

Unusual Reactivity Mode of Coordinated Oximes: Platinum(IV)-Assisted Ring Closure by Reaction with Acetone

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The platinum(II) complexes *trans*-[PtCl₂(RR'C=NOH)₂], where R = R' = Me, RR' = (CH₂)₄ and (CH₂)₅, react with *m*-chloroperoxybenzoic acid in Me₂CO to give the platinum(IV) complexes [PtCl₂(OCMe₂ON=CRR')₂] in 50–60% yields. The complexes [PtCl₂(OCMe₂ON=CRR')₂] were characterized by elemental analysis, EI-MS, and IR and Raman spectroscopies; X-ray structure analyses were performed for both *trans*-[PtCl₂(OCMe₂ON=CC₄H₈)₂] and *trans*-[PtCl₂(OCMe₂ON=CC₅H₁₀)₂]. The former compound crystallizes in the triclinic space group P1 with *a* = 8.088(2) Å, *b* = 8.327(2) Å, *c* = 8.475(2) Å, α = 103.54(3)°, β = 102.15(3)°, γ = 108.37(3)°, *V* = 501.0(2) Å³, *Z* = 1, and ρ_{calcd} = 1.917 g cm⁻³. The latter complex crystallizes in the monoclinic space group C2/c with *a* = 12.5260(10) Å, *b* = 9.3360(10) Å, *c* = 18.699(2) Å, β = 98.320(10)°, *V* = 2163.7(4) Å³, *Z* = 4, and ρ_{calcd} = 1.862 g cm⁻³. The structures of [PtCl₂(OCMe₂ON=CC₄H₈)₂] and [PtCl₂(OCMe₂ON=CC₅H₁₀)₂] show an octahedron of Pt where two Cl atoms and two chelate ligands are mutually *trans*, respectively.

Introduction

The coordination chemistry and reactivity of complexes containing so-called "simple" oximes, *e.g.* ligands which have merely one oxime group as the only coordination site,² is a relatively unexplored area. Nevertheless, nonsystematic and scattered works from different groups show that oxime-containing complexes display very interesting reactivity modes. Reported examples include deprotonation either preserving the Pt–N bond³ or leading to formation of Pt–O–N oximate and bridging oximate μ₂-η²-ONCR₂ complexes,⁴ the Beckmann rearrangement,⁵ deoxygenation,⁶ metal-ion assisted addition of oximes to nitriles,^{7,8} cleavage of the C=N bond,⁹ oxidative addition,¹⁰ ortho-palladation of aromatic oximes,¹¹ oxime-ligand-

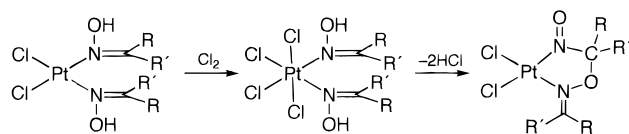
supported stabilization of Pt^{III}–Pt^{III} derivatives,¹² and dehydration with formation of metal-bonded organonitriles^{13,14} or azavynilidene-type complexes.^{14,15} In high-oxidation-state metal ion complexes, hydrolysis followed by oxidation is observed.¹⁶

Recently, we have demonstrated that the oxidation of *cis*-[PtCl₂(RR'C=NOH)₂], where R = R' = Me, RR' = (CH₂)₄ and (CH₂)₅, by molecular chlorine yields *cis*-[PtCl₄(RR'C=NOH)₂].¹⁷ The latter compounds, on standing in water–acetone solution, undergo an unusual spontaneous Pt(IV)-mediated redox coupling leading to the platinum(II) chelate [PtCl₂(N(=O)CRR'ONCRR')], shown in Scheme 1. We have no indication of participation of acetone as a reagent in this reaction.

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Scheme 1



As an extension of this study, we have found that *trans*- $[\text{PtCl}_2(\text{RR}'\text{C=NOH})_2]$ displays intriguing reactivity toward oxidation in acetone. We report herein the oxidation of *trans*- $[\text{PtCl}_2(\text{RR}'\text{C=NOH})_2]$ by *m*-chloroperoxybenzoic acid (MCPBA) in Me_2CO , where acetone acts as both the solvent and reagent.

Experimental Section

Materials and Instrumentation. The oxime ligands and $\text{K}_2[\text{PtCl}_4]$ were purchased from Aldrich and Reakhim, respectively, and used as received. MCPBA was purchased from Aldrich (57–86%; contains 7–10% 3-chlorobenzoic acid, the remainder being water) and was not titrated. *trans*- $[\text{PtCl}_2(\text{RR}'\text{C=NOH})_2]$ ($\text{RR}'=(\text{CH}_2)_4$ and $(\text{CH}_2)_5$) were prepared by heating the appropriate *cis*-isomers in the solid phase at 135 and 140 °C, respectively.¹⁸ *trans*- $[\text{PtCl}_2(\text{Me}_2\text{C=NOH})_2]$ was synthesized by the published method^{17a} from $\text{K}_2[\text{PtCl}_4]$ and excess $\text{Me}_2\text{C=NOH}$. All other chemicals and solvents were obtained from commercial sources and were used as received. C, H, and N elemental analyses were carried out by the Microanalytical Service, Universidad Autónoma de Madrid. Electron impact mass spectra (EI-MS) were obtained with a VG Autospec instrument. Decomposition points were determined in capillary. Infrared spectra (4000–220 cm^{-1}) were recorded on a Perkin-Elmer 1650 FT-IR instrument, using Nujol mulls between CsI windows. Raman spectra were measured on a Dilor XY spectrophotometer, using an Ar laser (5145 Å) with the powdered samples sealed in capillary tubes.

Synthetic Work and Characterization. Preparation of $[\text{PtCl}_2(\text{OCMe}_2\text{ON=CC}_4\text{H}_8)_2]$. Solid MCPBA (1.02 g, 4.2–6.4 mmol) was added in small portions during 15 min to a stirred suspension of *trans*- $[\text{PtCl}_2(\{\text{CH}_2\}_4\text{C=NOH})_2]$ (1.05 g, 2.3 mmol) in acetone (50 mL) at room temperature. The suspension was converted into a dark-orange solution 8–10 min after the beginning of the addition. The solution was left to stand in an open beaker at 20–25 °C. After evaporation of 35–40 mL (ca. 12 h), released crystals were collected on a filter, washed with acetone (2×1 mL) and diethyl ether (2×1 mL), and dried in air at 20–25 °C. Yield of $[\text{PtCl}_2(\text{OCMe}_2\text{ON=CC}_4\text{H}_8)_2] = 0.72$ g, 55% based on Pt. Complexes $[\text{PtCl}_2(\text{OCMe}_2\text{ON=CCMe}_2)_2]$ and $[\text{PtCl}_2(\text{OCMe}_2\text{ON=CC}_5\text{H}_{10})_2]$ were prepared analogously in 48 and 60% yields, respectively. All three compounds were obtained as bright-yellow crystals which are very poorly soluble in most common solvents. The latter property does not allow the measurement of NMR spectra of the complexes even with high accumulation.

$[\text{PtCl}_2(\text{OCMe}_2\text{ON=CC}_4\text{H}_8)_2]$ has no characteristic melting point. On heating it decomposes from ca. 120 °C. Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{Cl}_2\text{N}_2\text{O}_4\text{Pt}$: C, 33.2; H 4.9; N 4.8. Found: C, 33.1; H 5.2; N 4.7. EI-MS, m/z : 563 ($[\text{M} - \text{CH}_3]^+$). IR (selected bands, cm^{-1}): 1635 m $\nu_{\text{as}}(\text{C=N})$, 337 m-s $\nu_{\text{as}}(\text{Pt-Cl})$. Raman spectrum (selected bands, cm^{-1}): 1640 m-w $\nu_s(\text{C=N})$, 324 vs $\nu_s(\text{Pt-Cl})$. Crystals suitable for X-ray crystallography were grown directly from the reaction mixture.

$[\text{PtCl}_2(\text{OCMe}_2\text{ON=CCMe}_2)_2]$ has no characteristic melting point. On heating it decomposes from ca. 160 °C. Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{Cl}_2\text{N}_2\text{O}_4\text{Pt}$: C, 27.4; H 4.6; N 5.3. Found: C, 26.7; H 4.2; N 5.0. EI-MS, m/z : 511 ($[\text{M} - \text{CH}_3]^+$). IR (selected bands, cm^{-1}): 1639 m $\nu_{\text{as}}(\text{C=N})$, 334 m-s $\nu_{\text{as}}(\text{Pt-Cl})$. Raman spectrum (selected bands, cm^{-1}): 1648 m-w $\nu_s(\text{C=N})$, 327 vs $\nu_s(\text{Pt-Cl})$.

$[\text{PtCl}_2(\text{OCMe}_2\text{ON=CC}_5\text{H}_{10})_2]$ has no characteristic melting point. On heating, it decomposes from ca. 130 °C. Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{Cl}_2\text{N}_2\text{O}_4\text{Pt}$: C, 35.7; H 5.3; N 4.6. Found: C, 35.7; H 5.3; N 4.6. EI-MS, m/z : 519 ($[\text{M} - \text{CH}_3]^+$). IR (selected bands, cm^{-1}): 1668 m $\nu_{\text{as}}(\text{C=N})$, 336 s $\nu_{\text{as}}(\text{Pt-Cl})$. Raman spectrum (selected bands,

Table 1. Crystal Data and Structure Refinement for $[\text{PtCl}_2(\text{OCMe}_2\text{ON=CC}_4\text{H}_8)_2]$ and $[\text{PtCl}_2(\text{OCMe}_2\text{ON=CC}_5\text{H}_{10})_2]$

empirical formula	$\text{C}_{16}\text{H}_{28}\text{Cl}_2\text{N}_2\text{O}_4\text{Pt}$	$\text{C}_{18}\text{H}_{32}\text{Cl}_2\text{N}_2\text{O}_4\text{Pt}$
fw	578.39	606.45
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
<i>a</i> , Å	8.088(2)	12.5260(10)
<i>b</i> , Å	8.327(2)	9.3360(10)
<i>c</i> , Å	8.475(2)	18.699(2)
α , deg	103.54(3)	90
β , deg	102.15(3)	98.320(10)
γ , deg	108.37(3)	90
<i>V</i> , Å ³	501.0(2)	2163.7(4)
<i>Z</i>	1	4
$\rho(\text{calcd})$, g cm ⁻³	1.917	1.862
<i>T</i> , K	293(2)	293(2)
radiation, λ (Å)	Mo K α , Nb-filter,	Mo K α , Nb-filter,
	0.710 73	0.710 73
μ , mm ⁻¹	7.290	6.757
θ range, deg	2.60–24.97	2.20–24.95
no. of coll reflns	1927	1448
no. of reflns for calc	1759	975
$R1^a/wR2^b$	0.012/0.030	0.012/0.032

$$^a R1 = \sum(|F_o| - |F_c|)/\sum|F_o|. \quad ^b wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}.$$

cm^{-1}): 1672 m-w $\nu_s(\text{C=N})$, 328 vs $\nu_s(\text{Pt-Cl})$. Crystals suitable for X-ray crystallography were grown directly from the reaction mixture.

X-ray Structure Determination of *trans*- $[\text{PtCl}_2(\text{OCMe}_2\text{ON=CC}_4\text{H}_8)_2]$ and *trans*- $[\text{PtCl}_2(\text{OCMe}_2\text{ON=CC}_5\text{H}_{10})_2]$. (Data for the latter complex are given below in square brackets.) Diffraction data were collected on an Enraf-Nonius CAD 4 diffractometer. Cell parameters for both complexes were obtained from centered reflections with θ between 10 and 12.5°; 1891 [1448] independent reflections were measured up to 50° by the $\theta/2\theta$ scan technique. Range of *hkl*: *h* = −9 to +9, *k* = −9 to +9, *l* = −10 to 0 [*h* = −14 to +14, *k* = 0 to 11, *l* = 0 to 18]. Standard reflections were measured every 60 min and showed practically no change with time ($\pm 1\%$). Diffractometer data were processed by the program PROFIT¹⁹ with profile analysis of reflections. The structures were solved by means of Fourier synthesis based upon the Pt-atom coordinates obtained from the Patterson synthesis using the SHELXTL package.^{20a} After that, all reflections with $I < 3\sigma(I)$ were excluded from calculations. Refinement was done by full-matrix least squares based on F^2 using the SHELX-93 package.^{20b} All non-H atoms were treated anisotropically. H atoms were located in a difference Fourier map and refined isotropically [hydrogen coordinates were found from difference synthesis and were included in refinement with fixed coordinates and thermal parameters]. An extinction correction has been applied. Lorentz, polarization, and absorption corrections were made.²¹ Crystal size: $0.28 \times 0.24 \times 0.20$ [$0.15 \times 0.12 \times 0.12$] mm. T_{min} and T_{max} are 0.154 and 0.301 [0.197 and 0.302], respectively. Scattering factors were obtained from ref 22. Crystal data are given in Table 1, atomic parameters are given in Tables 2 and 3, and bond distances and angles are given in Tables 4 and 5.

Discussion

The reaction between *trans*- $[\text{PtCl}_2(\text{RR}'\text{C=NOH})_2]$ and an excess of MCPBA proceeds in a similar way for all three complexes studied. The process is fast at room temperature, and complete disappearance of the starting material was detected by TLC monitoring a few minutes after mixing the reagents. Crystals of the final products were released from the reaction mixtures after 3–12 h, and compounds were isolated in 50–

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_4\text{H}_8)_2]^a$

atom	x	y	z	U_{eq}
Pt	5000	5000	5000	27(1)
Cl	2073(1)	4004(1)	3147(1)	46(1)
O(1)	4727(3)	7168(2)	7960(2)	39(1)
O(2)	5309(3)	7571(2)	5457(2)	39(1)
N	4050(3)	5357(3)	7006(3)	32(1)
C(1)	2939(3)	4299(3)	7526(3)	33(1)
C(2)	2131(4)	2319(4)	6723(4)	46(1)
C(3)	1115(5)	1673(4)	7928(5)	51(1)
C(4)	575(4)	3198(4)	8689(4)	43(1)
C(5)	2241(4)	4871(4)	8970(3)	41(1)
C(6)	4636(4)	8186(3)	6758(3)	39(1)
C(7)	5913(5)	10082(4)	7818(5)	53(1)
C(8)	2666(4)	8003(4)	6111(4)	50(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_5\text{H}_{10})_2]^a$

atom	x	y	z	U_{eq}
Pt	5000	5000	5000	25(1)
Cl	6094(1)	5799(2)	6030(1)	40(1)
O(1)	4840(3)	7011(4)	4624(2)	34(1)
O(2)	6613(3)	6519(5)	4447(2)	33(1)
N	6277(3)	4966(28)	4457(2)	33(1)
C(1)	6802(4)	4167(7)	4133(3)	30(1)
C(2)	6510(5)	2620(6)	4113(3)	39(1)
C(3)	6194(5)	2181(6)	3319(3)	45(1)
C(4)	7094(6)	2533(7)	2881(3)	48(1)
C(5)	7380(5)	4113(6)	2932(3)	45(1)
C(6)	7685(4)	4582(6)	3715(3)	38(1)
C(7)	5661(4)	7438(6)	4252(3)	33(1)
C(8)	6048(5)	8918(6)	4494(3)	45(1)
C(9)	5342(5)	7316(8)	3429(3)	48(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond Lengths ($\text{\AA}$) and Angles (deg) for $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_4\text{H}_8)_2]$

Bond Lengths			
Pt—O(2)	2.007(2)	C(1)—C(2)	1.489(4)
Pt—N	2.007(2)	C(2)—C(3)	1.529(4)
Pt—Cl	2.3124(12)	C(4)—C(5)	1.529(4)
O(1)—N	1.396(3)	C(6)—C(8)	1.518(4)
O(2)—C(6)	1.392(3)	C(6)—C(7)	1.511(4)
O(1)—C(6)	1.475(3)	C(1)—C(5)	1.493(3)
N—C(1)	1.276(3)	C(3)—C(4)	1.518(4)
Bond Angles ^a			
O(2)—Pt—O(2)#1	180.0	O(2)—Pt—N#1	99.90(8)
O(2)—Pt—Cl	92.16(7)	O(2)—Pt—N	80.10(8)
N#1—Pt—N	180.0	O(2)#1—Pt—Cl	87.84(7)
N—Pt—Cl	90.54(7)	O(2)—Pt—Cl#1	92.16(7)
N—Pt—Cl#1	89.46(7)	N—O(1)—C(6)	107.9(2)
C(6)—O(2)—Pt	113.2(2)	C(1)—N—O(1)	115.7(2)
C(1)—N—Pt	133.5(2)	O(1)—N—Pt	110.78(14)
N—C(1)—C(2)	123.7(2)	N—C(1)—C(5)	125.0(2)
C(2)—C(1)—C(5)	111.3(2)	C(1)—C(2)—C(3)	103.3(2)
C(4)—C(3)—C(2)	104.3(2)	C(3)—C(4)—C(5)	103.6(2)
C(1)—C(5)—C(4)	102.8(2)	O(2)—C(6)—O(1)	109.6(2)
O(2)—C(6)—C(7)	109.2(2)	O(1)—C(6)—C(7)	104.0(2)
O(2)—C(6)—C(8)	113.1(2)	O(1)—C(6)—C(8)	108.0(2)
C(7)—C(6)—C(8)	112.6(2)		

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

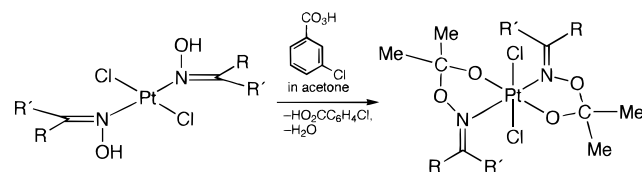
60% yields. It is possible to assume that the initial reaction is fast, but the formation of the final products must be slow because, being quite insoluble, they should precipitate as soon as they are formed. Elemental analyses, EI-MS, Raman and

Table 5. Bond Lengths ($\text{\AA}$) and Angles (deg) for $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_5\text{H}_{10})_2]$

Bond Lengths			
Pt—O(1)	2.004(4)	O(1)—C(7)	1.382(6)
Pt—Cl	2.3189(12)	Pt—N	2.015(4)
O(2)—N	1.51(2)	N—C(1)	1.21(2)
O(2)—C(7)	1.472(6)	C(1)—C(6)	1.496(8)
C(1)—C(2)	1.489(8)	C(3)—C(4)	1.523(9)
C(2)—C(3)	1.535(8)	C(5)—C(6)	1.522(8)
C(4)—C(5)	1.518(9)	C(7)—C(9)	1.538(8)
C(7)—C(8)	1.511(8)		
Bond Angles ^a			
O(1)—Pt—O(1)#1	180.0	O(2)—N—Pt	103.6(11)
O(1)—Pt—N	83.4(7)	O(1)—Pt—N#1	96.6(7)
O(1)—Pt—Cl	90.40(12)	O(1)#1—Pt—Cl	89.60(12)
N—Pt—Cl	90.4(3)	N#1—Pt—Cl	89.6(3)
Cl#1—Pt—Cl	180.0	C(7)—O(1)—Pt	113.8(3)
C(7)—O(2)—N	110.2(5)	C(1)—N—O(2)	114.3(7)
C(1)—N—Pt	142(2)	N—C(1)—C(6)	126.7(10)
N—C(1)—C(2)	117.4(11)	C(8)—C(7)—C(9)	113.1(5)
C(2)—C(1)—C(6)	115.8(5)	C(1)—C(2)—C(3)	108.1(5)
C(4)—C(3)—C(2)	110.9(5)	C(5)—C(4)—C(3)	111.2(5)
C(4)—C(5)—C(6)	111.4(5)	C(1)—C(6)—C(5)	109.0(4)
O(1)—C(7)—O(2)	110.1(4)	O(1)—C(7)—C(8)	110.0(4)
O(2)—C(7)—C(8)	104.2(4)	O(1)—C(7)—C(9)	112.2(4)
O(2)—C(7)—C(9)	106.8(4)		

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

Scheme 2



IR spectra, and X-ray data are in agreement with the proposed structure of Pt(IV) complexes with two newly formed chelate ligands; see Scheme 2.

Compounds *trans*- $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_4\text{H}_8)_2]$, **1**, and *trans*- $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_5\text{H}_{10})_2]$, **2**, have been structurally characterized. The coordination polyhedron of the complexes is a slightly distorted octahedron (Figures 1 and 2). The Pt atom in each case lies at an inversion center, and the two Cl atoms are mutually *trans*. The values of the Pt—Cl bond distances (2.312(1) for **1** and 2.319(1) $\text{\AA}$ for **2**) agree well with previously characterized platinum(IV) chloride compounds.²³ Two chelate ligands are *trans*, and the cycles containing the Pt atom are in an envelope-like conformation. In **1**, atoms Pt, N, C(6), and O(2) are coplanar within 0.02 $\text{\AA}$, the deviation of O(1) from this plane being 0.55 $\text{\AA}$. In **2**, atoms Pt, N, C(7), and O(1) are coplanar within 0.03 $\text{\AA}$, and O(2) deviates from this plane by 0.6 $\text{\AA}$. In the cyclopentanone oxime moiety of **1**, the atoms C(1), C(2), C(4), and C(5) are coplanar in the limits of 0.08 $\text{\AA}$, and atom C(3) deviates from this plane by 0.54 $\text{\AA}$. The cyclohexanone oxime ring of **2** adopts a chairlike conformation; atoms C(1), C(2), C(4), and C(5) are coplanar within 0.01 $\text{\AA}$, and atoms C(3) and C(6) deviate by -0.68 and 0.66 $\text{\AA}$, correspondingly. The X-ray structures for Pt(IV) complexes containing an oxime $\text{O}=\text{N}=\text{CRR}'$ fragment are unknown. Nevertheless, the Pt—N interatomic distances in **1** and **2** are 2.007(2) and 2.015(4) $\text{\AA}$, respectively, which is consistent with those in the platinum(II) complex $[\text{PtCl}(\text{N},\text{N}=\text{CMe}_2)\text{C}_2\text{H}_4]$

(23) For X-ray structures of Pt(IV)—Cl complexes see, for example: Kukushkin, V. Yu.; Zenkevich, I. G.; Belsky, V. K.; Kononov, V. E.; Moiseev, A. I.; Sidorov, E. O. *Inorg. Chim. Acta* **1989**, 166, 79 and references therein.

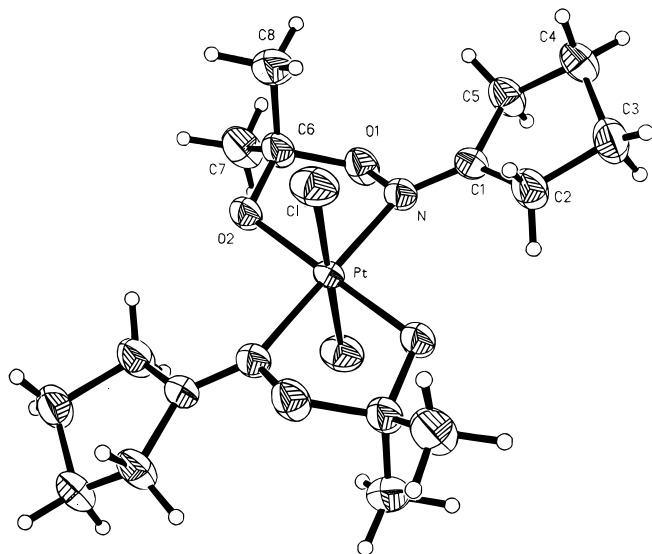


Figure 1. View of $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_4\text{H}_8)_2]$ with atomic numbering.

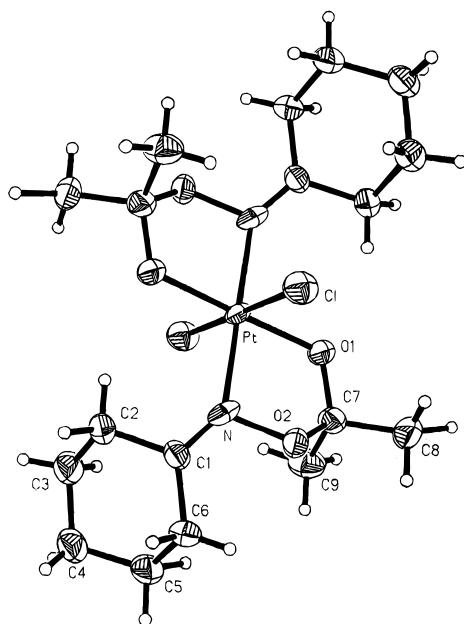


Figure 2. View of $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_5\text{H}_{10})_2]$ with atomic numbering.

$\text{NH}_2(\text{PBU}_3)]\text{Cl}$ ($2.08(1) \text{ \AA}^{24}$) and in some oxime-containing Pt(II) complexes ($1.97\text{--}2.02 \text{ \AA}^{17,25}$). The C(6)–O(1) bond length ($1.475(3) \text{ \AA}$) in **1** and C(7)–O(2) bond length ($1.472(6) \text{ \AA}$) in **2** agree within 3σ with the C–O bond distance ($1.55(3) \text{ \AA}$) found earlier in $[\text{PtCl}_2(\text{N}(\text{O})\text{CMe}_2\text{ONCMe}_2)]$.¹⁷ The Pt–O(2) and O(2)–C(6) bond lengths for **1** and Pt–O(1) and O(1)–

C(7) bond lengths for **2** correspond to those in platinum alkoxides.²⁶ All other bond lengths in both *trans*- $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_4\text{H}_8)_2]$ and *trans*- $[\text{PtCl}_2(\text{OCMe}_2\text{ON}=\text{CC}_5\text{H}_{10})_2]$ are usual.

In conclusion, it is worthwhile to mention the following: (i) we believe that the reactions reported here are the first oxidations of Pt(II) involving the use of a peroxybenzoic acid. Previous examples of the interaction of peroxybenzoic acids with platinum complexes include only reactions of coordinated ligands, *e.g.* oxygenation of the bridged sulfide in $\text{Pt}_2(\mu\text{-S})(\text{CO})_2(\text{P}^t\text{Bu}_2\text{Ph})_2$ ²⁷ and Pt–C oxidative splitting in $[\text{Pt}(\text{CH}_2\text{-Ph})\text{Cl}(\text{PPh}_3)_2]$ with no change in the Pt(II) oxidation state.²⁸ (ii) Accumulating data show that Me_2CO , one of the most common solvents, is far from being chemically inert. Both η^1 - and $\eta^2\text{-O}=\text{CMe}_2$ coordination modes,^{29–31} $\eta^1 \rightleftharpoons \eta^2$ linkage isomerization,³¹ template reactions,³² condensation with amines,²⁴ deprotonation and bonding to a S_2^{2-} bridged ligand,³³ addition to a (pyrazolyl)hydroborato ligand,³⁴ and self-condensation with the formation of $\text{HOCMe}_2\text{CH}_2\text{C}(\text{O})\text{Me}^{35}$ and $\text{CH}_2=\text{CMeCH}_2\text{C}(\text{O})\text{Me}^{36}$ chelate ligands have been reported. (iii) To the best of our knowledge, no other example of metal-assisted ring closure involving oxime ligands and ketones has been published to date. Studies on the mechanism of this reaction and similar reactions in other solvents³⁷ are under current investigation.

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Supporting Information Available: Atomic coordinates and equivalent isotropic displacement parameters (Tables 1 and 1a), anisotropic displacement parameters (Tables 2 and 2a), and hydrogen coordinates and isotropic displacement parameters (Tables 3 and 3a) (3 pages). Ordering information is given on any current masthead page.

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