A** and **2B** (Scheme 2) using 2D ^{1}H,^{1}H-COSY, and^{1}H,^{13}C-HSQC NMR correlation experiments indicates that the low yields for the (hydroxylamino$^\cap$oxime)Pt^{II} chelates can be explained by, on one hand, the significant residual solubility of **8**−**11** and, on the other hand, the insufficient selectivity of the process, when the chelate is contaminated with the *bis*-chelate and *vice versa*.

In 6 M HCl solution, **8** partially (ca. 10% after 1 d) transforms to the previously unreported compound [Pt(OHA)$_2$][PtCl$_4$] (R = Me, **12**; via **Route 2C**), and then to [Pt(OHA-H)$_2$] (R = Me, **10**; via **Route 2D**) (ca. 5% after 2 d). Attempts to perform a similar conversion for **9** did not result in the formation of [Pt(OHA)$_2$][PtCl$_4$] (R = Ph) but affords a mixture of yet unidentified products. Evaporation of a 6 M HCl solution of **8** in air for 1 d produces **12** (orange-yellow crystals) in a mixture with unreacted **8** (dark-red crystals); **8** and **12** were mechanically separated.

In addition to the obtained satisfactory microanalyses, **8**−**12** were characterized by IR and 1D ^{1}H, ^{13}C{^{1}H}, ^{195}Pt, and 2D ^{1}H,^{1}H-COSY,^{1}H,^{13}C-HSQC NMR spectroscopies, and **15** also by X-ray diffraction. The IR spectra of **8**−**12** display a medium intensity band in the range 1599−1636 cm^{-1}, assigned to the ν(C=N) stretching vibrations of the coordinated oxime group C=NOH, and medium intensity bands in the range between 3066 and 3249 cm^{-1} due to the ν(N−H) and ν(O−H) stretches. Complexes **8**−**12** appear to be sufficiently stable in both DMSO-*d$_6$* and DMSO to permit NMR measurements; the low rate of solvolysis was proved by repeated measurements of the spectra in 95:5 (v/v) mixture of DMSO-*d$_6$*:DMSO; no signals from Pt-bound DMSO[33] were observed after 3 h of incubation at 25 °C. The ^{1}H NMR spectra of **8**−**12** in DMSO-*d$_6$* exhibit two broad singlets in the range between 9.8 and 13.3 ppm (from the O*H* protons of the hydroxylamine and oxime NOH group) and a resonance in the range of 9.0−9.6 ppm (from the NH hydroxylamine proton). The ^{13}C{^{1}H} spectra of **8**−**12** indicate the presence of peaks from the coordinated oxime C=N moiety; they emerge in the range of 154−168 ppm, which is usual for the C=N groups.[25] The ^{195}Pt NMR spectra of **8**−**12** in DMSO-*d$_6$* display one peak between −2020 and −2270 ppm in the typical range for Pt^{II} species.[26]

In the ^{195}Pt NMR spectrum of **12** measured in DMSO-*d$_6$*, one more signal from [PtCl$_4$]$^{2-}$ (−1640 ppm) was detected. One should mention that typically in *aqueous* DMSO solutions the Pt−Cl bond is subject to solvation giving (DMSO)Pt^{II} species.[22,33] However, we observed that in *anhydrous* DMSO-*d$_6$*, which is conventionally used for NMR measurements, the rate of substitution is low and during 3 h

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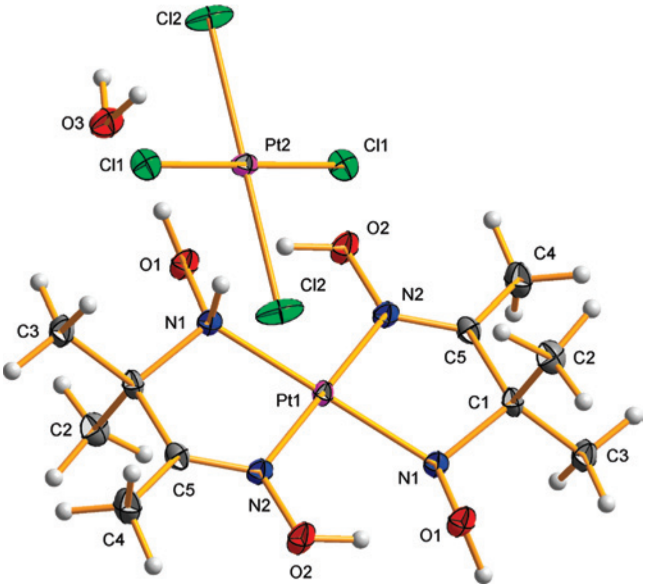

Figure 4. Thermal ellipsoid view of **12** with atomic numbering scheme (hydrogen labels are not shown for simplicity). Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(2) 1.992(2), Pt(1)−N(1) 2.025(2), Pt(2)−Cl(1) 2.3036(8), Pt(2)−Cl(2) 2.2956(8), O(1)−N(1) 1.438(3), O(2)−N(2) 1.376(3), N(2)−Pt(1)−N(1) 101.61(9), N(2)#1−Pt(1)−N(1) 78.39(9), Cl(2)−Pt(2)−Cl(1) 89.77(3). The symmetry transformation used to generate equivalent atom: #1 = $-x$, $-y$, $-z$.

at 20−25 °C only about 10% of $[PtCl_4]^{2-}$ converts to the known[22,33] $[PtCl_3(DMSO\text{-}d_6)]^-$ complex (−2980 ppm; obtained in this work).

In the X-ray structure of **12** (Figure 4), the coordination polyhedra of both metal centers are slightly distorted square planes. In the cation, two neutral ligands HO$\underline{\text{N}}$(H)-CMe$_2$C(Me)=$\underline{\text{N}}$OH are coordinated by the hydroxylamino and the oxime nitrogens thus forming two five-membered metallacycles with the hydroxylamino N atoms in the mutual *trans*-positions. The Pt(1)−N(2) 1.992(2) and Pt(1)−N(1) 2.025(2) Å bond lengths are normal, and O(1)−N(1) 1.438(3), O(2)−N(2) 1.376(3) Å are typical single O−N bonds.[29] The N(2)#1−Pt(1)−N(1) angle is 78.39(9)°, and this value agrees with those previously observed in related *N*,*N*-coordinated five-membered chelates of the type $[PtCl_2L]$, where L = bpy [79.1−83.1°],[34] phen [80.9−81.5°],[34] $H_2NCH_2CH_2NH_2$ [73.2−83.7°],[35] and $H_2NCH_2CH_2NMe_2$ [84.0°].[35] Inspection of the distances and angles between the oxime proton (H2O) of one of the chelating ligands and the hydroxylamine oxygen (O1) of the other one, clearly indicates the presence of two similar intramolecular hydrogen bonds between the two chelating species, stabilizing structure of **12**, with the following observed distances and angles: O(2)−H(2O) 0.95 Å, O(2)−H(2O)···O(1) 1.80 Å, and O(2)−H(2O)···O(1) 164.9°. Related intramolecular H-bondings were also observed in other *bis*-chelate complexes, namely, in [Pt{HO$\underline{\text{N}}$C(Me)C(Me)$\underline{\text{N}}$O}$_2$],[27] [Pd{HO$\underline{\text{N}}$(1,2-C$_6$H$_4$)$\underline{\text{N}}$=O}$_2$],[30] and [Ni{HO$\underline{\text{N}}$C(=O)C(=O)$\underline{\text{N}}$=O}$_2$].[31]

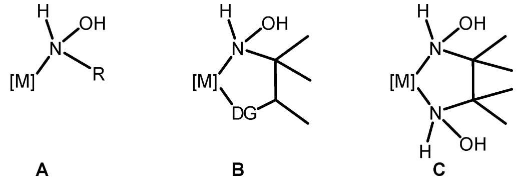

Figure 5. Types of metal complexes with alkylhydroxylamines. In **B**, DG denotes a donor group different from the N(H)OH.

Generation of the Dinitrosoalkane Ligand by Oxidation of (BHA)Pt^{II} Complexes. In general, oxidation of (HO$\underline{\text{N}}$H$_2$)Pt^{II} complexes can proceed at the metal, at the hydroxylamine ligand, or at both centers; some examples of oxidation of the unsubstituted NH_2OH ligands at Pt,[36] Mn,[37] and Re[38] centers to form nitrosyl, nitroxyl, or nitrogen oxides have been reported.[36–38] On the contrary, oxidation of *N*-bound alkylhydroxylamines RN(H)OH is substantially less studied.

The metal complexes having alkylhydroxylamine ligands can be divided into three categories (**A**−**C**, Figure 5). Group **A** is represented by compounds bearing monodentately *N*-bound RN(H)OH species. To our knowledge, no examples of intramolecular oxidation of RN(H)OH in complexes were reported, although a few cases of the oxidation of that species upon coordination to metal centers are known.[1] However, the nature of the oxidants in all these examples remains unknown. Group **B** exemplifies metal complexes with bidentate coordination of HO(H)N$^\cap$DG species (DG is a donor group which is different from the N(H)OH moiety, e.g., an oxime or amine functionality). The reported oxidations of type **B** compounds include the reaction of [PdCl$_2${HO(H)$\underline{\text{N}}$CMe$_2$C(R)=$\underline{\text{N}}$OH}] with 2,3,5,6-tetrachloro-*p*-benzoquinone that gives the nitrosoalkane compound [PdCl$_2${O=$\underline{\text{N}}$CMe$_2$C(R)=$\underline{\text{N}}$OH}] and the oxidation of [M{HO(H)$\underline{\text{N}}$CMe$_2$C(R)=$\underline{\text{N}}$OH}$_2$] (M = Pd, Ni) with the same reagent, which affords [M{$^\bullet$O$\underline{\text{N}}$CMe$_2$C(R)=$\underline{\text{N}}$OH}$_2$] with radical anion ligands.[39,40]

Group **C** is formally represented by metal complexes with the bidentate R{N(H)OH}$_2$ ligands, having two N(H)OH moieties. However, only one representative of Group **C**

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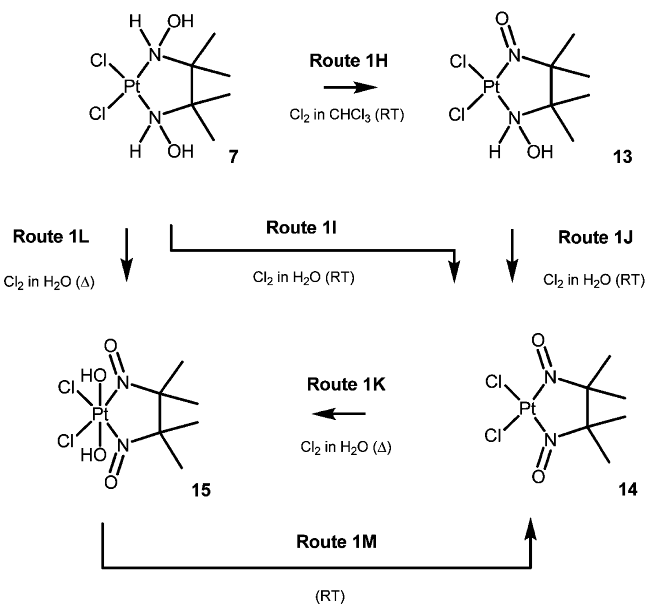
Scheme 3



complexes was so far described, that is, the nickel(II) *bis*-chelate [Ni^{II}Cl(BHA-H)(BHA)], which upon oxidation by PbO$_2$[20] gives [Ni^{II}{$^{\bullet}$O$\underline{\mathrm{N}}$CMe$_2$CMe$_2\underline{\mathrm{N}}$O}$_2$] as a product of the 2*e*-oxidation/deprotonation of the N(H)OH functionalities.[20]

In our experiments, the chlorination of the platinum(II) complex [PtCl$_2$(BHA)] (**7**) (Scheme 3) furnishes the nitrosoalkane ligands and shows a remarkable solvent dependence. Thus, in freshly distilled dry *chloroform*, a passage of dry Cl$_2$ leads to the oxidation of one N(H)OH group and yields the mononitrosoalkane complex [PtCl$_2${HO(H)$\underline{\mathrm{N}}$-CMe$_2$CMe$_2\underline{\mathrm{N}}$=O}] (**13**), where only one hydroxylamine moiety of the starting chelate was oxidized to the nitrosoalkane group (**Route 1H**). When the chlorination is performed in *water*, both N(H)OH functionalities of the starting complex are oxidized producing the dinitrosoalkane compound [PtCl$_2$(O=$\underline{\mathrm{N}}$CMe$_2$CMe$_2\underline{\mathrm{N}}$=O)] (**14**; **Route 1I**). Complex **14** can also be obtained from **13** upon its treatment with Cl$_2$ in water (**Route 1J**). The observed reactivity and solvent dependence is in good agreement with the fact that Cl$_2$ is a much stronger oxidant in highly polar aqueous media than in low-polar chloroform.[41] Hence, the usage of these two solvents, in the chlorination, allows the synthesis of two different nitrosoalkane products from the same starting material.

Furthermore, a prolonged (1 h) chlorination of **7** or **14** in water at 80−85 °C results in further oxidation, now of the Pt^{II} center, giving the platinum(IV) dihydroxo-dinitroso complex **15**. The latter compound is not stable in both solution and in the solid state and at room temperature (in the solid state 50% conversion occurred for 3 h, while in acetone-d_6 solution 95% conversion was observed already after ca. 5 min) undergoes reductive elimination along with some side-reactions yielding a mixture of **14** with yet unidentified products.

One should mention that although nitrosoalkane complexes of various metal centers are known,[3,4] reported (nitrosoalkane)Pt species are still quite rare. Their examples are limited exclusively to (i) the platinum(0) complexes [Pt(^{t}Bu$\underline{\mathrm{N}}$=O)$_2$(Ph$_3$P)$_2$], [Pt(CF$_3\underline{\mathrm{N}}$=O)(PPh$_3$)$_2$], and [Pt(Ph$\underline{\mathrm{N}}$=O)(PPh$_3$)$_2$] obtained via the reaction of the preprepared nitrosoalkanes with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] or [Pt(PPh$_3$)$_3$], correspondingly,[42] (ii) the platinum(II) complexes [PtCl$_2$(Me$\underline{\mathrm{N}}$=O)(bpy)],[43] [PtCl$_2$(^{t}Bu$\underline{\mathrm{N}}$=O)L] (L = various *N*-donor ligands),[43] and [PtCl$_2$(R$\underline{\mathrm{N}}$=O)$_2$] (R = ^{t}Bu, Ph),[44] obtained by substitution of chlorides in [PtCl$_4$]$^{2-}$ with the appropriate free nitrosoalkane,[43,44] and (iii) the chelates [PtX$_2$(O=$\underline{\mathrm{N}}$CRR′$_2$O$\underline{\mathrm{N}}$CRR′$_2$)] (X = Cl, Br; R/R′ = alkyls) generated via redox coupling of coordinated oximes and described by one of us.[8,9]

Liberation of the Ligand from the Dinitrosoalkane Complex. Treatment of **14** with 2 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) in CH$_2$Cl$_2$ at room temperature results in the formation of **20** (IUPAC name:[21] 3,3,4,4-tetramethyl-1,2-diazete-1,2-dioxide) in about 90% yield and the precipitation of the known *trans*-[Pt(dppe)$_2$](Cl)$_2$,[45] identified by ^{31}P NMR spectroscopy (Scheme 4, **Route 1M**). Compound **20** is generated from the liberated dinitrosoalkane O=NCMe$_2$CMe$_2$N=O upon cyclization giving the new N=N bond. The known alternative preparation of **20** includes the mild metal-free oxidation of free bis-hydroxylamine species **1** by bromine in aqueous solution (**Route 1N**).[46]

The results of these experiments clearly indicate that (i) the Pt^{II} center provides a stabilizing effect on the elusive dinitrosoalkane species; (ii) the dinitroso ligand shows a dramatic stabilizing effect by the metal center in a low oxidation state (Pt^{II} vs Pt^{IV}) probably because of the π-acceptor ability of the former.

Characterization of the Nitroso and Dinitrosoalkane Complexes Derived from the Oxidation of (BHA)Pt^{II} Complexes. The formulation of complexes **13** and **14** was supported by satisfactory C, H, and N microanalyses. These species were also characterized by IR and 1D ^{1}H, ^{13}C{^{1}H}, ^{195}Pt, and 2D ^{1}H,^{1}H-COSY,^{1}H,^{13}C-HSQC NMR spectroscopies, and X-ray diffraction while complex **15** was identified based on IR and ^{1}H NMR data.

The IR spectra of **13**−**15** display one very strong band each at 1525−1540 cm^{-1} due to the ν(N=O) from the nitroso group of the newly formed nitrosoalkane ligands. Moreover,

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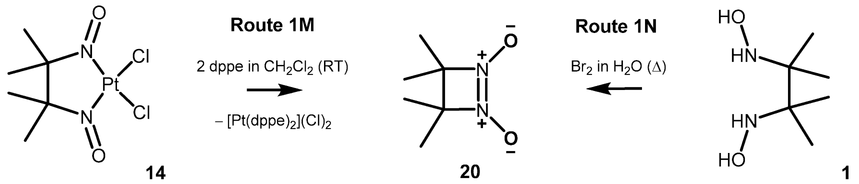
Scheme 4



compound **13** exhibits two strong bands in the 3220−2990 cm^{-1} range due to the ν(N−H) and ν(O−H) stretching vibrations of the hydroxylamine moieties.

The ^1H NMR spectrum of **13** in DMSO-d_6 displays two broad singlets from the NH and OH protons of the hydroxylamine N(H)OH moieties resonating at 7.6 and 10.3 ppm, correspondingly. In the $^{13}C\{^1H\}$ NMR spectra of **13** and **14** in DMSO-d_6, the CN carbons resonate at about 80 and 110 ppm, within the expected[25] range. The ^{195}Pt NMR spectra of **13** and **14** in DMSO-d_6 display one signal at about −2000 ppm, characteristic of Pt^{II} species.[26]

The structures of the nitroso complexes **13** and **14** have been determined by X-ray diffraction (Figures 6 and 7). We also determined the X-ray structure of **10** but the crystals were of insufficient quality probably because of the decomposition of this Pt^{IV} complex.

Complex **13** provides the first crystallographic evidence for a metal complex with the newly formed hybrid nitroso-hydroxylamino $O{=}NCMe_2CMe_2N(H)OH$ ligand. In **13**, the coordination polyhedron of the metal center is a slightly distorted square, while the bidentate $O{=}NCMe_2CMe_2N(H)OH$ ligand is coordinated by both hydroxylamino and nitroso nitrogens, forming a five-membered chelate ring similar to those observed in related Pt-chelates of the type $[PtCl_2(NN)]$.[34,35] In the ligand, the O(1)−N(1) (1.407(4) Å) bond length has a typical value for a single O−N bond while the measured O(2)−N(2) distance of the nitroso fragment is 1.207(3) Å. The latter value is normal for a O═N double bond, and agrees with those for the relevant Pt-nitrosoalkane complexes, that is, *trans*-$[PtCl_2({}^tBu\underline{N}{=}O)_2]$ (1.21(1) Å),[44] and $[PtCl_2(R_2C\underline{N}OR_2C\underline{N}{=}O)]$ (R = Me, C_5H_{10}) (1.21−1.24 Å).[8,9]

Complex **14**, as the others, shows a slightly distorted square coordination, with the bidentate dinitroso $O{=}\underline{N}CMe_2CMe_2\underline{N}{=}O$ ligand coordinated by both N-atoms, forming a five-membered chelating ring [N(1)Pt(1)−N(2) 82.7(3)°], similar to those observed in the two related metal dinitrosoalkane complexes.[5,6] The measured N═O bond distances at the nitroso fragments are equal within 3σ [O(1)−N(1) 1.205(8); O(2)−N(2) 1.202(8) Å] and these values agree with those for the Pt-nitrosoalkane complexes *trans*-$[PtCl_2({}^tBu\underline{N}{=}O)_2]$ (1.21(1) Å),[44] and $[PtCl_2(R_2C\underline{N}OR_2C\underline{N}{=}O)]$ (R = Me, C_5H_{10}) (1.21−1.24 Å).[8,9]

Generation of Nitrosoalkane Ligands by Oxidation of (OHA)Pt^{II} Complexes. We found that the complexes $[PtCl_2\{HO(H)\underline{N}C(Me)_2C(R){=}\underline{N}OH\}]$ (**8**, **9**) upon treatment with Cl_2 in $CHCl_3$ were easily oxidized to the nitrosoalkane compounds $[PtCl_2\{O{=}\underline{N}CMe_2C(R){=}\underline{N}OH\}]$ (R = Me **16**, Ph **17**) (Scheme 5, **Route 2E**), respectively, while the corresponding chlorination of the *bis*-chelates $[Pt\{HO(H)\underline{N}CMe_2C(R){=}\underline{N}O\}_2]$ (**10**, **11**) gives $[Pt\{O{=}\underline{N}CMe_2C(R){=}NO\}_2]$ (R = Me **18**, Ph **19**).

In case of **8**, the oxidation to **16** can also be performed using 30% aqueous H_2O_2 taken in a 10-fold excess while **9** is more stable toward oxidation than **8** and under similar conditions remains intact. In compounds **16**−**19**, the nitrosoalkane group originates from the 2*e*-oxidation of the hydroxylamino group HO(H)N. It is worthwhile mentioning that despite the oxidative deoximation of "HON═C"-type ligands is well-known,[8,9] the Pt^{II} center provides such a strong protection of the oxime group of the **OHA** ligands that it stays unreacted under the drastic reaction conditions.

It is worth mentioning that physicochemical data provided in the next section support the dinitroso structure of **18** and

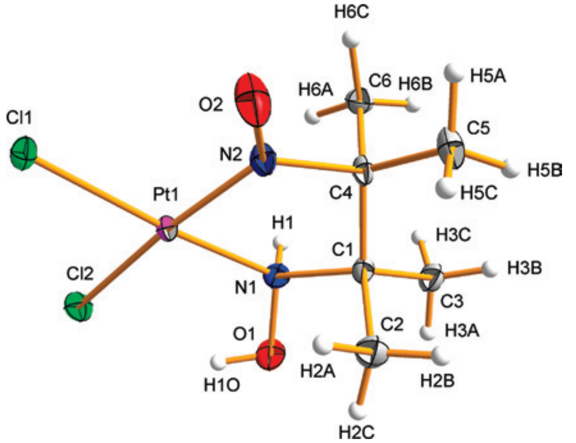


Figure 6. Thermal ellipsoid view of **13** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.033(3), Pt(1)−N(2) 1.924(3), Pt(1)−Cl(1) 2.2965(8), Pt(1)−Cl(2) 2.2953(8), O(1)−N(1) 1.407(4), O(2)−N(2) 1.207(3), N(1)−Pt(1)−N(2) 83.00(11).

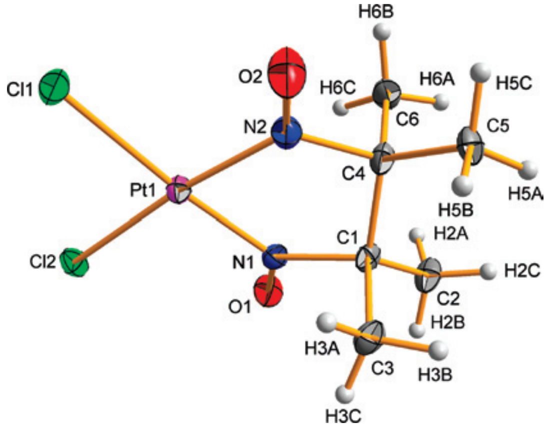
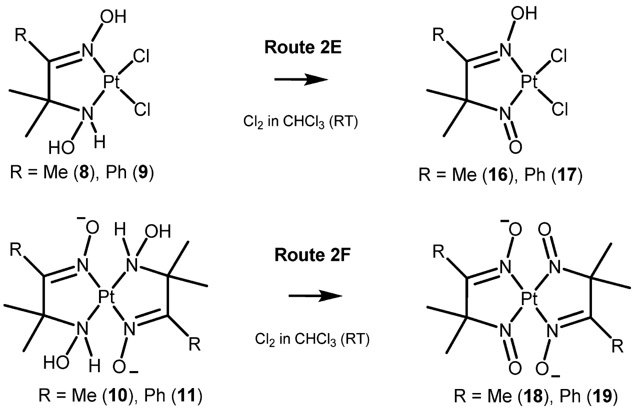


Figure 7. Thermal ellipsoid view of **14** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 1.944(6), Pt(1)−N(2) 1.946(7), Pt(1)−Cl(1) 2.2859(18), Pt(1)−Cl(2) 2.2817(18), O(1)−N(1) 1.205(8), O(2)−N(2) 1.202(8), N(1)−Pt(1)−N(2) 82.7(3).

Scheme 5



19. However, the radical ion structure [Pt{$^{\bullet}$O$\underline{N}$C-$Me_2C(R){=}NOH$}$_2$], which is similar to the previously reported radical ions [M{$^{\bullet}ONCMe_2C(R){=}NO$}$_2$] (M = Pd,[39] Ni[40]), cannot be ruled out. However, to distinguish between the nitroso and the radical structures of **18** and **19** further data, for example, X-ray structure determinations, would be needed to obtain quantitative information on the NO bond orders in N=O vs •N−O groups.

Characterization of the Nitrosoalkane Complexes Derived from the Oxidation of (OHA)Pt^{II} Complexes. The formulation of all complexes **16**−**19** was supported by satisfactory C, H, and N microanalyses. They were also characterized by IR and 1D ^{1}H, ^{13}C{^{1}H}, ^{195}Pt, and 2D ^{1}H,^{1}H-COSY,^{1}H,^{13}C-HSQC NMR spectroscopies. Compound **16** was recently synthesized by us via a different route[10] and the authenticity of our samples with those described previously[10] was confirmed by elemental analyses, IR, and X-ray single-crystal study.

The IR spectra of **16**−**19** display medium intensity bands in the range 1599−1636 cm^{-1} assigned to ν(C=N) stretching vibrations of the coordinated oxime group. The absence of the ν(O−H) stretches of the hydroxylamine moieties is logical for the deprotonated oxime group. The very strong band at 1547−1557 cm^{-1} is assigned to the ν(N=O) of the newly formed nitroso ligands.

The ^{1}H NMR spectra of **16** and **17** in DMSO-d_6 show one broad singlet at about 12.0 ppm (from the NOH protons of the oxime group). The ^{13}C{^{1}H} NMR spectra of **16**−**19** in DMSO-d_6 display the signal from the coordinated oxime C=N moiety at about 170 ppm, which is typical for a C=N groups.[25] The ^{195}Pt NMR spectra of **16**−**19** in DMSO-d_6 exhibit one resonance in the normal range for Pt^{II} species.[26]

Final Remarks

We report here on a novel synthetic route to the almost unexplored dinitrosoalkane species, which consists on the oxidation of the easy-to-obtain platinum complexes with the *bis*-hydroxylamine ligand. Chlorine appears to be a suitable oxidizing agent, and the extent of oxidation can be controlled by a proper choice of solvent. In fact, the chlorination of (*bis*-hydroxylamine)Pt^{II} complex shows a remarkable solvent dependence and produces, in freshly distilled dry *chloroform*, a Pt-mononitrosoalkane complex in which only one hydroxylamine group has been selectively oxidized to the nitroso functionality (Scheme 3). However, the corresponding process in *water* results in the oxidation of both hydroxylamino moieties and affords a (dinitrosoalkane)Pt complex (Scheme 3).

The liberation of the ligated dinitrosoalkane can be achieved by treatment of the complex with a diphosphine (dppe), and the free dinitroso compound is unstable and undergoes a fast cyclization giving the cyclic α-dinitrone 3,3,4,4-tetramethyl-1,2-diazete-1,2-dioxide (Scheme 4). The oxidation of (hydroxylamino$^\cap$oxime)Pt^{II} complexes occurs selectively at the hydroxylamino group affording a series of (nitroso$^\cap$oxime)Pt^{II} species, where the oxime group remains intact (Scheme 5). Further studies directed toward widening the family of metal dinitrosoalkanes by oxidation of *bis*-hydroxylamino ligands bound to various metal centers are underway in our group.

Experimental Section

Materials and Instrumentation. The compounds K[$PtCl_3$-($Me_2\underline{S}O$)],[22] *cis*-[$PtCl_2(Me_2\underline{S}O)_2$],[22] **1**,[14] **2**,[14] and **3**·$MeCO_2H$,[47] and **4**[47] were synthesized in accord with the published procedures. Solvents were obtained from commercial sources and used as received while chloroform was dried using standard methods.[41] C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. IR spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D (^{1}H, ^{13}C{^{1}H}, ^{195}Pt) NMR experiments and 2D (^{1}H,^{1}H-COSY, and^{1}H,^{13}C-HSQC) NMR correlation spectra were recorded on Bruker Avance II+ 300 and 400 MHz (UltraShield Magnet) and Varian UNITY 300 spectrometers at ambient temperature. ^{195}Pt NMR chemical shifts are given relatively to $K_2[PtCl_6]$ (0.0 ppm); half-width is given in parentheses.

X-ray Structure Determinations. The crystals were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 120 K. The X-ray diffraction data were collected by means of a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The Denzo-Scalepack[48] or EvalCCD[49] program packages were used for cell refinements and data reductions. All of the structures were solved by direct methods using the SHELXS-97,[50] SIR97,[51] SIR2002,[52] or SIR2004,[53] with the WinGX[54] graphical user interface. An empirical absorption correction was

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Table 1. Crystal Data

	5	**7**	**12**	**13**	**14**
empirical formula	$C_{12}H_{36}Cl_4N_4O_6Pt_2$	$C_6H_{16}Cl_2N_2O_2Pt$	$C_{10}H_{28}Cl_4N_4O_6Pt_2$	$C_6H_{14}Cl_2N_2O_2Pt$	$C_6H_{12}Cl_2N_2O_2Pt$
fw	864.43	414.20	832.34	412.18	410.17
temp (K)	120(2)	120(2)	120(2)	120(2)	120(2)
λ(Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	16.1477(10)	9.3515(9)	7.3585(5)	9.3692(8)	12.3005(3)
b (Å)	13.0342(9)	8.9988(9)	8.5897(5)	17.694(2)	16.7021(6)
c (Å)	11.6516(6)	13.9799(13)	9.6385(4)	13.4721(16)	10.8385(4)
α (deg)	90	90	104.471(4)	90	90
β (deg)	107.967(4)	106.604(5)	104.070(5)	99.641(8)	94.883(2)
γ (deg)	90	90	98.437(5)	90	90
V (Å^3)	2332.7(2)	1127.4(2)	558.06(6)	2201.8(4)	2218.63(13)
Z	4	4	1	8	8
ρ_{calc} (Mg/m^3)	2.461	2.440	2.477	2.487	2.456
μ(Mo Kα) (mm^{-1})	12.474	12.893	13.030	13.203	13.102
no. reflns.	7365	11285	10323	30127	39701
Unique reflns.	2679	2431	2812	5018	4362
$R_{int.}$	0.0220	0.0751	0.0285	0.0344	0.0544
R1^a ($I \geq 2\sigma$)	0.0270	0.0434	0.0167	0.0194	0.0299
wR2^b ($I \geq 2\sigma$)	0.0608	0.1087	0.0374	0.0304	0.0576

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

applied to all of the data (SADABS,[55] XPREP in SHELXTL[56]). Structural refinements were carried out using SHELXL-97.[57] The OH, H_2O hydrogen atoms, and NH hydrogens (except NH atoms in **7** and **12**) were located from the difference Fourier map but not refined. The coordinates were either fixed or the hydrogen atoms were constrained to ride on their parent atom with $U_{iso} = 1.5U_{eq}$ (parent atom). All other hydrogen atoms (including the NH hydrogen atom in **7** and **12**) were positioned geometrically and constrained to ride on their parent atoms, with C−H = 0.98 Å, NH = 0.93 Å, and $U_{iso} = 1.5U_{eq}$ (parent atom). The crystallographic details are summarized in Table 1. Selected bond lengths and angles are given in figure captions.

Synthetic Work. $[Pt\{HO(H)\underline{N}CMe_2CMe_2\underline{N}(H)OH\}_2][PtCl_4]\cdot H_2O$ (5). A solution of **2** (0.049 g, 0.2 mmol) in water (1 mL) was added to a solution of $K_2[PtCl_4]$ (0.042 g, 0.1 mmol) in water (5 mL). The reaction mixture was heated at 80 °C for about 1 d and then left to stand in air for 5 d at 20−25 °C. During this time the solvent was evaporated to about $^1/_2$, followed by a precipitation of a mixture of **5** (red crystals suitable for X-ray diffraction) and a colorless solid. The crystals of **5** were mechanically separated from the mixture, washed with two 5 mL portions of cold (10 °C) water and dried in air at 20−25 °C. Monitoring of the colorless residue and the filtrate by IR and NMR allows the identification of **5**−**7** in a mixture with KCl; these components were not separated because of their similar and high water solubilities. Yield of **5** is 0.039 g, 37%, based on Pt. Anal. Calcd for $C_{12}H_{34}N_4Cl_4O_5Pt_2$: C, 17.03; H, 4.05; N, 6.62%. Found: C, 17.21; H, 3.70; N, 6.50%. IR spectrum (selected bands), cm^{-1}: 3230 and 2995 mw ν(O−H) and ν(N−H). ^{1}H NMR (D_2O, δ): 1.25 (m, 12H, $NCMe_2$). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 17.6, 19.5 (Me), 72.0 (CMe_2). ^{195}Pt NMR (D_2O, δ): −1713 (120 Hz; $[PtCl_4]^{2-}$) and −2464 (380 Hz; $[Pt(BHA)_2]^{2+}$). Crystals suitable for X-ray study were obtained directly from the reaction mixture.

$[PtCl_2\{HO(H)\underline{N}CMe_2CMe_2\underline{N}(H)OH\}]$ (7). The solutions of **2** (0.049 g, 0.2 mmol) in water (1 mL) and $K[PtCl_3(Me_2\underline{S}O)]$ (0.084 g, 0.1 mmol) in water (1 mL) were mixed and left to stand in a closed vial at room temperature for 1d. The released pale yellow crystals were separated by filtration and washed with two 5 mL portions of cold (10 °C) water and dried in air at room temperature. An additional amount of **7** (0.010 g) can be obtained by evaporation of the filtrate in air up to about $^1/_4$ of the initial volume. The total yield is 0.038 g, 45%. Anal. Calcd for $C_6H_{16}N_2Cl_2O_2Pt$: C, 17.40; H, 3.89; N, 6.76%. Found: C, 17.30; H, 3.92; N, 6.70%. IR spectrum (selected bands), cm^{-1}: 3228 mw ν(O−H), 2918 m ν(N−H). ^{1}H NMR (DMSO-d_6, δ): 1.16, 1.23, 1.25, 1.27 (s, 12H, $NCMe_2$), 7.66 (s, br, 2H, NHO*H*), 9.45 (s, br, 2H, N*H*OH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 22.5, 22.7, 23.8, 24.5 (Me), 77.0 (CMe_2). ^{195}Pt NMR (DMSO-d_6, δ): −2492 (340 Hz).

Reaction of 1 equiv Hydroxylamino$^\cap$oximes ($3\cdot MeCO_2H$ and 4) with $K_2[PtCl_4]$. A suspension of hydroxylamino$^\cap$oximes $3\cdot MeCO_2H$ or **4** (0.96 mmol) in 40% (v/v) ethanol−water solution (1.5 mL) was added to a solution of $K_2[PtCl_4]$ (0.40 g, 0.96 mmol) in water (2 mL), and the reaction mixture was stirred at 80 °C for about 30 min resulting in the release of a pale-beige precipitate. Then, aqueous HCl (6 M, 1.6 mL) was added to the reaction mixture, and the latter was evaporated to about $^1/_2$ of the initial volume. The precipitate formed was filtered off, and washed with one 5 mL portion of water, one 1.5 mL portion of EtOH, and two 2 mL portions of Et_2O. Yields are 100 mg, 25% (R = Me **8**); 120 mg, 26% (R = Ph **9**). In the case of **3**, when the reaction mixture after addition of HCl was left to stand for 1 d, a mixture of dark-red (**8**) and orange-yellow (**12**) crystals was formed and filtered off. Crystals of two types were mechanically separated, and they were characterized by IR, ^{1}H NMR spectroscopies, and X-ray diffraction.

$[PtCl_2\{HO(H)\underline{N}CMe_2C(Me){=}\underline{N}OH\}]$ (8). Anal. Calcd for $C_5H_{12}N_2Cl_2O_2Pt$: C, 15.08; H, 3.04; N, 7.04%. Found: C, 15.02; H, 3.28; N, 6.59%. IR (KBr, selected bands, cm^{-1}): 3199 w and 3090 mw ν(N−H and/or O−H); 1621 m ν(C=N). ^{1}H NMR (DMSO-d_6, δ): 10.45 and 9.88 (s, br, 2H, NOH and NHO*H*), 9.45 (s, br, 1H, NH), 1.84 (s, 3H), 1.53 (s, 3H), 1.39 (s, 3H) (Me). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 159.1 (C=N), 72.3 (CMe_2), 24.4, 21.1, 12.1 (Me). ^{195}Pt NMR (DMSO-d_6, δ): −2267 (420 Hz).

$[Pt\{HO(H)\underline{N}CMe_2C(Me){=}\underline{N}OH\}_2][PtCl_4]$ (12). IR (KBr, selected bands, cm^{-1}): 3227 mw and 3087 ms ν(N−H and/or O−H); 2969 w and 2929 w ν(C−H from CH_3); 1623 mw ν(*C*=N). ^{1}H NMR (DMSO-d_6, δ): 10.48 and 9.92 (s, br, 2H, NOH and NHO*H*), 9.52 (s, br, 1H, NH), 1.78 (s, 6H), 1.53 (s, 6H), 1.40 (s, 6H) (Me).

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^{13}C{^{1}H} NMR (DMSO-d_6, δ): 165.1 (C=N), 74.9 (*C*Me$_2$), 22.4, 20.5, 13.1 (Me). ^{195}Pt NMR (DMSO-d_6, δ): −2110 (220 Hz) and −1641(150 Hz).

[PtCl$_2${HO(H)$\underline{\mathrm{N}}$CMe$_2$C(Ph)=$\underline{\mathrm{N}}$OH}]·1/2H$_2$O (9). Anal. Calcd for $C_{10}H_{15}N_2Cl_2O_{2.5}Pt$: C, 25.60; H, 3.22; N, 5.97%. Found: C, 25.02; H, 3.15; N, 6.12%. IR (KBr, selected bands, cm^{-1}): 3249 mw ν(N−H and/or O−H); 3111 mw ν(N−H and/or O−H and/or C−H from Ph); 2989 w, 2937 w and 2816 w ν(C−H from CH$_3$); 750 and 705 s δ(C−H from Ph). ^{1}H NMR (DMSO-d_6, δ): 10.53 (s, br, 1H, NOH) and 10.00 (s, br, 1H, NHO*H*), 9.55 (s, br, 1H, NH), 7.52−7.48 (m, 3H), 7.36−7.34 (s, 2H) (Ph's), 1.79 (s, 3H), 1.19 (s, 3H) (Me). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 167.8 (C=N), 130.7, 130.3, 128.9, 128.7, 128,5, 127.7, 127.1 (carbons in Ph), 77.6 (*C*Me$_2$), 24.7, 21.3 (Me).^{195}Pt NMR (DMSO-d_6, δ): −2269 (520 Hz).

Reaction of 4 equiv Hydroxylamino∩oximes (3·MeCO$_2$H and 4) with K$_2$[PtCl$_4$]. A suspension of the hydroxylamino∩oxime **3**·MeCO$_2$H or **4** (2.89 mmol) in 40% ethanol−water mixture (3 mL) was added to a solution of K$_2$[PtCl$_4$] (0.30 g, 0.72 mmol) in water (2 mL) and then heated (80 °C) with stirring for 1.5 h. The pink precipitate released was separated by filtration, washed with two 5 mL portions of water, one 2 mL portion of EtOH, and two 2 mL portions of Et$_2$O. Yields are 175 mg, 53% (R = Me **10**); 210 mg, 50% (R = Ph **11**).

[Pt{HO(H)$\underline{\mathrm{N}}$CMe$_2$C(Me)=$\underline{\mathrm{NO}}$}$_2$] (10). Anal. Calcd for $C_{10}H_{22}N_4O_4Pt$: C, 26.26; H, 4.85; N, 12.25%. Found: C, 25.98; H, 4.80; N, 12.01%. IR (KBr, selected bands, cm^{-1}): 3242 w and 3066 mw ν(N−H and/or O−H); 2979 w, 2919 w, and 2827 mw ν(C−H from CH$_3$); 1632 m ν(*C*=N). ^{1}H NMR (DMSO-d_6, δ): 13.23 (s, br, 2H, NHO*H*), 9.04 (s, 2H, NH), 1.77 (s, 6H), 1.50 (s, 6H), 1.36 (s, 6H) (Me). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 154.1 (C=N), 73.0 (*C*Me$_2$), 24.4, 21.1, 10.5 (Me). ^{195}Pt NMR (DMSO-d_6, δ): −2022 (140 Hz).

[Pt{HO(H)$\underline{\mathrm{N}}$CMe$_2$C(Ph)=$\underline{\mathrm{NO}}$}$_2$] (11). Anal. Calcd for $C_{20}H_{26}N_4O_4Pt$: C, 41.31; H, 4.51; N, 9.64%. Found: C, 41.61; H, 4.52; N, 9.70%. IR spectrum (selected bands), cm^{-1}: 3130 mw ν(N−H and/or O−H); 3054 w ν(C−H from Ph); 2986 mw, 2934 w, 2865 w and 2822 mw ν(C−H from CH$_3$); 1636 m ν(C=N and/or C=C from Ph); 750 and 700 s δ(C−H from Ph). ^{1}H NMR (DMSO-d_6, δ): 13.09 (s, br, 2H, NHO*H*), 9.39 (s, 2H, NH), 7.45−7.38 (m, 6H), 7.34 (d, 2H), 7.32 (t, 2H) (Ph's), 1.81 (s, 6H), 1.21 (s, 6H) (Me). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 158.8 (C=N), 132.2, 129.0, 128.7 (carbons from Ph), 73.6 (*C*Me$_2$), 26.16, 22.67 (Me).^{195}Pt NMR (DMSO-d_6, δ): −2028 (280 Hz).

Generation of Nitrosoalkane and Dinitrosoalkane Species upon Treatment of 7 with Excess Cl$_2$. [PtCl$_2${HO(H)-$\underline{\mathrm{N}}$CMe$_2$CMe$_2$$\underline{\mathrm{NO}}$}] (13). Gaseous Cl$_2$ was passed through a suspension of **7** (0.041 g, 0.1 mmol) in CHCl$_3$ (10 mL) for 5 min. During the chlorination the color of the precipitate changed from pale yellow to dark red. The obtained red crystalline solid was filtered off, washed with two 5 mL portions of CHCl$_3$, and dried in air at room temperature. Yield is 0.033 g, 80%. Anal. Calcd for $C_6H_{14}N_2Cl_2O_2Pt$: C, 17.48; H, 3.42; N, 6.80%. Found: C, 17.56; H, 3.67; N, 6.62%. IR spectrum (selected bands), cm^{-1}: 3238 mw ν(O−H), 1527 vs ν(N=O). ^{1}H NMR (DMSO-d_6, δ): 10.28 (s, br, 1H, N*H*OH), 7.55 (s, br, 1H, N*H*OH), 1.68, 1.77 (s, 12H, NCMe$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 22.5, 22.7, 23.8, 24.5 (Me), 80.2 and 102.8 (*C*Me$_2$). ^{195}Pt NMR (DMSO-d_6, δ): −2003 (420 Hz).

[PtCl$_2${O$\underline{\mathrm{N}}$CMe$_2$CMe$_2$$\underline{\mathrm{NO}}$}] (14). Gaseous Cl$_2$ was passed through a suspension of **7** or **13** (0.1 mmol) in water (10 mL) for 30 or 15 min, respectively. In both cases, the released red compound was filtered off, washed with two 5 mL portions of CHCl$_3$, and dried in air. Yield is 0.034 g, 83% (for **7**) or 0.032 g, 79% (for **13**), correspondingly. Anal. Calcd for $C_6H_{12}N_2Cl_2O_2Pt$: C, 17.57; H, 2.95; N, 6.83%. Found: C, 17.34; H, 2.90; N, 6.91%. IR spectrum (selected bands), cm^{-1}: 3216 mw ν(O−H), 1538 vs ν(N=O). ^{1}H NMR (DMSO-d_6, δ): 1.39 (s, 12H, NCMe$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 107.7 (*C*Me$_2$), 21.6 (Me). ^{195}Pt NMR (DMSO-d_6, δ): −2008 (360 Hz).

Further Conversions of 8−11 upon Treatment with Excess Cl$_2$. A suspension of any of the complexes **8**−**11** (0.07 mmol) in CHCl$_3$ (9 mL) was chlorinated by a slow passage of dry Cl$_2$ through the reaction mixture for about 5 min. In the case of **8** and **9**, the starting bright-orange suspension gave a dark-red solution, which upon evaporation of the solvent gave a dark-crimson solid residue of **16** and **17**, correspondingly. The treatment of **10** with Cl$_2$ leads to the formation of a crimson precipitate of **18** during the chlorination while in the case of **11** the color of the released precipitate **19** is brown-beige. All the obtained products were filtered off, washed with two 3 mL portions of CHCl$_3$ and dried at 20−25 °C under vacuum. Yields are 16 mg, 59% (**16**); 6 mg, 18% (**17**); 31 mg, 96% (**18**); 26 mg, 65% (**19**).

[PtCl$_2${O=$\underline{\mathrm{N}}$CMe$_2$C(Me)=$\underline{\mathrm{N}}$OH}] (16). Anal. Calcd for $C_5H_{10}N_2Cl_2O_2Pt$: C, 15.16; H, 2.54; N, 7.07%. Found: C, 15.00; H, 2.44; N, 7.20%. IR (KBr, selected bands, cm^{-1}): 3210 mw ν(O−H); 2999 w, 2932 w and 2860 w ν(C−H from CH$_3$); 1637 w ν(C=N); 1555 vs ν(N=O). ^{1}H NMR (DMSO-d_6, δ): 12.12 (s, br, 1H, NOH), 2.04 (s, 3H, Me), 1.49 (s, 6H, CMe$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 167.8 (C=N), 107.8 (*C*Me$_2$), 21.3, 13.4 (Me). ^{195}Pt NMR (DMSO-d_6, δ): −2118 (190 Hz).

[PtCl$_2${O=$\underline{\mathrm{N}}$Me$_2$C(Ph)=$\underline{\mathrm{N}}$OH}] (17). Anal. Calcd for $C_{10}H_{12}N_2Cl_2O_2Pt$: C, 26.21; H, 2.64; N, 6.11%. Found: C, 26.15; H, 2.52; N, 6.00%. IR (KBr, selected bands, cm^{-1}): 3233 w ν(O−H); 3059 w ν(C−H from Ph); 2994 mw, 2936 w and 2864 w ν(C−H from CH$_3$); 1599 ms ν(C=N and/or C=C from Ph); 1544 vs ν(N=O); 755 and 715 s δ(C−H from Ph). ^{1}H NMR (DMSO-d_6, δ): 12.04 (s, br, 1H, NOH), 7.60–7.57 (m, 3H), 7.53−7.51 (m, 2H) (Ph's), 1.47 (Me). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 130.7, 128.9, 127.4 (carbons from Ph), 108.9 (*C*Me$_2$), 22.8 (Me). ^{195}Pt NMR (DMSO-d_6, δ): −2018 (200 Hz).

[Pt{O=$\underline{\mathrm{N}}$CMe$_2$C(Me)$\underline{\mathrm{NO}}$}$_2$] (18). Anal. Calcd for $C_{10}H_{18}N_4O_4Pt$: C, 26.49; H, 4.00; N, 12.36%. Found: C, 25.92; H, 4.02; N, 12.32%. IR (KBr, selected bands, cm^{-1}): 2996 w, 2937 w and 2863 (w), ν(C−H from CH$_3$); 1624 m ν(*C*=N); 1557 vs ν(N=O). ^{1}H NMR (DMSO-d_6, δ): 2.30 (s, 6H, Me), 1.48 (s, 12H, CMe$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 169.2 (C=N), 108.9 (*C*Me$_2$), 22.0, 13.0 (Me). ^{195}Pt NMR (DMSO-d_6, δ): −2436 (190 Hz).

[Pt{O=$\underline{\mathrm{N}}$CMe$_2$C(Ph)$\underline{\mathrm{NO}}$}$_2$] (19). Anal. Calcd for $C_{20}H_{22}N_4O_4Pt$: C, 41.60; H, 3.84; N, 9.70%. Found: C, 40.52; H, 3.62; N, 8.98%. IR (KBr, selected bands, cm^{-1}): 3065 w ν(C−H from Ph); 2979 mw, 2930 w and 2869 w ν(C−H from CH$_3$); 1638 w ν(C=N and/or C=C from Ph); 1553 vs ν(N=O); 754 and 714 s δ(C−H from Ph). ^{1}H NMR (DMSO-d_6, δ): 7.59−7.57 (m, 5H), 7.53−7.50 (m, 5H) (Ph's), 1.46 (s, 12*H*, Me). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 131.1, 129.3, 128.2, 127.8 (carbons from Ph), 109.3 (*C*Me$_2$), 23.2 (Me). ^{195}Pt NMR (DMSO-d_6, δ): −2409 (220 Hz).

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