Reactivity of *trans*-$[PtX_2(ketoxime)_2]$ Complexes toward *m*-Chloroperoxybenzoic Acid: An Efficient Route to Coordinated Nitrosoalkanes and Solvent Dependence of the Reaction

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The platinum(II) compounds *trans*-$[PtX_2(RR'C{=}NOH)_2]$ [$X = Cl$, $R = R' = Me$, $RR' = (CH_2)_4$, $(CH_2)_5$; $X = Br$, $R = R' = Me$] react with *m*-chloroperoxybenzoic acid (MCPBA) in dimethylformamide to give the platinum(II) complexes $[PtX_2\{N({=}O)CRR'ONCRR'\}]$ containing coordinated nitrosoalkane ligands. The complexes $[PtX_2\{N({=}O)CRR'ONCRR'\}]$ were characterized by elemental analysis, EI-MS, IR, electronic absorption, and ^1H NMR spectroscopy; X-ray structure analysis was performed for $[PtCl_2\{N({=}O)CC_5H_{10}ONCC_5H_{10}\}]$. The latter compound crystallizes in the triclinic $P\bar{1}$ space group with $a = 9.214(2)$ Å, $b = 9.577(2)$ Å, $c = 10.367(2)$ Å, $\alpha = 109.14(2)°$, $\beta = 91.87(2)°$, $\gamma = 115.62(2)°$, $V = 762.8(3)$ Å^3, $Z = 2$, and $\rho_{calcd} = 2.135$ g cm^{-3}. The reaction between *trans*-$[PtX_2(RR'C{=}NOH)_2]$ and MCPBA displays a solvent dependence: interaction of these reagents in ketones, $R_1R_2C{=}O$, yields the platinum(IV) chelates $[PtX_2(OCR_1R_2ON{=}CRR')_2]$, while the oxidation state of the oxime N atom remains unchanged. Heating $[PtCl_2(OCR_1R_2ON{=}CRR')_2]$ in DMF or in DMF-d_7 at 100 °C leads to the extrusion of $R_1R_2C{=}O$ and the formation of $[PtCl_2\{N({=}O)CRR'ONCRR'\}]$.

Introduction

The syntheses, structures, and solution chemistry of metal oxime and oximato complexes have been extensively studied and described in a large number of reviews.[2,3] However, metal-ion assisted reactions of oximes and reactivity of oxime-containing metal complexes have received much less attention. Despite this, data gradually accumulated in the literature show that the reactivity of coordinated $RR'C{=}NOH$ ligands and their complexes is impressively rich.[4]

As far as the redox chemistry of oxime ligands is concerned, the oxime nitrogen has the formal oxidation state 1− and, like the parent hydroxylamine, can be either reduced or oxidized. In contrast to reduction of oximes,[5−8] metal-ion assisted oxidation of $RR'C{=}NOH$ is an essentially unexplored area, and only oxidative deoximation involving high oxidation state metal ions has been reported for a variety of *free* oximes.[9,10] Moreover, apart from data presented recently by two of us,[11] no other reports have been published on the oxidation of *coordinated* oxime ligands. In the latter work,[11] it was demonstrated that the oxidation of *cis*-$[PtCl_2(Me_2C{=}NOH)_2]$ by molecular chlorine yields *cis*-$[PtCl_4(Me_2C{=}NOH)_2]$ (reaction (*i*) in Scheme 1). The ketoxime ligands survive the reaction conditions, although it is known that free ketoximes can be easily converted into the nitroso compounds, $RR'ClC{-}NO$, by chlorination with Cl_2.[12] The platinum(IV) complex *cis*-$[PtCl_4$-

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(2) (a) Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 1. (b) Singh, A.; Gupta, V. D.; Srivastava, G.; Mehrotra, R. C. *J. Organomet. Chem.* **1974**, *64*, 145. (c) Haldar, B. C. *J. Indian Chem. Soc.* **1974**, *51*, 224. (d) Bose, K. S.; Patel, C. C. *J. Indian Chem. Soc.* **1974**, *51*, 315. (e) Mehrotra, R. C.; Rai, A. K.; Singh, A. K.; Bohra, R. *Inorg. Chim. Acta* **1975**, *13*, 91. (f) Varhelyi, C.; Firta, Z. *Kem. Kozl.* **1976**, *45*, 79. (g) Bertrand, J. A.; Eller, P. G. *Prog. Inorg. Chem.* **1976**, *21*, 29. (h) Schrauzer, G. N. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 417; *Angew. Chem.* **1976**, *88*, 465. (i) Dixit, N. S.; Patel, C. C. *J. Indian Chem. Soc.* **1977**, *54*, 176. (j) Yamada, S.; Kuma, H. *Kagaku (Kyoto)* **1978**, *33*, 231; *Chem. Abstr.* **1978**, *88*, 202252m. (k) Shafranskii, V. N.; Fasu, I. L.; Buburuz, D. D.; Dranka, I. V.; Kharitonov, Yu. Ya. *Koord. Khim.* **1981**, *7*, 1123; *Chem. Abstr.* **1981**, *95*, 161127y. (l) Voiculescu, N.; Dominte, L. *Rev. Chim. (Bucharest)* **1983**, *34*, 973.

(3) (a) Simonov, Yu. A.; Shkurpelo, A. I.; Budnikov, S. S.; Botoshanskii, M. M.; Malinovskii, T. I. *Kristallokhimiya Neorg. i Organ. Soedinenii* **1982**, 35; *Chem. Abstr.* **1983**, *98*, 64547q. (b) Keeney, M. E.; Osseo-Asare, K.; Woode, K. A. *Coord. Chem. Rev.* **1984**, *59*, 141. (c) Chakravorty, A. *Proc. Indian Acad. Sci., Chem. Sci.* **1984**, *93*, 741. (d) Mehrotra, R. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 2, p 269. (e) Shirotani, I. *Kino Zairyo* **1987**, *7*, 60; *Chem. Abstr.* **1987**, *107*, 123300h. (f) Stynes, D. V. *Pure Appl. Chem.* **1988**, *60*, 561. (g) Singh, R. P.; Singh, N. K. *Asian J. Chem. Rev.* **1991**, *2*, 62. (h) Dash, K. C. *Adv. Organomet., Proc. Indo−Sov. Symp. "Organomet. Chem.", 1st* **1988**, 82; *Chem. Abstr.* **1991**, *115*, 125450w. (i) Garnovsky, A. D. *Koord. Khim.* **1993**, *19*, 394. (j) Gerasimchuk, N. N.; Bowman-James, K. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: Chichester, U.K., 1994; Vol. 5, p 2254.

(4) (a) Kukushkin, V. Yu.; Tudela, D.; Pombeiro, A. J. L. *Coord. Chem. Rev.*, in press. (b) Davies, J. A.; Hockensmith, C. M.; Kukushkin, V. Yu.; Kukushkin Yu. N. *Synthetic Coordination Chemistry: Principles and Practice*; World Scientific: Singapore, 1996.

(5) For reduction of coordinated oximes involving metal carbonyls see: (a) Alper, H.; Edward, J. T. *Can. J. Chem.* **1970**, *48*, 1543. (b) Charalambous, J.; Haines, L. I. B.; Morgan, J. S.; Peat, D. S.; Campbell, M. J. M.; Bailey, J. *Polyhedron* **1987**, *6*, 1027. (c) Dondoni, A.; Barbaro, G. *J. Chem. Soc., Chem. Commun.* **1975**, 761. (d) Nitta, M.; Sasaki, I.; Miyano, H.; Koboyashi, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3357. (e) Langenbahn, M.; Stoeckli-Evans, H.; Süss-Fink, G. *Helv. Chim. Acta* **1991**, *74*, 549. (f) Kaneda, K.; Doken, K.; Imanaka, T. *Chem. Lett.* **1988**, 285. (g) Kaneda, K.; Fujita, K.; Takemoto, T.; Imanaka, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 602. (h) Akazome, M.; Tsuji, Y.; Watanabe, Y. *Chem. Lett.* **1990**, 635.

(6) For reduction with formation of azavinylidene complexes see: (a) Werner, H.; Knaup, W.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 248; *Angew. Chem.* **1987**, *99*, 277. (b) Daniel, T.; Müller, M.; Werner, H. *Inorg. Chem.* **1991**, *30*, 3118. (c) Meyer, U.; Werner, H. *Chem. Ber.* **1990**, *123*, 697. (d) Werner, H.; Daniel, T.; Knaup, W.; Nürnberg, O. *J. Organomet. Chem.* **1993**, *462*, 309. (e) Daniel, T.; Knaup, W.; Dziallas, M.; Werner, H. *Chem. Ber.* **1993**, *126*, 1981.

(7) For reduction with formation of imine and μ_2-imido complexes see: (a) Fischer, E. O.; Knauss, L. *Chem. Ber.* **1970**, *103*, 1262. (b) Carofiglio, T.; Stella, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1957. (c) Deeming, A. J.; Owen, D. W.; Powell, N. I. *J. Organomet. Chem.* **1990**, *398*, 229. (d) Czarkie, D.; Shvo, Y. *J. Organomet. Chem.* **1985**, *280*, 123.

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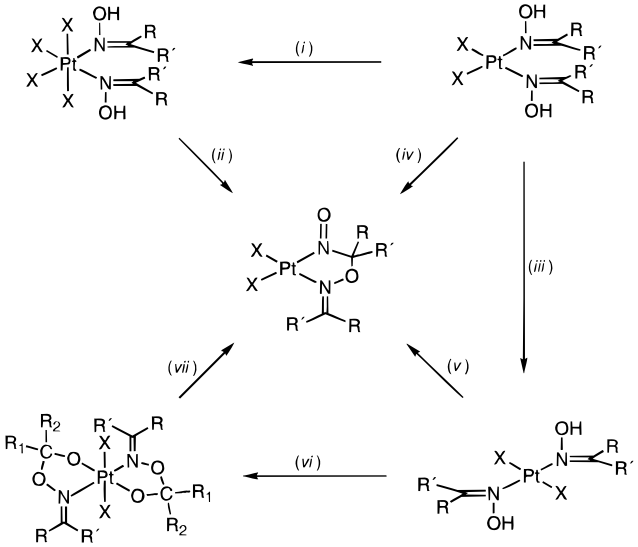
Scheme 1. Studied Conversions of the Oxime Complexes[a]



[a] Key: (*i*) Cl_2, R = R′ = Me; X = Cl. (*ii*) Spontaneous reaction in a water−acetone mixture; R = R′ = Me; X = Cl. (*iii*) Δ, solid state; R = R′ = Me; RR′ = $(CH_2)_4$, $(CH_2)_5$; X = Cl; R = R′ = Me, X = Br. (*iv*) MCPBA in Me_2CO; R = R′ = Me; R = Me, R′ = Et, RR′ = $(CH_2)_4$, $(CH_2)_5$; X = Cl; R = R′ = Me, X = Br. (*v*) MCPBA in DMF; R = R′ = Me; X = Cl, Br; RR′ = $(CH_2)_4$, $(CH_2)_5$; X = Cl. (*vi*) MCPBA in the ketones R_1R_2CO; R = R′ = Me; RR′ = $(CH_2)_4$, $(CH_2)_5$; X = Cl, R = R′ = Me, X = Br, ketone = Me_2CO; R = R′ = Me, RR′ = $(CH_2)_5$; X = Cl, ketone = MeEtCO; R = R′ = Me; X = Cl, ketone = Et_2CO. (*vii*) Δ, DMF; $R_1 = R_2$ = R = R′ = Me; R_1 = Me, R_2 = Et, R = R′ = Me; $R_1 = R_2$ = Et, R = R′ = Me; R_1 = Me, R_2 = Et, RR′ = C_5H_{10}; X = Cl.

($Me_2C{=}NOH)_2$], on standing in water−acetone solution, undergoes a spontaneous Pt(IV)-mediated redox coupling leading to the platinum(II) chelate [$PtCl_2\{N({=}O)CMe_2ONCMe_2\}$] (reaction (*ii*) in Scheme 1).

In continuation of the work on the oxidation of ketoxime ligands in Pt complexes, we have studied the reactions of *trans*-[$PtCl_2(RR'C{=}NOH)_2$] with another oxidant—*m*-chloroperoxybenzoic acid (MCPBA)—in dimethylformamide (DMF) solution. We report herein the reaction between the *trans*-ketoxime platinum(II) complexes and MCPBA in DMF, which results in oxidation of the ligands to afford the chelates [$PtX_2\{N({=}O)CRR'ONCRR'\}$] while the Pt(II) oxidation state remains the same (reaction (*v*) in Scheme 1).[13] This reaction is of synthetic utility and can be used for the preparation of very little studied Pt(II) complexes with nitrosoalkane species.

Previously, we have observed that the same platinum(II) complexes *trans*-[$PtCl_2(RR'C{=}NOH)_2$], where R = R′ = Me and RR′ = $(CH_2)_4$ and $(CH_2)_5$, react with MCPBA in Me_2CO to give the platinum(IV) compounds [$PtCl_2(OCMe_2ON{=}CRR')_2$] without change in the oxidation state of the oxime N atom.[14] We have now observed that the reaction proceeds in the same way in the ketones R_1R_2CO (R_1 = Me, R_2 = Et; $R_1 = R_2$ = Et). This remarkable solvent dependence and the unusual conversion of [$PtCl_2(OCR_1R_2ON{=}CRR')_2$] into [$PtCl_2\{N({=}O)CRR'ONCRR'\}$] will also be the subject of this article.

Experimental Section

Materials and Instrumentation. The oxime ligands were purchased from Aldrich and used as received. $K_2[PtCl_4]$ was obtained from Reakhim and recrystallized from water. MCPBA was purchased from Aldrich (57−86%; contains 7−10% 3-chlorobenzoic acid, the remainder being water) and was not titrated. *trans*-[$PtX_2(RR'C{=}NOH)_2$] complexes (X = Cl, R = R′ = Me, RR′ = $(CH_2)_4$, $(CH_2)_5$; X = Br, R = R′ = Me) were prepared by heating the appropriate *cis*-isomers in the solid phase at 140, 135, 140, and 140 °C, respectively (reaction (*iii*) in Scheme 1).[15] 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. For TLC, Riedel−deHaën 60 F 254 SiO_2 plates with layer thickness 0.2 mm have been used. Infrared spectra (4000−220 cm^{-1}) were recorded on a Perkin-Elmer 1650 FT-IR instrument, using Nujol mulls between CsI windows. ^1H NMR and electronic absorption spectra were recorded on a Bruker AMX-300 and Pye Unicam SP8-100 instruments, respectively.

Synthetic Work and Characterization. Reaction of *trans*-[$PtX_2(RR'C{=}NOH)_2$] (R = R′ = Me, RR′ = $(CH_2)_4$, $(CH_2)_5$, X = Cl; R = R′ = Me, X = Br) with MCPBA in DMF (General Method), Reaction (*v*) in Scheme 1. A 0.6−0.7 mmol amount of *trans*-[$PtX_2(RR'C{=}NOH)_2$] was dissolved at 40 °C in the minimum amount of DMF, and to this solution an excess of solid MCPBA (0.27−0.30 g, 0.9−1.5 mmol according to purity range) was added. Immediately after addition, the color of the solution turned from yellow to dark-red. The nitrosoalkane complexes [$PtX_2\{N({=}O)CRR'ONCRR'\}$] were isolated by vapor diffusion of Et_2O (R = R′ = Me; X = Cl, Br) or by addition of water (RR′ = $(CH_2)_4$, $(CH_2)_5$; X = Cl). Yields were 50−60%.

[$PtCl_2\{N({=}O)CMe_2ONCMe_2\}$]: Dark-red needlelike crystals formed from a water−acetone solution, mp = 125 °C (dec). EI-MS, *m/z*: 409 $[M - H]^+$. Anal. Calcd for $C_6H_{12}Cl_2N_2O_2Pt$: C, 17.6; H, 3.0; N, 6.8. Found: C, 17.8; H, 3.1; N, 6.7. IR data (Nujol), cm^{-1}: 1625 m $\nu(C{=}N)$, 1543 vs $\nu(N{=}O)$, 354 ms and 336 ms $\nu(Pt{-}Cl)$. ^1H NMR

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(8) For reduction of oximes involving low- or medium-oxidation-state metal ions see: (a) McMurry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281. (b) Timms, G. H.; Wildsmith, E. *Tetrahedron Lett.* **1971**, 195. (c) Christofis, O.; Habeeb, J. J.; Steevensz, R.; Tuck, D. G. *Can. J. Chem.* **1978**, *56*, 2269. (d) Barton, D. H. R.; Bowles, T.; Husinec, S.; Forbes, J. E.; Llobera, A.; Porter, A. E. A.; Zard, S. Z. *Tetrahedron Lett.* **1988**, *29*, 3343. (e) Leeds, J. P.; Kirst, H. A. *Synth. Commun.* **1988**, *18*, 777. (f) Kamochi, Y.; Kudo, T. *Nippon Kagaki Kaishi* **1993**, 500. (g) Kamochi, Y.; Kudo, T. *Tetrahedron Lett.* **1991**, *32*, 3511. (h) Kudo, T.; Kamochi, Y. *Kidorui* **1991**, *18*, 150. (i) Souppe, J.; Danon, L.; Namy, J. L.; Kagan, H. B. *J. Organomet. Chem.* **1983**, *250*, 227. (j) Corey, E. J.; Richmann, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 5276. (k) Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *Synthesis* **1980**, 220. (l) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 824. (m) Balicki, R.; Kaczmarek, L.; Malinowski, M. *Liebigs Ann. Chem.* **1989**, 1139. (n) Vakatkar, V. V.; Tatake, J. G.; Sunthankar, S. V. *Chem. Ind. (London)* **1977**, 742.

(9) (a) McKillop, A.; Hunt, J. D.; Naylor, R. D.; Taylor, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 4918. (b) Firouzabadi, H.; Mohammadpoor-Baltork, I. *Synth. Commun.* **1994**, *24*, 489. (c) Prasada Rao, L. V. S.; Brahmaji Rao, S. *J. Indian Chem. Soc.* **1988**, *65*, 404. (d) Aizpurua, J. M.; Palomo, C. *Tetrahedron Lett.* **1983**, *24*, 4367. (e) Aizpurua, J. M.; Juaristi, M.; Lecea, B.; Palomo, C. *Tetrahedron* **1985**, *41*, 2903. (f) Firouzabadi, H.; Sardarian, A. R.; Moosavipour, H.; Afshari, G. M. *Synthesis* **1986**, 285. (g) Firouzabadi, H.; Iranpoor, N.; Kiaeezadeh, F.; Toofan, J.*Tetrahedron* **1986**, *42*, 719. (h) Ramakrishnan, K.; Sankaran, K. R.; Srinivasan, V. S. *Indian J. Chem.* **1990**, *29A*, 843. (i) Rao, V. V.; Sethuram, B.; Rao, T. N. *Indian J. Chem.* **1980**, *19A*, 1127. (j) Firouzabadi, H.; Mottghinejad, E.; Seddighi, M. *Synthesis* **1989**, 378. (k) Firouzabadi, H.; Sardarian, A. *Synth. Commun.* **1983**, *13*, 863. (l) Firouzabadi, H.; Sardarian, A. R.; Naderi, M.; Vessal, B. *Tetrahedron* **1984**, *40*, 5001.

(10) (a) Vankar, P.; Rathore, R.; Chandrasekaran, S. *J. Org. Chem.* **1986**, *51*, 3063. (b) Kumar, H.; Kaur, B.; Kumar, B. *Indian J. Chem.* **1991**, *30B*, 869. (c) Olah, G. A.; Welch, J.; Henninger, M. *Synthesis* **1977**, 308. (d) Olah, G. A.; Welch, J. *J. Am. Chem. Soc.* **1978**, *100*, 5396. (e) Ho, T.-L. *Synthesis* **1973**, 347. (f) Shilov, V. P.; Krot, N. N.; Stepanova, E. S. *Radiokhimia* **1976**, *18*, 355. (g) Tananaev, I. G.; Shilov, V. P.; Krot, N. N. *Radiokhimia* **1986**, *28*, 92.

(11) Kukushkin, V. Yu.; Belsky, V. K.; Aleksandrova, E. A.; Konovalov, V. E.; Kirakosyan, G. A. *Inorg. Chem.* **1992**, *31*, 3836.

(12) Barnes, M. W.; Patterson, J. M. *J. Org. Chem.* **1976**, *41*, 733 and references therein.

(13) A preliminary communication concerning part of this work has been published: Kukushkin, V. Yu.; Izotova, Yu. A.; Tudela, D. *Zh. Obsch. Khim.* **1995**, *65*, 1918.

(14) Kukushkin, V. Yu.; Belsky, V. K.; Tudela, D. *Inorg. Chem.* **1996**, *35*, 510.

(15) Kukushkin, V. Yu.; Tudela, D.; Izotova, Yu. A.; Belsky, V. K.; Stash, A. I. Unpublished results (1996).

in acetone−d_6, δ, ppm: 1.55 ($OC(CH_3)_2$), 2.63 ($^4J_{PtH}$ 5.5 Hz) and 2.71 ($^4J_{PtH}$ 9.5 Hz) ($N{=}C(CH_3)_2$).

$[PtCl_2\{N(=O)C(C_4H_8)ONC(C_4H_8)\}]$: Dark-red rhombic crystals formed from a $MeNO_2$/2-PrOH mixture, mp = 134 °C (dec). EI-MS, *m/z*: 462 $[M]^+$. Anal. Calcd for $C_{10}H_{16}Cl_2N_2O_2Pt$: C, 26.0; H, 3.5; N, 6.1. Found: C, 25.7; H, 3.3; N, 5.9. IR data (Nujol), cm^{-1}: 1651 m $\nu(C{=}N)$, 1540 vs $\nu(N{=}O)$, 345 ms and 337 ms $\nu(Pt{-}Cl)$. ^1H NMR in CD_2Cl_2, δ, ppm: complex multiplet at 1.75−2.10, triplet 2.95 (J_{HH} 7.4 Hz) and triplet 3.07 (J_{HH} 7.0 Hz) (α−CH_2 within the oxime moiety).

$[PtCl_2\{N(=O)C(C_5H_{10})ONC(C_5H_{10})\}]$: Dark-red rodlike crystals formed from acetone, mp = 136 °C (dec). EI-MS, *m/z*: 489 $[M-H]^+$. Anal. Calcd for $C_{12}H_{20}Cl_2N_2O_2Pt$: C, 29.4; H, 4.1; N, 5.7. Found: C, 29.4; H, 3.8; N, 5.5. IR data (Nujol), cm^{-1}: 1618 m $\nu(C{=}N)$, 1538 vs $\nu(N{=}O)$, 349 ms and 342 ms $\nu(Pt{-}Cl)$. ^1H NMR in nitromethane−d_3, δ, ppm: complex multiplet at 1.2−2.1, triplet 3.11 (J_{HH} 6.2 Hz) and triplet 3.19 (J_{HH} 6.3 Hz) (α-CH_2 within the oxime moiety).

$[PtBr_2\{N(=O)CMe_2ONCMe_2\}]$: Dark-red needle- and plateslike crystals from a water−acetone mixture, mp = 122−124 °C. EI-MS, *m/z*: 469 $[M-NO]^+$. Anal. Calcd for $C_6H_{12}Br_2N_2O_2Pt$: C, 14.5; H, 2.4; N, 5.6. Found: C, 14.4; H, 2.6; N, 5.8. IR data (Nujol), cm^{-1}: 1630 m $\nu(C{=}N)$, 1550 vs $\nu(N{=}O)$, 227 m and 224 mw $\nu(Pt{-}Br)$. ^1H NMR in nitromethane−d_3, δ, ppm: 1.51 ($OC(CH_3)_2$), 2.58 ($^4J_{PtH}$ 7.3 Hz) and 2.71 ($^4J_{PtH}$ 10.5 Hz) ($N{=}C(CH_3)_2$).

Reaction of *trans*-$[PtX_2(RR'C{=}NOH)_2]$ (R = R′ = Me, RR′ = $(CH_2)_4$, $(CH_2)_5$, X = Cl; R = R′ = Me, X = Br) with MCPBA in the Ketones Me_2CO, MeEtCO, and Et_2CO (General Method), Reaction (*vi*) in Scheme 1. The procedure is similar to that described for the preparation of $[PtCl_2(OCMe_2ON{=}CC_4H_8)_2]$.[14] Yields were 30−60% based on Pt. All compounds 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. The complexes $[PtCl_2(OCMe_2ON{=}CRR')_2]$ (R = R′ = Me, RR′ = $(CH_2)_4$ and $(CH_2)_5$) were previously characterized.[14]

$[PtBr_2(OCMe_2ON{=}CMe_2)_2]$ was prepared from *trans*-$[PtBr_2(Me_2C{=}NOH)_2]$ and MCPBA in Me_2CO. The complex forms small rhombic dark-orange crystals from the reaction mixture. The compound has no characteristic melting point. On heating it decomposes from *ca*. 140 °C. Anal. Calcd for $C_{12}H_{24}Br_2N_2O_4Pt$: C, 23.4; H, 3.9; N, 4.6. Found: C, 23.8; H, 3.8; N, 4.6. EI-MS, *m/z*: 601 ($[M-CH_3]^+$). IR (selected bands), cm^{-1}: 1645 m $\nu(C{=}N)$, 253 s $\nu(Pt{-}Br)$.

$[PtCl_2(OCMeEtON{=}CMe_2)_2]$ was prepared from *trans*-$[PtCl_2(Me_2C{=}NOH)_2]$ and MCPBA in MeEtCO. The complex forms small orange crystals from the reaction mixture, mp = 190−192 °C. Anal. Calcd for $C_{14}H_{28}Cl_2N_2O_4Pt$: C, 30.3; H, 5.1; N, 5.1. Found: C, 30.2; H, 4.8; N, 4.8. EI-MS, *m/z*: 525 (100%) $[M-C_2H_5]^+$, 467 (15%) $[M-C_2H_5-CH_2]^+$ and 453 (85%) $[M-2CH_3-CCH_3C_2H_5]^+$. IR (selected bands), cm^{-1}: 1645 ms $\nu(C{=}N)$, 337 s $\nu(Pt{-}Cl)$.

$[PtCl_2(OCEt_2ON{=}CMe_2)_2]$ was prepared from *trans*-$[PtCl_2(Me_2C{=}NOH)_2]$ and MCPBA in Et_2CO. The complex forms square-planar bright orange crystals from the reaction mixture, mp = 186−188 °C. Anal. Calcd for $C_{16}H_{32}Cl_2N_2O_4Pt$: C, 33.0; H, 5.5; N, 4.8. Found: C, 32.7; H, 5.3; N, 4.5. EI-MS, *m/z*: 553 (65%) $[M-C_2H_5]^+$, 467 (15%) $[M-C_2H_5-C_2H_4]^+$. IR (selected bands), cm^{-1}: 1644 ms $\nu(C{=}N)$, 337 s $\nu(Pt{-}Cl)$.

$[PtCl_2(OCMeEtON{=}CC_5H_{10})_2]$ was prepared from *trans*-$[PtCl_2(C_5H_{10}C{=}NOH)_2]$ and MCPBA in MeEtCO. The complex forms platelike bright orange crystals from the reaction mixture, mp = 115−117 °C (dec). Anal. Calcd for $C_{20}H_{36}Cl_2N_2O_4Pt$: C, 37.9; H, 5.7; N, 4.4. Found: C, 38.1; H, 5.8; N, 4.2. EI-MS, *m/z*: 605 ($[M-C_2H_5]^+$). IR (selected bands), cm^{-1}: 1636 m $\nu(C{=}N)$, 337 s $\nu(Pt{-}Cl)$.

Thermal Conversion of the $[PtX_2(OCR_1R_2ON{=}CMe_2)_2]$ Complexes in DMF-d_7, Reaction (*vii*) in Scheme 1. In a typical experiment *ca*. 0.01 g of the complex was placed in a NMR tube and 0.5 mL of DMF-d_7 was added, whereafter the tube was closed and heated at 100 °C for 15 min with periodical shaking. During this time the solid gradually disappeared and a dark-red solution was formed. The solution was cooled down until room temperature, and the ^1H NMR spectrum was measured. The same sample was used for TLC monitoring and, after dilution with DMF, for measuring the electronic absorption spectrum. The following products were identified from NMR: From $[PtCl_2(OCMe_2ON{=}CMe_2)_2]$ to $[PtCl_2\{N(=O)CMe_2ONCMe_2\}]$, 1.55 (6*H*, $OCMe_2$), 2.62 (3*H*, $NCMe_2$) and 2.71 ppm (3*H*, $NCMe_2$); Me_2CO, 2.08 ppm; *trans*-$[PtCl_2(Me_2C{=}NOH)_2]$, 2.15 (3*H*), 2.67 (3*H*) and 11.86 ppm (broad, OH); from $[PtCl_2(OCMeEtON{=}CMe_2)_2]$ to $[PtCl_2\{N(=O)CMe_2ONCMe_2\}]$, 1.55 (6*H*, $OCMe_2$), 2.62 (3*H*, $NCMe_2$) and 2.71 ppm (3*H*, $NCMe_2$); MeEtCO, triplet 0.93 (J_{1-2} 7.3 Hz, CH_2CH_3, 3*H*), quartet 2.46 (J_{1-3} 7.3 Hz, CH_2CH_3, 2*H*) and 2.084 ppm (CH_3, 3*H*); Me_2CO, 2.083 ppm; *trans*-$[PtCl_2(Me_2C{=}NOH)_2]$, 2.15 (3*H*), 2.67 (3*H*) and 11.86 ppm (broad, OH); from $[PtCl_2(OCEt_2ON{=}CMe_2)_2]$ to $[PtCl_2\{N(=O)CMe_2ONCMe_2\}]$, 1.55 (6*H*, $OCMe_2$), 2.62 (3*H*, $NCMe_2$) and 2.71 ppm (3*H*, $NCMe_2$); Et_2CO, triplet 0.94 (J_{1-2} 7.3 Hz, CH_2CH_3, 6H) and quartet 2.44 (J_{1-3} 7.3 Hz, CH_2CH_3, 4*H*); Me_2CO, 2.083 ppm; *trans*-$[PtCl_2(Me_2C{=}NOH)_2]$, 2.15 (3*H*), 2.67 (3*H*) and 11.86 ppm (broad, OH).

In all reactions the TLC (Me_2CO:$CHCl_3$ = 1:1) displays an orange-red spot with $R_f = 0.62$ due to $[PtCl_2\{N(=O)CMe_2ONCMe_2\}]$ and a spot of small intensity in UV_{254} with $R_f = 0.70$ due to *trans*-$[PtCl_2(Me_2C{=}NOH)_2]$. Electronic spectrum, λ_{max}, nm: 414 for $[PtCl_2\{N(=O)CMe_2ONCMe_2\}]$.

The thermal conversion of $[PtCl_2(OCMeEtON{=}CC_5H_{10})_2]$ resulted in the formation of $[PtCl_2\{N(=O)C(C_5H_{10})ONC(C_5H_{10})\}]$ [TLC, Me_2CO:$CHCl_3$ = 1:5, $R_f = 0.65$] and MeEtCO [^1H NMR spectrum in DMF-d_7, δ, ppm: triplet 0.93 (J_{1-2} 7.3 Hz, CH_2CH_3, 3*H*), quartet 2.46 (J_{1-3} 7.3 Hz, CH_2CH_3, 2*H*) and 2.084 ppm (CH_3, 3*H*)]. Cyclohexanone was not detected by means of ^1H NMR spectroscopy due to the complexity of signals and overlapping with peaks from $[PtCl_2\{N(=O)C(C_5H_{10})ONC(C_5H_{10})\}]$, but it was unambiguously identified by means of EI mass spectrometry.

X-ray Structure Determination of $[PtCl_2\{N(=O)CC_5H_{10}ONCC_5H_{10}\}]$. Crystals suitable for X-ray analysis were grown by slow evaporation of an acetone−toluene solution. Diffraction data were collected on an Enraf-Nonius CAD 4 diffractometer. Cell parameters were obtained from 12 centered reflections with θ between 10 and 12.5°; 1914 independent reflections with 1836 with $I \geq 3\sigma(I)$ were measured up to 50° by the $\theta/2\theta$ scan technique. Range of *hkl*: $h = 0$ to $+8$, $k = -11$ to $+10$, $l = -12$ to $+12$. Diffractometer data were processed by the program PROFIT[16] with profile analysis of reflections. The structure was solved by means of Fourier synthesis based upon the Pt atom coordinates obtained from the Patterson synthesis using the SHELXTL package.[17] 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.[18] All non-H atoms were treated anisotropically. 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.[19] Crystal size: 0.28 × 0.10 × 0.06 mm. The crystal was packed in Cyacrine glue to prevent decomposition. In spite of the safety coating, the crystal decayed by 30% and that affects the *R*-factor value and standard deviations in bond lengths and angles. T_{min} and T_{max} are 0.349 and 0.607, respectively. Scattering factors were obtained from ref 20. Crystal data are given in Table 1, and bond lengths and angles, in Table 2.

Discussion

Reaction between *trans*-$[PtX_2(RR'C{=}NOH)_2]$ and MCPBA in DMF. Primary and secondary nitrosoalkanes are usually irreversibly rearranged to give the corresponding oximes.[21] This reactivity mode is preserved when nitrosoalkane species are

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(16) Strel'tsov, V. A.; Zavodnik, V. E. *Kristallografia* **1989**, *34*, 1369.

(17) Sheldrick, G. M. *SHELXTL User Manual*, Revision 3; Nicolet XRD Corp.: Cupertino, CA, 1981.

(18) Sheldrick, G. M. *SHELX-93*; University of Göttingen: Göttingen, Germany, 1993.

(19) Axelrud, L. G.; Grin, Yu. N.; Zavalii, P. Yu.; Pecharsky, V. K.; Fundamensky, V. S. CSD-universal program package for single crystal and/or powder structure data treatment. *Collected Abstracts*, XIIth European Crystallographic Meeting, Moscow, Aug 1989; USSR Academy of Sciences: Moscow, 1989; p 155.

(20) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

Table 1. Crystal Data and Structure Refinement for [$PtCl_2\{N({=}O)CC_5H_{10}ONCC_5H_{10}\}$]

empirical formula	$C_{12}H_{20}Cl_2N_2O_2Pt$
fw	490.29
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	9.214(2)
b, Å	9.577(2)
c, Å	10.367(2)
α, deg	109.14(2)
β, deg	91.87(2)
γ, deg	115.62(2)
V, Å^3	762.8(3)
Z	2
ρ(calcd), mg m^{-3}	2.135
T, K	293(2)
radiation, λ (Å)	Mo Kα, 0.71073
μ, mm^{-1}	9.547
θ range, deg	2.12−24.96
no. of collcd reflcns	2743
no. of reflcns for calc	1836
$R1^a$	0.0609
w$R2^b$	0.1636

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

Table 2. Bond Lengths (Å) and Angles (deg) for [$PtCl_2\{N({=}O)CC_5H_{10}ONCC_5H_{10}\}$]

Bond Lengths

Pt−N(1)	1.907(13)	C(2)−C(3)	1.52(3)
Pt−N(2)	2.063(10)	C(3)−C(4)	1.50(3)
Pt−Cl(1)	2.279(5)	C(4)−C(5)	1.50(3)
Pt−Cl(2)	2.277(4)	C(5)−C(6)	1.56(2)
N(1)−O(2)	1.21(2)	C(7)−C(8)	1.45(3)
N(1)−C(1)	1.51(2)	C(7)−C(12)	1.51(2)
N(2)−C(7)	1.25(2)	C(8)−C(9)	1.55(3)
N(2)−O(1)	1.44(2)	C(9)−C(10)	1.52(3)
O(1)−C(1)	1.45(2)	C(10)−C(11)	1.53(3)
C(1)−C(6)	1.52(2)	C(11)−C(12)	1.55(3)
C(1)−C(2)	1.52(2)		

Bond Angles

N(1)−Pt−N(2)	80.8(5)	O(1)−C(1)−C(2)	103.7(14)
N(1)−Pt−Cl(2)	177.0(4)	N(1)−C(1)−C(6)	112.5(14)
N(2)−Pt−Cl(2)	97.1(4)	C(6)−C(1)−C(2)	111.2(13)
N(1)−Pt−Cl(1)	92.9(4)	C(3)−C(2)−C(1)	115(2)
N(2)−Pt−Cl(1)	170.4(3)	C(4)−C(3)−C(2)	110(2)
Cl(2)−Pt−Cl(1)	88.9(2)	C(5)−C(4)−C(3)	112(2)
O(2)−N(1)−C(1)	115.6(13)	C(4)−C(5)−C(6)	110(2)
O(2)−N(1)−Pt	129.9(11)	C(1)−C(6)−C(5)	112(2)
C(1)−N(1)−Pt	114.3(10)	N(2)−C(7)−C(8)	121(2)
C(7)−N(2)−O(1)	116.4(13)	N(2)−C(7)−C(12)	121(2)
C(7)−N(2)−Pt	137.7(11)	C(8)−C(7)−C(12)	118(2)
O(1)−N(2)−Pt	104.1(8)	C(7)−C(8)−C(9)	115(2)
N(2)−O(1)−C(1)	106.2(11)	C(10)−C(9)−C(8)	111(2)
O(1)−C(1)−N(1)	107.0(12)	C(9)−C(10)−C(11)	111(2)
O(1)−C(1)−C(6)	113.3(14)	C(10)−C(11)−C(12)	115(2)
N(1)−C(1)−C(6)	109.0(14)	C(7)−C(12)−C(11)	109(2)

coordinated to a metal center. It has been shown that *N*-coordinated ligands $R_1R_2HC{-}N{=}O$ ($R_1 = R_2$ = alkyl; R_1 = alkyl, R_2 = H) undergo a spontaneous tautomerization into the oxime ligands, $R_1R_2C{=}NOH$.[22] Tertiary nitrosoalkanes are commonly stable toward conversion into oximes. However, some of these nitrosoalkanes still can be used as precursors for the generation of oximato complexes, *e.g.* the treatment of $NaMo(CO)_3Cp$ with excess of 2-bromo-2-nitrosopropane gives rise to Mo(η^2-*O,N*-ON=CMe_2)$(CO)_2$Cp complex containing a η^2-2-propanone oximato ligand.[23]

The *formally* or *schematically* reverse reaction, *i.e.* the conversion of coordinated oximes into nitrosoalkane species, was observed for the first time on studying the redox coupling of the neighboring ketoxime ligands in *cis*-[$PtCl_4(Me_2C{=}NOH)_2$].[11] To the best of our knowledge, no other works on oxidation of coordinated oximes and their transformation into nitrosoalkanes have been published to date.[24] Furthermore, complexes of platinum(II) with *tert*-nitrosoalkane ligands—which cannot tautomerize to the appropriate oximes—are very scarce and restricted only to a few derivatives of ^{t}BuN=O which were prepared earlier by direct addition of the *C*-nitroso compound to a complex.[24,25]

We have now found that the reaction of *trans*-[$PtX_2(RR'C{=}NOH)_2$] (X = Cl, Br) and MCPBA in dimethylformamide results in oxidation of the ketoxime ligands to afford complexes [$PtX_2\{N({=}O)CRR'ONCRR'\}$] containing coordinated nitrosoalkane species (reaction (*v*) in Scheme 1) and this reaction is of synthetic importance.

It has been observed that the starting *trans*-ketoxime complexes undergo a complete transformation in DMF almost immediately after addition of MCPBA to the reaction mixtures. The color of the solutions changes from pale yellow to dark red; *trans*-[$PtX_2(RR'C{=}NOH)_2$] complexes were not found by TLC a few minutes after mixing the reagents, but orange-red spots which correspond to the final products (*see below*) were detected. Further addition of diethyl ether or water to the reaction mixtures results in the formation of solids which, on the basis of elemental analyses and EI-MS, IR, and ^{1}H NMR spectra, were formulated as [$PtX_2\{N({=}O)CRR'ONCRR'\}$]. It is noteworthy that all the complexes are red in color, which is unusual for [$Pt^{II}X_2L_2$] compounds but seems to be characteristic of platinum(II) nitrosoalkane complexes.[11,25] The complex [$PtCl_2\{N({=}O)CMe_2ONCMe_2\}$] is identical to that prepared earlier on redox coupling of the ketoxime ligands in *cis*-[$PtCl_4(Me_2C{=}NOH)_2$].[11] Compound [$PtCl_2\{N({=}O)C(C_5H_{10})ONC(C_5H_{10})\}$] has been structurally characterized. A plot of the molecular structure is shown in Figure 1, and bond distances and angles are collected in Table 2. The coordination polyhedron of the Pt atom is a slightly distorted square plane. The chelate ligand is coordinated to platinum *via* the N atom of the nitrosoalkane group and the N atom of the *O*-alkylated oxime. The resulting Pt containing five-membered ring is in an envelope-like conformation. The Pt−N(oxime) bond is significantly longer than the Pt−N(nitroso) bond. This was also observed in the structure of [$PtCl_2\{N({=}O)CMe_2ONCMe_2\}$], but the difference was not significant.[11] While the fairly large standard deviations in the structure of [$PtCl_2\{N({=}O)CMe_2ONCMe_2\}$] precluded any meaningful comparison of the Pt−Cl bond lengths,[11] both distances are essentially identical in the present compound, thus pointing to similar *trans*-influences of the nitrosoalkane and alkyloxime ligands. Most distances and angles in the structure of [$PtCl_2\{N({=}O)C(C_5H_{10})ONC(C_5H_{10})\}$]

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(21) (a) Coombes, R. G. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 2 (Sutherland, I. O., Ed.), p 305. (b) Boyer, J. H. In *The Chemistry of the Nitro and Nitroso Groups*; Feuer, H., Ed.; Interscience Publishers: New York, 1969; p 215. (c) Senechal-Tocquer, M.-C.; Senechal, D.; Le Bihan, J.-Y.; Gentric, D.; Caro, B.; Gruselle, M.; Jaouen, G. *J. Organomet. Chem.* **1992**, *433*, 261.

(22) (a) Waters, W. A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 732. (b) Schoonover, M. W.; Baker, E. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1979**, *101*, 1880. (c) Legzdins, P.; Wassink, B.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 317. (d) Legzdins, P.; Richter-Addo, G. B.; Wassink, B.; Einstein, F. W. B.; Jones, R. H.; Willis, A. C. *J. Am. Chem. Soc.* **1989**, *111*, 2097. (e) Chang, J.; Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3258.

(23) Khare, G. P.; Doedens, R. J. *Inorg. Chem.* **1977**, *16*, 907.

(24) (a) Cameron, M.; Gowenlock, B. G.; Vasapollo, G. *Chem. Soc. Rev.* **1990**, *19*, 355. (b) Vasapollo, G. Private communication (1995).

(25) (a) Mansuy, D.; Drême, M.; Chottard, J. C.; Guilhem, J. *J. Organomet. Chem.* **1978**, *161*, 207. (b) Boyd A. S. F.; Browne, G.; Gowenlock, B. G.; McKenna P. *J. Organomet. Chem.* **1988**, *345*, 217.

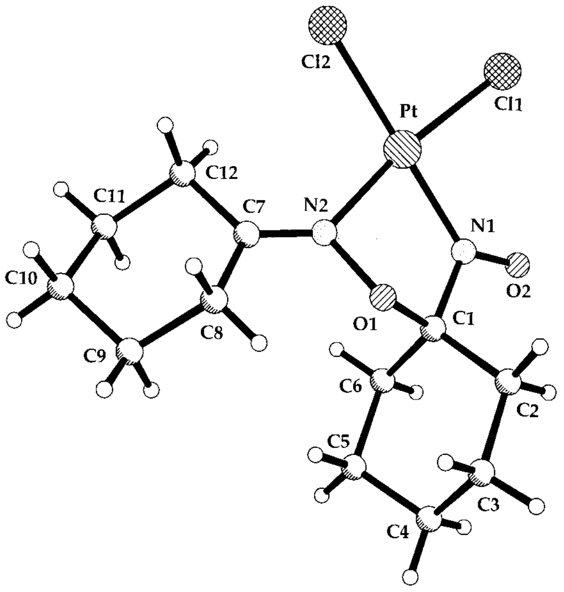

Figure 1. View of $[PtCl_2\{N(=O)CC_5H_{10}ONCC_5H_{10}\}]$ with atomic numbering.

and $[PtCl_2\{N(=O)CMe_2ONCMe_2\}]$[11] are close to each other; the most noticeable differences being in the Pt−N(oxime) distance [2.063(10) *vs* 1.97(2) Å] and Pt−N(oxime)−O angle [104.1(8) *vs* 110(1)°].

Thus, it has been established that oxidation of the *trans*-oximes of platinum(II) by MCPBA in dimethylformamide results in oxidation of the oxime ligands with formation of nitrosoalkane chelates $[PtX_2\{N(=O)CRR'ONCRR'\}]$, while the Pt(II) oxidation state remains the same. The overall reaction includes $2e^-$ oxidation of one of the oxime ligand, change in the relative positions of *N*-donor species around the Pt atom, and the ring-closure. The formation of $[PtX_2\{N(=O)CRR'ONCRR'\}]$ can also be achived starting from the isomeric *cis*-$[PtX_2(RR'C{=}NOH)_2]$ and MCPBA in acetone (reaction (*iv*) in Scheme 1).[26] Oxidations of both *trans*- and *cis*-$[PtX_2(ketoxime)_2]$ complexes by MCPBA provide a good synthetic method for the preparation of unusual and little investigated nitrosoalkane complexes of platinum.

Solvent Dependence of the Reaction between *trans*-$[PtX_2(RR'C{=}NOH)_2]$ and MCPBA. Our experiments demonstrate that the reaction between *trans*-$[PtX_2(RR'C{=}NOH)_2]$ and MCPBA displays an intriguing solvent-dependent path. Indeed, recently we have reported that the platinum(II) complexes *trans*-$[PtCl_2(RR'C{=}NOH)_2]$ [R = R′ = Me; RR′ = $(CH_2)_4$, $(CH_2)_5$] react with MCPBA in Me_2CO to give the platinum(IV) complexes $[PtCl_2(OCMe_2ON{=}CRR')_2]$ (reaction (*vi*) in Scheme 1).[14] As an extension of this work, we have now performed this reaction with *trans*-$[PtBr_2(Me_2C{=}NOH)_2]$ and isolated the appropriate platinum(IV) bromide complex $[PtBr_2(OCMe_2ON{=}CMe_2)_2]$. Furthermore, we have found that the MCPBA oxidation of *trans*-$[PtCl_2(RR'C{=}NOH)_2]$ proceeds also in some other ketones; *e.g.* interaction of *trans*-$[PtCl_2(Me_2C{=}NOH)_2]$ and MCPBA in either methyl ethyl ketone or diethyl ketone gives rise to $[PtCl_2(OCR_1R_2ON{=}CMe_2)_2]$ (R_1 = Me, R_2 = Et; R_1 = R_2 = Et), while treatment of *trans*-$[PtCl_2\{(C_5H_{10})C{=}NOH\}_2]$ with MCPBA in methyl ethyl ketone leads to $[PtCl_2\{OCMeEtON{=}CC_5H_{10}\}_2]$. All these observations indicate that the reaction (*vi*) has a general character for different *trans*-ketoxime complexes of platinum(II). These experiments also additionally prove that the R_1R_2CO ketones play the role of both the solvents and reagents in the reactions studied and that the reactions are solvent dependent because they follow a different path in DMF and ketones. The reactions carried out are among the first oxidations of Pt(II) complexes involving the use of a peroxybenzoic acid.[27]

Generation of $[PtCl_2\{N(=O)CRR'ONCRR'\}]$ by Thermal Conversion of $[PtCl_2(OCR_1R_2ON{=}CRR')_2]$. Complexes $[PtCl_2(OCR_1R_2ON{=}CRR')_2]$ are very poorly soluble in most common solvents (*i.e.* H_2O, MeOH, EtOH, Me_2CO, $MeNO_2$, CH_2Cl_2, $CHCl_3$, and C_6H_6) even on boiling of their suspensions. In search of an appropriate solvent for $[PtCl_2(OCR_1R_2ON{=}CRR')_2]$, we have established that keeping the solid compounds in DMF or DMF-d_7 at 100 °C for *ca.* 15 min leads to chemical reactions rather than just dissolution. In all cases, the bright orange solids $[PtCl_2(OCR_1R_2ON{=}CMe_2)_2]$ gradually disappeared on heating with the formation of red solutions. TLC and spectrophotometric monitoring provide evidence for the generation of the nitrosoalkane chelates $[PtCl_2\{N(=O)CRR'ONCRR'\}]$ described above. The products of the thermal conversion of $[PtCl_2(OCR_1R_2ON{=}CMe_2)_2]$ (R_1 = R_2 = Me, Et; R_1 = Me, R_2 = Et) in DMF-d_7 were subject to ^1H NMR analysis. Apart from the complex $[PtCl_2\{N(=O)CMe_2ONCMe_2\}]$ and small (<5%) amounts of *trans*-$[PtCl_2(Me_2C{=}NOH)_2]$, the ketones R_1R_2CO and Me_2CO were unambiguously identified. In the case of the thermal conversion of $[PtCl_2(OCMeEtON{=}CC_5H_{10})_2]$, the complex $[PtCl_2\{N(=O)C(C_5H_{10})ONC(C_5H_{10})\}]$ and MeEtCO were found. Cyclohexanone was not detected by means of ^1H NMR spectroscopy, due to the complexity of signals and overlapping with peaks from the nitrosoalkane complex, but it was identified by means of EI mass spectrometry.

In the reactions studied, the ketones R_1R_2CO are probably formed by thermal extrusion from the chelate ligand in $[PtCl_2(OCR_1R_2ON{=}CMe_2)_2]$, while acetone, as a byproduct, can be generated by either uncontrolled hydrolysis of the C=N bond or oxidative deoximation[9,10] by the Pt(IV) ion. The hydrolysis could proceed due to an extremely strong electrophilic activation of the ligands by the quadruply-charged Pt ion—a so-called Lewis superacid.[28] Examples of Pt(II)- and Pt(IV)-mediated hydrolysis of ligands containing the C=N and C≡N bonds are well-documented.[29] Oxidative deoximation of RR′C=NOH by platinum(IV) has not been studied so far. However, Bleaupré and Holland have investigated the extraction of $H_2[PtCl_6]$ from aqueous solutions at low pH by methyl ethyl ketone oxime and 4-heptanone oxime.[30] It was reported that, in very acidic solutions, Pt(IV) species are reduced to give Pt(II) species. Apparently, this observation supports the possibility of oxidative deoximation mediated by Pt(IV).

Hence, heating of $[PtCl_2(OCR_1R_2ON{=}CRR')_2]$ in DMF or in DMF-d_7 results at least in two reactions. The first process formally involves extrusion of the ketone from the chelate, $2e^-$ oxidation of one of the *N*-donor species formed, $2e^-$ reduction of platinum(IV), and ring-closure. The second transformation is the hydrolysis of the C=N bond and/or oxidative deoximation.

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[26] Kukushkin, V. Yu.; Oskarsson Å., Elding, L.-I. Unpublished results (1993).

[27] (a) Browning, C. S.; Farrar, D. H. *Organometallics* **1989**, *8*, 813. (b) Harvie, I. J.; McQuillin, F. J. *J. Chem. Soc., Chem. Commun.* **1977**, 241. (c) Tomohiro, T.; Laitalainen, T.; Shimura, T. *Stud. Org. Chem. (Amsterdam)* **1988**, 33; *Chem. Abstr.* **1988**, *108*, 230949u.

[28] Paul, P.; Nag, K. *Inorg. Chem.* **1987**, *26*, 1586.

[29] (a) Kukushkin, V. Yu.; Zenkevich, I. G.; Belsky, V. K.; Konovalov, V. E.; Moiseev, A. I.; Sidorov, E. O. *Inorg. Chim. Acta* **1989**, *166*, 79. (b) Rochon, F. D.; Kong, P. C.; Melanson, R. C. *Inorg. Chem.* **1990**, *29*, 1352. (c) Erxleben, A.; Mutikainen, I.; Lippert, B. *J. Chem. Soc., Dalton Trans.* **1994**, 3667. (d) Cross, R. J.; Davidson, M. F.; Rocamora, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1147.

[30] Bleaupré, P. W.; Holland, W. J. *Mikrochim. Acta* **1983**, *3*, 341.

In conclusion, it is worthwhile to mention that the MCPBA oxidation of bis(ketoxime) complexes of platinum(II) both in DMF and in the ketones provides a route for the preparation of new types of unusual chelates (all reactions and products studied are depicted in Scheme 1). However, the mechanisms of these processes are not yet clear. In fact, it is not established whether oxidation of the oxime ligands by MCPBA proceeds directly or *via* intermediate oxidation of Pt(II). Undoubtedly, this information would be important not only for the correct choice of starting materials and reaction conditions but also for predicting the occurrence of some other metal-ion-assisted reactions of oximes.

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

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