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Iminoacylation. 1. Addition of Ketoximes or Aldoximes to Platinum(IV)-Bound Organonitriles

Vadim Yu. Kukushkin,*,[1a] Tatyana B. Pakhomova,[1b] Yuri N. Kukushkin,*,[1b]
Rudolf Herrmann,[1c,d] Gabriele Wagner,[1c] and Armando J. L. Pombeiro*,[1c]

Department of Chemistry, St. Petersburg State University, 198904 Stary Petergof, Russian Federation,
Inorganic Chemistry, St. Petersburg State Technological Institute, Zagorodny Pr. 49,
198013 St. Petersburg, Russian Federation, and Complexo I, Instituto Supérior Técnico,
Av. Rovisco Pais, 1096 Lisbon Codex, Portugal

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The metal-mediated iminoacylation reaction of ketoximes or aldoximes upon treatment with the organonitrile platinum(IV) complexes *trans*-[$PtCl_4(RCN)_2$] proceeds under relatively mild conditions in acetonitrile (R = Me) or in chloroform (R = CH_2Ph, Ph) to give *trans*-[$PtCl_4(NH{=}C(R)ON{=}CR_1R_2)_2$] ($R_1 = R_2$ = Me; $R_1R_2 = C_4H_8$, $R_1R_2 = C_5H_{10}$, R_1R_2 = (H)Ph, R_1R_2 = (H)C_6H_4(OH)-*o*; **1**−**14**) in 90−95% yield. All these compounds were characterized by elemental analyses (C, H, N, Cl, Pt), FAB mass spectrometry, and IR and ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectroscopies. X-ray structure determinations of [$PtCl_4(NH{=}C(Me)ON{=}CMe_2)_2$] (**1**) and [$PtCl_4\{NH{=}C(Me)ON{=}C(C_5H_{10})\}_2$] (**3**) disclosed their overall *trans*-configuration and the amidine one-end rather than *N*,*N*-bidentate coordination mode of the *N*-donor ligands. The iminoacyl species are in *E*-conformation which is held by a rather weak N−H···N hydrogen bond between the amidine =N*H* atom and the oxime nitrogen with the following observed distances and angles for **1** and [**3**]: N(1)···N(2), and N(1)−H, N(1)H···N(2) are 2.605 [2.592], 0.74 [0.71], and 2.20 [2.25] Å; N(1)−H···N(2) is 115° [111°]. No evidence of the *Z*-conformation in solution was obtained by NMR spectroscopy. Compounds *trans*-[$PtCl_4(NH{=}C(R)ON{=}CR_1R_2)_2$] are unexpectedly stable toward hydrolysis both in the solid state and in solutions.

Introduction

Despite a great number of experimental works on synthetic and structural chemistry of oximes and oxime complexes,[2−5] their metal-mediated reactions received unexpectedly little attention. An overview of this chemistry, which has fairly recently been published by two of us,[6] shows an amazing variety of reactivity modes displayed by oxime species in metal-assisted reactions. Moreover, apart from the data analyzed in the review,[6] new interesting examples, e.g. stepwise deprotonation accompanied by self-assembly of oxime/oximato species formed,[7] oxidation of coordinated oximes to give nitrosoalkanes,[8] nitrosylation of metal centers,[9] the redox duality of oxime species toward one and the same metal,[10] observation of N−O bond cleavage in oxidative addition of oximes,[11] and facile dehydration and formation of coordinated nitriles,[12] have been reported in the last 3 years.

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(1) (a) St. Petersburg State University. Fax: +7-812-428 6939. E-mail: kukushkin@VK2100.spb.edu. (b) St. Petersburg State Technological Institute. E-mail: inorg@tu.spb.ru. (c) Instituto Supérior Técnico. E-mail: pombeiro@alfa.ist.utl.pt. Fax: +351-1-846-4455. (d) Permanent address: Institut für Organische Chemie und Biochemie der Technischen Universität München, Lichtenbergstr. 4, D-85 747 Garching, Germany. E-mail: rherrman@nucleus.org.chemie.tu-muenchen.de.

(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.

(3) (a) Schrauzer, G. N. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 417; *Angew. Chem.* **1976**, *88*, 465. (b) Dixit, N. S.; Patel, C. C. *J. Indian Chem. Soc.* **1977**, *54*, 176. (c) Yamada, S.; Kuma, H. *Kagaku (Kyoto)* **1978**, *33*, 231; *Chem. Abstr.* **1978**, *88*, 202252m. (d) 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. (e) Voiculescu, N.; Dominte, L. *Rev. Chim. (Bucharest)* **1983**, *34*, 973.

(4) (a) Simonov, Yu. A.; Shkurpelo, A. I.; Budnikov, S. S.; Botoshanskii, M. M.; Malinovskii, T. I. *Kristallokhim. 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.

(5) (a) Stynes, D. V. *Pure Appl. Chem.* **1988**, *60*, 561. (b) Singh, R. P.; Singh, N. K. *Asian J. Chem. Rev.* **1991**, *2*, 62. (c) Dash, K. C. *Adv. Organomet., Proc. Indo-Sov. Symp. Organomet. Chem.* **1988**, *1*, 82; *Chem. Abstr.* **1991**, *115*, 125450w. (d) Garnovsky, A. D. *Koord. Khim.* **1993**, *19*, 394. (e) 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. (f) Sakharov, S. G.; Buslaev, Yu. A. *Koord. Khim.* **1994**, *20*, 3. (g) Watanabe, Y.; Akazome, M.; Kondo, T. *Yuki Gosei Kagaku Kenkyusho Koenshu* **1994**, *8*, 50; *Chem. Abstr.* **1984**, *121*, 56944v.

(6) Kukushkin, V. Yu.; Tudela, D.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **1996**, *156*, 333 and references therein.

(7) Kukushkin, V. Yu.; Nishioka, T.; Tudela, D.; Isobe, K.; Kinoshita, I. *Inorg. Chem.* **1997**, *36*, 6157.

(8) Kukushkin, V. Yu.; Tudela, D.; Izotova, Y. A.; Belsky, V. K.; Stash, A. I. *Inorg. Chem.* **1996**, *35*, 4926.

(9) (a) Kukushkin, Yu. N.; Bavina, M. V.; Zinchenko, A. V. *Zh. Obshch. Khim.* **1996**, *66*, 1572. (b) Kukushkin, Yu. N.; Bavina, M. V.; Zinchenko, A. V. *Zh. Obstch. Khim.* **1996**, *66*, 1591.

(10) Guedes da Silva, M. F. C.; Izotova, Yu. A.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chim. Acta* **1998**, *277*, 83.

(11) (a) Ferreira, C. M. P.; Guedes da Silva, M. F. C.; Kukushkin, V. Yu.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1998**, 325. (b) Tillack, A.; Arndt, P.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Z. Anorg. Allg. Chem.* **1998**, *624*, 737.

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As far as addition reactions of oximes are concerned, it is well-documented that oximes are ambidentate nucleophiles and their *N*- or *O*-alkylation, acylation, and arylation have been extensively studied and reviewed[13] in organic chemistry. Similar processes involving metal complexes are also known although scarce.[14,15] Metal-mediated *iminoacylation* of oximes is an even lesser explored area, and only one example of such a reaction has been published so far. Thus, Grigg et al.[16] and concurrently Zerbib et al.[17] reported one-pot multistep processes between oxovanadium(IV) aldoxime and ketoxime complexes, for example [$VO\{C_6H_4(O)CH{=}NOH\}_2$], under treatment with acetonitrile. In the course of oxidation of the vanadium center, loss of one oxime ligand, and addition of MeCN, the iminoacyl oxovanadium complex [$VO_2\{C_6H_4(O)CH{=}NOC(Me){=}NH\}$] is formed.

Despite the appearance of the above-mentioned publications,[16,17] research in the field of metal-mediated iminoacylation was pioneered by Natile and co-workers.[18] They reported at a conference[18] that when $^tBuMeC{=}NOH$ reacts with [$PdCl_2(PhCN)_2$], the product of addition of the oxime to coordinated $PhC{\equiv}N$, e.g. [$PdCl_2(NH{=}CPhON{=}CMeBu^t)_2$], is formed along with other substituted and cyclometalated species; the iminoacyl complex was detected but not structurally characterized. These certainly intriguing findings were not further developed.[19] Taking into account our ongoing interest in the chemistry of both oximes[6−11,20] and nitriles,[21−23] we felt that such additions deserve additional studies. We now report on a high-yield systematic way for facile metal-assisted addition of oximes to coordinated nitriles to give iminoacylated species.

Experimental Section

Materials and Instrumentation. Oximes were purchased from Aldrich. Solvents were obtained from commercial sources and used as received. C, H, and N elemental analyses were carried out by the Microanalytical Services of the Instituto Supérior Técnico and St. Petersburg Technological Institute, while Cl and Pt were analyzed by the authors. Decomposition points were determined on a Kofler table. For TLC, Silufol UV 254 SiO_2 plates have been used. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrixes of samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Mass calibration for the data system acquisition was achieved using CsI. Infrared spectra (4000−220 cm^{-1}) were recorded on a Nicolet FT 360 instrument in KBr pellets. ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature. ^{195}Pt spectra were recorded without ^1H decoupling at a frequency of 64.507 MHz and a spectral width of 100 kHz, using a 90° pulse (12.2 μs), an acquisition time of 0.64 s, and a delay of 0.05 s. Chemical shifts are quoted relative to $Na_2[PtCl_6]$ (0 ppm) and were measured versus aqueous $K_2[PtCl_4]$ (−1630 ppm), the half-height line width being given in parentheses.

Synthetic Work and Characterization. Complexes [$PtCl_4(RCN)_2$] (R = Me, Ph) were prepared according to the published methods.[24,25] Starting material for preparation of [$PtCl_4(PhCH_2CN)_2$], e.g. the platinum(II) compound *trans*-[$PtCl_2(PhCH_2CN)_2$],[26] was synthesized similarly to [$PtCl_2(PhCN)_2$],[27] i.e. by heating [$PtCl_2(MeCN)_2$] in benzyl cyanide. [$PtCl_4(PhCH_2CN)_2$] was prepared by treatment of *trans*-[$PtCl_2(PhCH_2CN)_2$] with Cl_2 in chloroform at room temperature.

[$PtCl_4(PhCH_2CN)_2$]. Anal. Calcd for $C_{16}H_{14}N_2Cl_4Pt$: C, 33.6; H, 2.5; N, 4.9; Cl, 24.8; Pt, 34.2. Found: C, 32.9; H, 2.3; N, 5.3; Cl, 25.0; Pt, 34.4. FAB$^+$-MS, *m/z*: 465 [M − 3Cl]$^+$, 429 [M − 4Cl −H]$^+$. Mp = 166−167 °C. TLC on SiO_2: $R_f = 0.62$ (eluent 2:1 Me_2CO/$CHCl_3$). IR spectrum (selected bands), cm^{-1}: 2337 m-w $\nu(C{\equiv}N)$, 355 m-s, and 347 m-s $\nu(Pt{-}Cl)$. ^1H NMR spectrum in $CDCl_3$, δ: 4.56 (s, 2*H*, CH_2), 7.28−7.45 (m, 5*H*, Ph). Solubility of the complex in weak donor $CDCl_3$ is insufficient to measure the $^{13}C\{^1H\}$ NMR spectrum at reasonable accumulation time.

Reaction of [$PtCl_4(RCN)_2$] (R = Me, CH_2Ph, Ph) with $Me_2C{=}NOH$, $(C_4H_8)C{=}NOH$, $(C_5H_{10})C{=}NOH$, $PhC(H){=}NOH$, or *o*-$(HO)C_6H_4C(H){=}NOH$. In a typical experiment, [$PtCl_4(MeCN)_2$] (0.15 g, 0.36 mmol) is suspended in acetonitrile (10 mL) at room temperature, the oxime (0.90 mmol) is added, and the reaction mixture is heated with stirring at 55−60 °C for 10 min until homogenization of the reaction mixture. A bright yellow solution formed is evaporated to dryness and washed with diethyl ether (five 3-mL portions) to remove the excess of the oxime. Complexes **6**−**14** derived from [$PtCl_4(RCN)_2$] (R = CH_2Ph, Ph) can be prepared analogously but with the use of chloroform as a solvent. Yields are 90−95%.

[$PtCl_4(NH{=}C(Me)ON{=}CMe_2)_2$] (1). Anal. Calcd for $C_{10}H_{20}N_4Cl_4O_2Pt$: C, 21.3; H, 3.6; N, 9.9; Cl, 25.1; Pt, 34.5. Found: C, 21.3; H, 2.7; N, 9.4; Cl, 25.3; Pt, 34.0. FAB$^+$-MS, *m/z*: 529 [M − Cl]$^+$, 494 [M − 2Cl]$^+$, 460 [M − 3Cl + H]$^+$. Mp = 194 °C. TLC on SiO_2: $R_f = 0.63$ (eluent $CHCl_3$). IR spectrum (selected bands), cm^{-1}: 3290 m-w $\nu(N{-}H)$, 1655 and 1633 s $\nu(C{=}N)$, 1192 m $\nu(C{-}O)$, 347 m-s $\nu(Pt{-}Cl)$. ^1H NMR spectrum in $CDCl_3$, δ: 2.64 (s, 3*H*, $={C}{\mathit{Me}}O$), 2.09 and 2.11 (two s, 3*H* each, $={C}{\mathit{Me}}_2$), 8.45 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$

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(12) Kukushkin, Yu. N.; Bavina, M. V.; Zinchenko, A. V.; Belsky, V. K.; Kukushkin, V. Yu. *Polyhedron* **1997**, *16*, 2429.

(13) Metzger, H. In *Houben-Weyl's Methoden der organischen Chemie*, 4th ed.; Müller, E., Ed.; G. Thieme Verlag: Stuttgart, Germany, 1968; Stickstoffverbindungen I, Teil 4, Vol. 10/4, p 217.

(14) (a) Kazankov, G. M.; Dyachenko, O. G.; Nemukhin, A. V.; Ryabov, A. D. *Mendeleev Commun.* **1997**, 159. (b) Maeda, K.; Hosokawa, T.; Murahashi, S.-I.; Moritani, I. *Tetrahedron Lett.* **1973**, 5075. (c) Hosokawa, T.; Shimo, N.; Maeda, K.; Sonoda, A.; Murahashi, S.-I. *Tetrahedron Lett.* **1976**, 383. (d) Baker, R.; Nobbs, M. S. *Tetrahedron Lett.* **1977**, 3759. (e) Hutton, A. T.; McEwan, D. M.; Show, B. L.; Wilkinson, S. W. *J. Chem. Soc., Dalton Trans.* **1983**, 2011. (f) Alemagna, A.; Baldoli, C.; Del Buttero, P.; Licandro, E.; Maiorana, S. *Synthesis* **1987**, 192. (g) Alemagna, A.; Baldoli, C.; Del Buttero, P.; Licandro, E.; Maiorana, S. *J. Chem. Soc., Chem. Commun.* **1985**, 417. (h) Constable, A. G.; McDonald, W. S.; Sawkins, L. C.; Show, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1992.

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

(16) Grigg, J.; Collison, D.; Garner, C. D.; Helliwell, M.; Tasker, P. A.; Thorpe, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1807.

(17) Zerbib, V.; Robert, F.; Gouzerh, P. *J. Chem. Soc., Chem. Commun.* **1993**, 2179.

(18) Caglioti, L.; Galli, B.; Gasparrini, F.; Natile, G. In *Congresso Interdivisionale della Societa Chimica Italiana*, San Benedetto del Tronto, Atti, Italy; Soc Chim Ital: Rome, 1990; p 521.

(19) Natile, G. Personal Communication, **1998**.

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

(21) (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) Kukushkin, V. Yu.; Aleksandrova, E. A.; Kukushkin, Yu. N. *Zh. Obshch. Khim.* **1995**, *65*, 1937; *Russ. J. Gen. Chem. (Engl. Transl.)* **1995**, *65*, 1777. (c) Kukushkin, V. Yu.; Nishioka, T.; Nakamura, S.; Kinoshita, I.; Isobe, K. *Chem. Lett.* **1997**, 189.

(22) (a) Kukushkin, Yu. N. *Koord. Khim.* **1998**, *24*, 185 and references therein. (b) Pearson, C.; Beauchamp, A. L. *Inorg. Chem.* **1998**, *37*, 1242. (c) Kukushkin, Yu. N.; Larionova Yu. E. *Zh. Obshch. Khim.* **1994**, *64*, 1409.

(23) (a) Pombeiro, A. J. L. *New J. Chem.* **1994**, *18*, 163. (b) Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1996**, *526*, 237. (c) Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1994**, 3299. (d) Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Amatore, C.; Verpeaux, J.-N. *Organometallics* **1994**, *13*, 3943. (e) Fraústo da Silva, J. J. R.; Guedes da Silva, M. F. C.; Henderson, R. A.; Pombeiro, A. J. L.; Richards, R. L. *J. Organomet. Chem.* **1993**, *461*, 141. (f) Guedes da Silva, M. F. C.; Ferreira, C. M. P.; Branco, E. M. P. R. P.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Michelin, R. A.; Belluco, U.; Bertani, R.; Mozzon, M.; Bombieri, G.; Benetollo, F.; Kukushkin, V. Yu. *Inorg. Chim. Acta* **1997**, *265*, 267.

(24) Kukushkin, V. Yu.; Tkachuk, V. M. *Z. Anorg. Allg. Chem.* **1992**, *613*, 123.

(25) *Synthesis of Complex Compounds of the Platinum Group Metals* [in Russian], Chernyaev, I. I., Ed.; Nauka: Moscow, 1964; p 130.

(26) (a) Kukushkin, V. Yu.; Tkachuk, V. M.; Vorobiov-Desiatovsky, N. V. *Inorg. Synth.* **1998**, *32*, 144. (b) Kukushkin, V. Yu. *Platinum Met. Rev.* **1998**, *42*, 1.

(27) Kukushkin, Yu. N.; Pakhomova, T. B. *Zh. Obshch. Khim* **1995**, *65*, 330.

NMR spectrum in CDCl$_3$, δ: 174.3 (=*C*MeO), 166.8 (=*C*Me$_2$), 21.8, 18.0, and 17.6 (*Me* groups). ^{195}Pt NMR spectrum in CDCl$_3$, δ: −160 (780 Hz).

[PtCl$_4${NH=C(Me)ON=C(C$_4$H$_8$)}$_2$] (2). Anal. Calcd for $C_{14}H_{24}N_4Cl_4O_2Pt$: C, 27.2; H, 3.9; N, 9.1; Cl, 23.0; Pt, 31.6. Found: C, 28.5; H, 4.0; N, 9.1; Cl, 22.8; Pt, 31.5. FAB$^+$-MS, *m/z*: 581 [M − Cl]$^+$, 546 [M − 2Cl]$^+$, 510 [M − 3Cl]$^+$. Mp = 191 °C. TLC on SiO$_2$: R_f = 0.71 (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3283 m-w ν(N−H), ca. 1655 (sh) and 1637 s ν(C=N), 1175 m ν(C−O), 354 m-s and 342 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 2.61 (s, 3*H*, =C*Me*O), 1.85 and 2.55 (two m, 4*H* each, =C{C$_4$*H*$_8$}), 8.39 (s, br, 1*H*, N*H*). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$, δ: 174.4 (=*C*MeO), 178.2 (=*C*{C$_4$H$_8$}), 31.6, 30.1, 24.9, 24.3 (*C*$_4$H$_8$), 18.0 (*Me*). ^{195}Pt NMR spectrum in CDCl$_3$, δ: −155 (780 Hz).

[PtCl$_4${NH=C(Me)ON=C(C$_5$H$_{10}$)}$_2$] (3). Anal. Calcd for $C_{16}H_{28}N_4Cl_4O_2Pt$: C, 29.8; H, 4.4; N, 8.7; Cl, 22.0; Pt, 30.2. Found: C, 30.2; H, 4.4; N, 8.8; Cl, 22.4; Pt, 30.3. FAB$^+$-MS, *m/z*: 538 [M − 3Cl + H]$^+$. Mp = 182 °C. TLC on SiO$_2$: R_f = 0.75 (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3295 m-w ν(N−H), 1656 and 1633 s ν(C=N), 1196 m ν(C−O), 348 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 2.74 (s + d, $^4J_{PtH}$ 3.3 Hz, 3*H*, =C*Me*O), 1.66 (m, 2*H*), 1.75 (m, 4*H*), 2.38 (“t”, J_{HH} 4.4 Hz, 2*H*) and 2.58 (“t”, J_{HH} 4.4 Hz, 2*H*) (=C{C$_5$*H*$_{10}$}), 8.63 (s, br, 1*H*, N*H*.). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$, δ: 174.1 (=*C*MeO), 170.5 (=*C*{C$_5$H$_{10}$}), 31.8, 27.2, 26.6, 25.6, 25.0 (*C*$_5$H$_{10}$), 18.3 (*Me*). ^{195}Pt NMR spectrum in CDCl$_3$, δ: −156 (970 Hz).

[PtCl$_4$(NH=C(Me)ON=C(H)Ph)$_2$] (4). Anal. Calcd for $C_{18}H_{20}N_4Cl_4O_2Pt$: C, 32.7; H, 3.1; N, 8.5; Cl, 21.5; Pt, 29.5. Found: C, 32.8; H, 3.1; N, 8.4; Cl, 22.0; Pt, 29.7. All our attempts to detect in a FAB$^+$ mass spectrum any group of peaks which belong to platinum-containing species failed. Mp = 190 °C. TLC on SiO$_2$: R_f = 0.65 (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3294 m-w ν(N−H), 1668 and 1621 s ν(C=N), 1192 m ν(C−O), 347 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 2.85 (s, 3*H*, =C*Me*O), 7.49 (m, 2*H*), 7.56 (m, 1*H*) and 7.73 (“d”, J_{HH} 4.8 Hz, 2*H*) (=CH*Ph*), 8.53 (s, 1*H*, =C*H*−), 8.74 (s, br, 1*H*, N*H*). The solubility of the complex is insufficient to measure the ^{13}C{^{1}H} and ^{195}Pt NMR spectra at a reasonable accumulation time.

[PtCl$_4${NH=C(Me)ON=C(H)C$_6$H$_4$(OH)-*o*}$_2$] (5). Anal. Calcd for $C_{18}H_{20}N_4Cl_4O_4Pt$: C, 31.2; H, 2.9; N, 8.1; Cl, 20.5; Pt, 28.1. Found: C, 31.3; H, 2.8; N, 8.2; Cl, 20.7; Pt, 27.8. FAB$^+$-MS, *m/z*: 621 [M − 2Cl]. This complex does not have a characteristic melting point. On heating it decomposes above 205 °C. TLC on SiO$_2$: R_f = 0.54 (eluent 4:1 CHCl$_3$/Me$_2$CO, v/v). IR spectrum (selected bands), cm^{-1}: 3467 m ν(O−H), 3292 m-w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1659 and 1616 s; 344 m-s ν(Pt−Cl). ^{1}H NMR spectrum in DMSO-d_6, δ: 2.75 (s, 3*H*, =C*Me*O), 6.93 (“t”, J_{HH} 5.0 Hz, 1*H*), 7.00 (“d”, J_{HH} 5.6 Hz, 1*H*), 7.43 (“t”, J_{HH} 4.8 Hz, 1*H*) and 7.63 (“d”, J_{HH} 5.2 Hz, 1*H*) (C$_6$*H*$_4$OH), 9.02 (s, 1*H*, =C*H*−), 9.12 (s + d, $^2J_{PtH}$ 28.1 Hz, 1*H*, N*H*), 10.71 (s, 1*H*, O*H*). ^{13}C{^{1}H} NMR spectrum in DMSO-d_6, δ: 174.4 (=*C*(Me)O), 155.0 (=*C*H−), 158.2, 134.6, 127.8, 119.7, 116.8, 114.6 (*C*$_6$H$_4$OH), 17.8 (*Me*). ^{195}Pt NMR spectrum in DMSO-d_6, δ: −90 (780 Hz).

[PtCl$_4$(NH=C(CH$_2$Ph)ON=CMe$_2$)$_2$] (6). Anal. Calcd for $C_{22}H_{28}N_4Cl_4O_2Pt$: C, 36.8; H, 3.9; N, 7.8; Cl, 19.8; Pt, 27.2. Found: C, 36.4; H, 3.9; N, 7.6; Cl, 20.2; Pt, 26.8. FAB$^+$-MS, *m/z*: 646 [M − 2Cl]$^+$, 611 [M − 3Cl]$^+$. Mp = 177 °C. TLC on SiO$_2$: R_f = 0.48 (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3278 m-w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1657 m-s and 1626 s; 353 and 340 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 1.76 and 2.03 (two s, 3*H* each, =C*Me*$_2$), 4.65 (s, 2*H*, C*H*$_2$Ph), 7.30 (m, 3*H*) and 7.41 (m, 2*H*) (CH$_2$*Ph*), 8.80 (s, br, 1*H*, N*H*). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$, δ: 173.9 (=*C*(CH$_2$Ph)), 166.6 (=*C*Me$_2$), 132.9, 130.0, 128.4, 127.3 (CH$_2$*Ph*), 37.8 (*C*H$_2$Ph), 21.8 and 17.3 (*Me* groups).^{195}Pt NMR spectrum in CDCl$_3$, δ: −174 (quint., $^1J_{Pt^{14}N}$ 220 Hz).

[PtCl$_4${NH=C(CH$_2$Ph)ON=C(C$_4$H$_8$)}$_2$] (7). Anal. Calcd for $C_{26}H_{32}N_4Cl_4O_2Pt$: C, 40.6; H, 4.2; N, 7.3; Cl, 18.4; Pt, 25.4. Found: C, 40.3; H, 4.2; N, 7.4; Cl, 18.2; Pt, 25.0. FAB$^+$-MS, *m/z*: 699 [M − 2Cl]$^+$. Mp = 164 °C. TLC on SiO$_2$: R_f = 0.56 (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3285 m-w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1627 and 1607 s; 355 m-s and 343 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 1.74 (m, 4*H*), 2.23 (“t”, J_{HH} 6.9 Hz, 2*H*) and 2.49 (“t”, J_{HH} 6.6 Hz, 2*H*) (=C{C$_4$*H*$_8$}), 4.59 (s, 2*H*, C*H*$_2$Ph), 7.30 (m, 3*H*) and 7.40 (m, 2*H*) (CH$_2$*Ph*), 8.73 (s + d, $^2J_{PtH}$ 29 Hz, 1*H*, NH). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$, δ: 178.0 (=*C*{C$_4$H$_8$}), 173.9 (=*C*CH$_2$Ph), 132.9, 130.0, 128.3, and 127.3 (CH$_2$*Ph*), 37.7 (*C*H$_2$Ph), 31.5, 29.7, 25.0, and 24.3 (*C*$_4$H$_8$). ^{195}Pt NMR spectrum in CDCl$_3$, δ: −163 (900 Hz).

[PtCl$_4${NH=C(CH$_2$Ph)ON=C(C$_5$H$_{10}$)}$_2$] (8). Anal. Calcd for $C_{28}H_{36}N_4Cl_4O_2Pt$: C, 42.2; H, 4.6; N, 7.0; Cl, 17.8; Pt, 24.5. Found: C, 42.3; H, 3.9; N, 7.3; Cl, 17.9; Pt, 24.6. FAB$^+$-MS, *m/z*: 760 [M − Cl − H]$^+$, 726 [M − 2Cl]$^+$, 691 [M − 3Cl]$^+$, 654 [M − 4Cl − H]$^+$. Mp = 182 °C. TLC on SiO$_2$: R_f = 0.67 (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3278 m-w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1657 and 1633 s; 354 and 345 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 1.57 (m, 4*H*), 1.72 (m, 2*H*), 2.22 (m, 2*H*) and 2.33 (m, 2*H*) (=C{C$_5$*H*$_{10}$}), 4.64 (C*H*$_2$Ph), 7.26 (m, 2*H*), 7.31 (m, 1*H*) and 7.40 (m, 2*H*) (CH$_2$*Ph*), 8.81 (s + d, $^2J_{PtH}$ ca. 38 Hz, 1*H*, N*H*). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$, δ: 174.7 (=*C*(CH$_2$Ph)), 171.7 (=*C*{C$_5$H$_{10}$}), 133.5, 130.5, 128.9, 127.8 (CH$_2$*Ph*), 38.4 (*C*H$_2$Ph), 32.3, 27.7, 27.1, 26.1, 25.5 (*C*$_5$H$_{10}$).^{195}Pt NMR spectrum in CDCl$_3$, δ: −166 (840 Hz).

[PtCl$_4${NH=C(CH$_2$Ph)ON=C(H)Ph}$_2$] (9). Anal. Calcd for $C_{30}H_{28}N_4Cl_4O_2Pt$: C, 44.3; H, 3.5; N, 6.9; Cl, 17.4; Pt, 24.0. Found: C, 44.1; H, 3.8; N, 6.9; Cl, 17.7; Pt, 24.2. FAB$^+$-MS, *m/z*: 742 [M − 2Cl]$^+$, 707 [M − 3Cl]$^+$. The compound has no characteristic melting point. On heating it decomposes above 200 °C. TLC on SiO$_2$: R_f = 0.64 (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3255 m-w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1695 and 1678 s; 353 m-s and 344 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 4.71 (s, 2*H*, C*H*$_2$Ph), 7.33 (m, 3*H*) and 7.47 (m, 2*H*) (CH$_2$*Ph*), 7.47 (m, 3*H*) and 7.67 (“d”, J_{HH} 8.1 Hz, 2*H*) (=CH*Ph*), 8.35 (s, 1*H*, =C*H*−), 9.03 (s + d, $^2J_{PtH}$ 35 Hz, 1*H*, N*H*). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$, δ: 174.2 (=*C*CH$_2$Ph), 157.3 (=*C*H−), 133.5, 129.9, 128.5, and 127.4 (CH$_2$*Ph*), 132.5, 129.2, 128.9, and 128.0 (=CH*Ph*), 37.6 (*C*H$_2$Ph). ^{195}Pt NMR spectrum in CDCl$_3$, δ: −202 (900 Hz).

[PtCl$_4${NH=C(CH$_2$Ph)ON=C(H)C$_6$H$_4$(OH)-*o*}$_2$] (10). Anal. Calcd for $C_{30}H_{28}N_4Cl_4O_4Pt$: C, 42.6; H, 3.3; N, 6.6; Cl, 16.8; Pt, 23.1. Found: C, 42.7; H, 4.5; N, 6.3; Cl, 17.3; Pt, 22.6. FAB$^+$-MS, *m/z*: 774 [M − 2Cl]$^+$, 739 [M − 3Cl]$^+$. The compound has no characteristic melting point. On heating it decomposes above 200 °C. TLC on SiO$_2$: R_f = 0.45 (eluent 1:14 Me$_2$CO/CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3390 m ν(O−H), 3255 m-w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1669 and 1650 s; 349 m-s and 345 m-s ν(Pt−Cl). ^{1}H NMR spectrum in DMSO-d_6, δ: 4.64 (s, 2*H*, C*H*$_2$Ph), 7.31 (m, 1*H*), 7.36 (m, 2*H*), and 7.46 (m, 2*H*) (CH$_2$*Ph*), 6.91 (“t”, J_{HH} 7.2 Hz, 1*H*), 6.96 (“d”, J_{HH} 8.7 Hz, 1*H*), 7.39 (m, 1*H*), and 7.59 (“d”, J_{HH} 8.1 Hz, 2*H*) (C$_6$*H*$_4$OH), 8.84 (s, 1*H*, =C*H*−), 8.96 (s + d, $^2J_{PtH}$ 35 Hz, 1*H*, N*H*), O*H* was not observed. ^{13}C{^{1}H} NMR spectrum in DMSO-d_6, δ: 174.3 (=*C*CH$_2$Ph), 155.1 (=*C*H−), 133.0, 129.5, 128.5, and 127.3 (CH$_2$*Ph*), 158.2, 134.6, 128.0, 119.6, 116.7, and 114.2 (*C*$_6$H$_4$-OH), 36.5 (*C*H$_2$Ph). ^{195}Pt NMR spectrum in DMSO-d_6, δ: −94 (800 Hz).

[PtCl$_4$(NH=C(Ph)ON=CMe$_2$)$_2$] (11). Anal. Calcd for $C_{20}H_{24}N_4Cl_4O_2Pt$: C, 34.9; H, 3.5; N, 8.1; Cl, 20.6; Pt, 28.30. Found: C, 34.7; H, 3.6; N, 8.5; Cl, 20.8; Pt, 28.4. FAB$^+$-MS, *m/z*: 618 [M − 2Cl]$^+$, 583 [M − 3Cl]$^+$. Mp = 199 °C. TLC on SiO$_2$: R_f = 0.38 (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3210 m-w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1610, 1590, and 1575 s; 350 m-s and 343 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 2.05 and 2.10 (two s, 3*H* each, =C*Me*$_2$), 7.43 (m, 2*H*), 7.55 (m, 1*H*), and 7.90 (m, 2*H*) (=C*Ph*), 9.21 (s, br, 1*H*, N*H*). The solubility of the complex in CDCl$_3$ is insufficient to measure ^{13}C{^{1}H} and ^{195}Pt NMR spectra at reasonable accumulation time, while in a better solvent, e.g. DMSO-d_6, this complex is unstable.

[PtCl$_4${NH=C(Ph)ON=C(C$_4$H$_8$)}$_2$] (12). Anal. Calcd for $C_{24}H_{28}N_4Cl_4O_2Pt$: C, 38.9; H, 3.8; N, 7.6; Cl, 19.1; Pt, 26.3. Found: C, 39.1; H, 4.0; N, 7.4; Cl, 19.4; Pt, 26.1. FAB$^+$-MS, *m/z*: 635 [M − 3Cl]$^+$. Mp = 163 °C. TLC on SiO$_2$: R_f = 0.44 (eluent Me$_2$CO). IR spectrum (selected bands), cm^{-1}: 3274 m-w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1600, 1579, and 1575 s; 356 m-s and 347 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 1.82 and 2.56 (two m, 4*H* each, =C{C$_4$*H*$_8$}), 7.41 (“t”, J_{HH} 6.9 Hz, 2*H*), 7.53 (“t”, J_{HH} 6.0 Hz, 1*H*), and 7.89 (“d”, J_{HH} 6.9 Hz, 2*H*) (=C*Ph*), 9.10 (s, br, 1*H*, N*H*).

Table 1. Crystallographic Data for *trans*-[PtCl$_4$(NH=C(Me)ON=CMe$_2$)$_2$] (**1**) and *trans*-[PtCl$_4${NH=C(Me)ON=C(C$_5$H$_{10}$)}$_2$] (**3**)

	1	**3**
empirical formula	$C_{10}H_{20}N_4Cl_4O_2Pt$	$C_{16}H_{28}N_4Cl_4O_2Pt$
fw	565.19	645.31
temp, °C	20(2)	20(2)
λ, Å	0.710 73	0.710 73
space group	*C*2/*c* (No. 16)	*Pbca* (No. 61)
a, Å	17.767(4)	10.383(2)
b, Å	8.602(2)	12.615(3)
c, Å	12.234(2)	17.844(4)
β, deg	104.34(3)	90
V, Å^3	1811.5(7)	2337.2(9)
Z	4	4
ρ_{calcd}, g/cm^3	2.072	1.834
μ(Mo Kα) cm^{-1}	83.43	64.79
$R_1{}^a$	0.0266	0.0263
w$R_2{}^b$	0.0615	0.0673

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$ (for **1**), $w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 1.4083P]$ (for **3**).

^{13}C{^{1}H} NMR spectrum in CDCl$_3$, δ: 177.9 (=*C*{C$_4$H$_8$}), 172.0 (=*C*Ph), 132.1, 130.1, and 127.2 (=C*Ph*; one carbon was not observed), 31.7, 30.2, 25.0, and 24.3 (*C*$_4$H$_8$). ^{195}Pt NMR spectrum in CDCl$_3$, δ: −120 (780 Hz).

[PtCl$_4${NH=C(Ph)ON=C(C$_5$H$_{10}$)}$_2$] (13). Anal. Calcd for $C_{26}H_{32}N_4Cl_4O_2Pt$: C, 40.6; H, 4.2; N, 7.3; Cl, 18.4; Pt, 25.4. Found: C, 40.4; H, 4.3; N, 6.9; Cl, 18.0; Pt, 25.0. FAB$^+$-MS, *m*/*z*: 699 [M − 2Cl]$^+$, 663 [M − 3Cl]$^+$. Mp = 169−170 °C. TLC on SiO$_2$: $R_f = 0.46$ (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3230 w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1630, 1605, and 1585 s; 345 m-s ν(Pt−Cl). ^{1}H NMR spectrum in CDCl$_3$, δ: 1.65 (m, 4*H*), 1.76 (m, 2*H*), 2.38 ("t", J_{HH} 6.6 Hz, 2*H*), and 2.52 ("t", J_{HH} 6.0 Hz, 2*H*) (=C{C$_5$*H*$_{10}$}), 7.42 ("t", J_{HH} 7.5 Hz, 2*H*), 7.45 (m, 1*H*), and 7.89 (m, 2*H*) (=C*Ph*), 9.22 (s + d, $^2J_{\mathrm{PtH}}$ 36 Hz, 1*H*, N*H*). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$, δ: 172.2 (=*C*Ph), 171.1 (=*C*{C$_5$H$_{10}$}), 132.0, 130.1, and 127.2 (=C*Ph*; one carbon was not observed), 31.9, 27.5, 26.6, 25.7, and 25.0 (*C*$_5$H$_{10}$). ^{195}Pt NMR spectrum in CDCl$_3$, δ: −120 (970 Hz).

[PtCl$_4${NH=C(Ph)ON=C(H)Ph}$_2$] (14). Anal. Calcd for $C_{28}H_{24}N_4Cl_4O_2Pt$: C, 42.8; H, 3.1; N, 7.1; Cl, 18.1; Pt, 24.8. Found: C, 42.7; H, 3.5; N, 6.7; Cl, 18.4; Pt, 24.5. All our attempts to detect in a FAB$^+$ mass-spectrum any group of peaks which belong to platinum-containing species failed. The compound has no characteristic melting point. On heating it decomposes above 200 °C. TLC on SiO$_2$: $R_f = 0.54$ (eluent CHCl$_3$). IR spectrum (selected bands), cm^{-1}: 3254 w ν(N−H); peaks in the ν(C=N) + ν(C=C) area are 1636, 1613, and 1602 s; 346 m-s ν(Pt−Cl). ^{1}H NMR spectrum in DMSO-d_6, δ: 7.54 (m, 3*H*) and 7.93 ("d", J_{HH} 8.1 Hz, 2H) (=C*Ph*), 7.54 (m, 3H) and 7.75 (m, 2*H*) (=CH*Ph*), 9.06 (s, 1*H*, =C*H*−); N*H* was not observed. Solubility of the complex in both CDCl$_3$ and DMSO-d_6 is insufficient to measure ^{13}C{^{1}H} and ^{195}Pt NMR spectra at reasonable accumulation time.

X-ray Structure Determination of *trans*-[PtCl$_4$(NH=C(Me)-ON=CMe$_2$)$_2$] (1) and *trans*-[PtCl$_4${NH=C(Me)ON=C(C$_5$H$_{10}$)}$_2$] (3). (Note: data for the latter complex are given below in brackets.) Bright-yellow plates of **1** and prisms of **3** were obtained directly from the reaction mixtures. Diffraction data were collected on an Enraf-Nonius CAD 4 [Syntex P$\bar{1}$] diffractometer. Cell parameters for both complexes were obtained from centered reflections with θ between 10 and 13°. Range of *hkl*: h = −20 to 20, *k* = 0 to 10, *l* = 0 to 14 [*h* = 0 to 12, *k* = 0 to 14, *l* = 0 to 20]. Standard reflections were measured every 60 min and showed practically no change with time (±1%). Diffractometer data were processed by the program PROFIT[28] 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 SHELXTL package.[29] 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.[30] All non-H atoms were treated anisotropically. H atoms were located in a difference Fourier map and refined isotropically. An extinction correction has been applied. Lorentz, polarization, and absorption corrections were made.[31] Crystal size: 0.30 × 0.28 × 0.08 [0.42 × 0.30 × 0.10] mm. $T_{\min}$ and $T_{\max}$ are 0.555 and 0.189 [0.512 and 0.119], respectively. Scattering factors are from ref 32. Crystal data are given in Table 1, and bond distances and angles, in Tables2 and 3.

Table 2. Bond Lengths (Å) and Angles (deg) for *trans*-[PtCl$_4$(NH=C(Me)ON=CMe$_2$)$_2$] (**1**)^a

Pt−N(1)	2.027(5)	N(1)−C(1)	1.268(7)
Pt−Cl(1)	2.314(2)	N(2)−C(3)	1.269(7)
Pt−Cl(2)	2.3106(16)	C(1)−C(2)	1.483(9)
Pt−Cl(3)	2.3195(18)	C(3)−C(4)	1.471(10)
O(1)−C(1)	1.335(7)	C(3)−C(5)	1.494(11)
O(1)−N(2)	1.454(6)		
N(1)#1−Pt−N(1)	174.7(3)	C(1)−O(1)−N(2)	113.3(4)
N(1)#1−Pt−Cl(2)	93.40(15)	C(1)−N(1)−Pt	135.1(4)
N(1)−Pt−Cl(2)	86.50(15)	C(3)−N(2)−O(1)	108.3(5)
Cl(2)−Pt−Cl(2)#1	177.94(7)	N(1)−C(1)−O(1)	122.6(5)
N(1)−Pt−Cl(1)	87.34(13)	N(1)−C(1)−C(2)	126.8(5)
Cl(2)−Pt−Cl(1)	88.97(4)	O(1)−C(1)−C(2)	110.6(5)
N(1)−Pt−Cl(3)	92.66(13)	N(2)−C(3)−C(4)	127.5(6)
Cl(2)−Pt−Cl(3)	91.03(4)	N(2)−C(3)−C(5)	115.1(7)
Cl(1)−Pt−Cl(3)	180.0	C(4)−C(3)−C(5)	117.5(6)

^{a} Symmetry transformations used to generate equivalent atoms: #1, $-x, y, -z + {}^1/_2$.

Table 3. Bond Lengths (Å) and Angles (deg) for *trans*-[PtCl$_4${NH=C(Me)ON=C(C$_5$H$_{10}$)}$_2$] (**3**)^a

Pt−N(1)	2.043(6)	C(1)−C(2)	1.489(12)
Pt−Cl(2)	2.313(2)	C(3)−C(8)	1.456(10)
Pt−Cl(1)	2.315(2)	C(3)−C(4)	1.504(12)
O−C(1)	1.340(8)	C(4)−C(5)	1.527(14)
O−N(2)	1.461(7)	C(5)−C(6)	1.53(2)
N(1)−C(1)	1.240(9)	C(6)−C(7)	1.50(2)
N(2)−C(3)	1.286(10)	C(7)−C(8)	1.509(13)
N(1)#1−Pt−N(1)	180.0	N(1)−C(1)−O	122.1(8)
N(1)#1−Pt−Cl(2)	87.0(2)	N(1)−C(1)−C(2)	128.9(8)
N(1)−Pt−Cl(2)	93.0(2)	O−C(1)−C(2)	109.0(8)
N(1)#1−Pt−Cl(1)	93.2(2)	N(2)−C(3)−C(8)	116.7(7)
N(1)−Pt−Cl(1)	86.8(2)	N(2)−C(3)−C(4)	126.5(8)
Cl(2)−Pt−Cl(1)	89.11(7)	C(8)−C(3)−C(4)	116.7(8)
Cl(2)#1−Pt−Cl(1)	90.89(7)	C(3)−C(4)−C(5)	110.3(9)
N(1)#1−Pt−Cl(1)#1	86.8(2)	C(6)−C(5)−C(4)	113.9(9)
Cl(1)−Pt−Cl(1)#1	180.0	C(7)−C(6)−C(5)	110.0(10)
C(1)−O−N(2)	113.0(6)	C(8)−C(7)−C(6)	110.4(9)
C(1)−N(1)−Pt	135.0(6)	C(3)−C(8)−C(7)	111.9(8)
C(3)−N(2)−O	109.5(6)		

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

Results and Discussion

Iminoacylation Reactions. The starting hypothesis for this work is that the addition of oximes to metal-bound nitriles should be facilitated in the case of strong electrophilic activation of RCN species. The latter property could be, in particular, reached by introducing acceptor groups R to RCN, use of

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

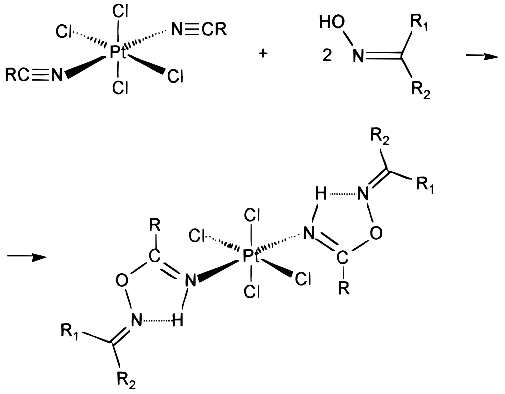
(29) Sheldrick, G. M. *SHELXTL User Manual*, rev. 3; Nicolet XRD Corp.: Madison, WI, 1981.

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

(31) 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.

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

Scheme 1. Iminoacylation of the Oximes



supporting ligands with pronounced π-acceptor properties, increasing the overall positive charge on a complex ion, and application of metal ions in the high and highest oxidation states.

Recently two of us found that the addition of NH_3 to coordinated nitriles in $[PtCl_n(MeCN)_2]$ ($n = 2, 4$) proceeds 10 times faster in the platinum(IV) compound as compared to the appropriate platinum(II) complex.[33] Moreover, electrophilic activation of acetonitrile by platinum(IV) ion is such that this ligand is subject to facile two-step hydrolysis leading to $[Pt^{IV}]-NH_3$ complexes and $MeCO_2H$.[34] These experimental observations stimulated our current studies on the addition of oximes to platinum(IV)-bound nitriles. We have found that the reaction of ketoxime or aldoxime with the platinum(IV) complexes *trans*-$[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph, Ph) proceeds under relatively mild conditions to yield stable iminoacyl compounds *trans*-$[PtCl_4(NH{=}C(R)ON{=}CR_1R_2)_2]$ (R = Me: $R_1 = R_2 =$ Me, **1**; $R_1R_2 = C_4H_8$, **2**; $R_1R_2 = C_5H_{10}$, **3**; $R_1R_2 =$ (H)Ph, **4**; $R_1R_2 =$ (H)C_6H_4(OH)-*o*, **5**. R = CH_2Ph: $R_1 = R_2 =$ Me, **6**; $R_1R_2 = C_4H_8$, **7**; $R_1R_2 = C_5H_{10}$, **8**; $R_1R_2 =$ (H)Ph, **9**; $R_1R_2 =$ (H)C_6H_4(OH)-*o*, **10**. R = Ph: $R_1 = R_2 =$ Me, **11**; $R_1R_2 = C_4H_8$, **12**; $R_1R_2 = C_5H_{10}$, **13**; $R_1R_2 =$ (H)Ph, **14**), and these results are reported in paragraphs that follow.

On treatment of the nitrile-based platinum(IV) complexes *trans*-$[PtCl_4(RCN)_2]$ with the oximes in MeCN (R = Me) or $CHCl_3$ (R = CH_2Ph, Ph) at 55−60 °C the reactions were completed in ca. 10 min. The iminoacyl complexes *trans*-$[PtCl_4(NH{=}C(R)ON{=}CR_1R_2)_2]$ (**1**−**14**) were isolated in 90−95% yields. Elemental analyses, FAB-MS (see Experimental Section), IR and ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectra, and X-ray data for **1** and **3** (see below) agree well with the proposed structure of Pt(IV) complexes with two newly formed ligands (Scheme 1).

The process is metal-mediated; e.g., interaction of *trans*-$[PtCl_4(MeCN)_2]$ and the oximes in *acetonitrile as a solvent* led almost quantitatively to the metal-bound iminoacylated oximes despite incomparably higher concentration of free MeCN. The ^1H NMR experiment shows that neither MeCN nor PhCN and $PhCH_2CN$ react with the oximes under the reaction or even more harsh (56 °C, 10 d) conditions, and this also supports the idea of the metal-mediated reaction. On the basis of these experiments, we suggest a similar reaction path for the additions with both *trans*-$[PtCl_4(MeCN)_2]$ and *trans*-$[PtCl_4(RCN)_2]$ (R = CH_2Ph, Ph). Complexes are presumably formed by nucleophilic attack of the oxime oxygen on the highly electrophilically activated carbon atom of the organonitrile. Previously, the additions of such protic nucleophiles as water−hydroxide, alcohols, sp^3-amines,[22a,35] sp^2-amines,[22b] and mercaptans[22c] to coordinated RCN species were reported.

IR and NMR Spectroscopic Results. Comparison of IR spectra of all the products with that of the starting materials shows disappearance of the C≡N stretching vibrations at ca. 2340 cm^{-1}. In **1**−**4** appearance of the two strong ν(C=N) vibrations at ca. 1660 and ca. 1625 cm^{-1}, a new medium-intensity band at ca. 1190 cm^{-1} which might be attributed[36a] to ν(C−O), and, eventually, appearance of N−H stretching vibrations which emerge at 3270−3300 cm^{-1} were observed. For **5**−**14** attribution of ν(C=N) and ν(C−O) peaks is less obvious because of overlapping with bands due to phenyl ring(s).

Both ^1H and $^{13}C\{^1H\}$ NMR spectra of the iminoacyl platinum(IV) compounds show typical patterns from the amidine and oxime moieties of the ligands. In $^{13}C\{^1H\}$ NMR spectra, the chemical shifts of the oxime N=*C* carbon show a relatively high variation (155.0−178.2 ppm) due to different environments introduced by the substituents R_1 and R_2. The amidine carbon shows the least variation in a fairly narrow range (172.0−174.4 ppm). In ^1H NMR spectra, the chemical shifts of the NH protons also fall in a comparatively narrow range, independent from the solvent (8.39−9.22 ppm); $^2J_{PtH}$ (ca. 28−36 Hz) was observed in some cases. This observation indicates similar overall structures in all the compounds and confirms the existence of a, albeit weak, hydrogen bond between the amidine hydrogen and oxime nitrogen in the ligand *E*-conformation not only in the solid state (see below) but also in solution.

For the compounds **1**−**5** derived from *trans*-$[PtCl_4(MeCN)_2]$, the ^1H-methyl resonance appears in a very narrow range (2.61−2.85 ppm) and occasionally shows a $^4J_{PtH}$ coupling (3.3 Hz for **3**). The ^{195}Pt NMR spectra show in general a broad signal of a half-height peak width of 780−970 Hz due to the nonresolved coupling to the ^{14}N nuclei, except for compound **6**, in which a quintet with a coupling constant $^1J_{^{195}Pt^{14}N}$ of 220 Hz was observed. The chemical shift range of −90 to −202 ppm is similar to that of complexes of the type $[PtCl_4(amine)_2]$[36b] or platinum(IV) porphyrins.[36c] No evidence for a *Z*-conformation can be derived from the NMR data.

X-ray Structure Determinations. Structures of compound **1** and **3** were determined by X-ray single-crystal diffraction. The coordination polyhedron of both **1** and **3** is a slightly distorted octahedron (Figures 1 and 2).

In **1**, the Pt atom is situated on a 2-fold axis, while in **3** it is in the center of symmetry. The two iminoacyl ligands in both **1** and **3** are in a trans configuration which is the thermodynami-

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(33) (a) Kukushkin, Yu. N.; Aleksandrova, E. A.; Pakhomova, T. B.; Vlasova, R. A. *Zh. Obshch. Khim.* **1994**, *64*, 705. (b) Kukushkin, Yu. N.; Aleksandrova, E. A.; Pakhomova, T. B. *Zh. Obshch. Khim.* **1994**, *64*, 151.

(34) Kukushkin, V. Yu.; Zenkevich, I. G.; Belsky, V. K.; Konovalov, V. E.; Moiseev, A. I.; Sidorov, E. O. *Inorg. Chim. Acta* **1989**, *166*, 79 and references therein.

(35) (a) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299. (b) Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1. (c) Endres, H. In *Comprehensive Coordination Chemistry*; G., Wilkinson, R. D., Gillard, J. A., McCleverty, Pergamon Press: Oxford, U.K., 1987; Vol. 2, p 261. (d) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic Press: London, 1976. (e) Hay, R. W. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1989; Vol. 2, p 280. (g) Kukushkin, Yu. N. *Reactivity of Coordination Compounds*; Khimiya: Leningrad, 1987; p 145 (in Russian). (h) Constable, E. C. *Metals and Ligand Reactivity. An Introduction to the Organic Chemistry of Metal Complexes*; VCH: Weinheim, Germany, 1995; p 65. (i) Parkins, A. W. *Platinum Met. Rev.* **1996**, *40*, 169.

(36) (a) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 2nd ed.; Methuen: London, 1996. (b) Hope, E. G.; Levason, W.; Powell, N. A. *Inorg. Chim. Acta* **1986**, *115*, 187. (c) Milgrom, L. R.; Zuurbier, R. J.; Gascoyne, J. M.; Thompsett, D.; Moore, B. C. *Polyhedron* **1994**, *13*, 209.

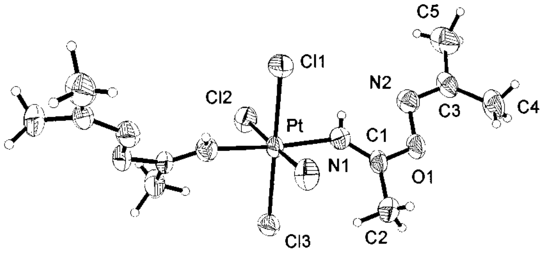


Figure 1. ORTEP drawing of *trans*-$[PtCl_4(NH{=}C(Me)ON{=}CMe_2)_2]$ (**1**) with atomic numbering scheme.

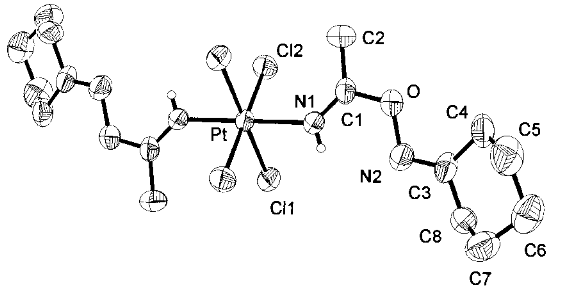
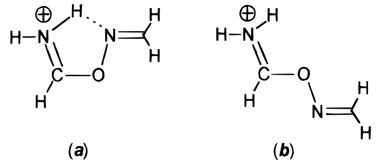


Figure 2. ORTEP drawing of *trans*-$[PtCl_4\{NH{=}C(Me)ON{=}C(C_5H_{10})\}_2]$ (**3**) with atomic numbering scheme.

cally stable form for metals in high oxidation state.[37] The values of the Pt−Cl bond distances (2.31−2.32 Å) agree well with previously characterized platinum(IV) chloride compounds.[34] In the iminoacyl ligands in their *E*-conformation, values of the two C═N bonds are almost identical and correspond to the mean values of the C═N double bonds.[38] All other bonds and angles are normal and perfectly agree with values of bond lengths in the structure of the *N*-acylamidinium salt $[^iPr(H)N{=}C(Ph)ON{=}CMe_2][SbCl_6]$, where the *E*-conformation was also observed.[39]

Hydrogen Bonding and Calculations. The structures of **1** and **3** were determined with relatively high accuracy; H coordinates are found from difference syntheses and were refined. The data obtained indicate intramolecular hydrogen bonding between imino hydrogen and uncoordinated oxime nitrogen. Indeed, the HN(1)C(1)O(1)N(2) skeletons are planar with maximum deviation 0.006 Å for the C(1) atom in **1** and 0.040 Å for the C(1) atom in **3**. In both **1** and **3**, the H atom is turned toward the lone pair of the N atom. Distances N(1)···N(2), and N(1)−H, N(1)H···N(2) are 2.605, 0.74, and 2.20 Å for **1** and 2.592, 0.71, and 2.25 Å for **3**, respectively; N(1)−H···N(2) angles are 115 and 111°, correspondingly. Values of the van der Waals radii for H and N ($1.20 + 1.55 = 2.75$ Å [40]) and some reported N···N (2.94−3.15 Å) and H···N (2.20 Å) distances in the case of NH···N bonding[41] also support this conclusion. In the context of the hydrogen bond observation in **1** and **3**, it is worthwhile to mention the results of X-ray structure determination of *E*-$[^iPr(H)N{=}C(Ph)ON{=}CMe_2][SbCl_6]$, where the $^iPr(H)N{=}$ hydrogen was calculated.[39] The existence of the *N*-acylamidinium in the *E*-conformation is believed[39] to be a result of the H-bonding.



(*a*) (*b*)

Figure 3. *E*-conformation (***a***) and *Z*-conformation (***b***) of the simplified ligand.

It might be perhaps reasonable to assume that the formation of the NH···N bond in $[Pt]{-}NH{=}C(R)ON{=}CR_1R_2$ species might be a reason for their one-end rather than bidentate *N,N*-coordination to platinum(IV). To clarify the influence of the hydrogen bond on the stabilization of the one-end-coordinated iminoacyls, calculations on a model compound, $H_2C{=}N{-}O{-}CH{=}NH_2^+$, were performed, using the program GAMESS-(US).[42] In this model, all substituents including the platinum site were replaced by hydrogens. The stretched *Z*-form, without a possibility to form the ═NH···N hydrogen bond, was compared with the hydrogen-bonded *E*-form (Figure 3), employing a double-ζ basis set[43a] with d-functions at the heavy atoms.

The geometry optimization led to stationary points with no imaginary frequencies in both cases. No other energy minima were found for conformations obtained by rotation around the C−O bond. The hydrogen-bonded form turned out to be 1.1 kcal/mol more stable, a quite low value. In comparison with the X-ray structure results, the N−N distance is well reproduced in the model (2.609 Å vs 2.605 Å in **1**), as well as the general tendencies in the N−C−O−N−C core. Although the model makes significant simplifications, in particular replacing platinum with hydrogen, the calculated values for the distances and angles of the core of heavy atoms remain in the range of 3σ of the observed ones. In detail, the model distinguishes the C═N bond lengths more (1.256 and 1.287 Å vs 1.268(7) and 1.269(7) Å in **1**) and suggests a somewhat shorter N−O bond (1.420 vs 1.454(6) Å in **1**). With respect to the hydrogen bond of the model (***a*** in Figure 3), the N−H distances are calculated to be 1.004 and 2.298 Å, respectively, with a N−H···N angle of 96.5°. This means that the hydrogen bond must be relatively weak, compared with the ideal situation where both donor atoms and the hydrogen are almost on a straight line. In fact, to get energies which allow for comparison, this ideal situation was approximated by calculating $H_2C{=}NH{\cdots}H{-}NH{=}CH_2^+$ (with an ideal N−H···N hydrogen bond) and comparing it with $H_2C{=}NH{\cdots}CH_2{=}NH_2^+$ (where the NH and CH groups are in the vicinity and do not allow for a N−H···N hydrogen bond, leading to a N−N distance of 3.998 Å and a C−H···N angle of 171.3°). The hydrogen-bonded species has a N−N distance of 2.832 Å and N−H distances of 1.042 and 1.790 Å with an N−H···N angle of 177.0°. For the two N−H bonds, the bond order analysis gives values of 0.590 and 0.169, respectively, whereas the bond order in the hydrogen bond of the model compound ***a*** in Figure 3 is 0.739 for the shorter bond and below the calculation threshold of 0.05 for the longer one. The energy difference between the two forms ($H_2C{=}NH{\cdots}H{-}NH{=}CH_2^+$

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(37) Kukushkin, V. Yu. *Zh. Neorg. Khim.* **1988**, *33*, 1905; *Russ. J. Inorg. Chem. (Engl. Transl.)* **1988**, *33*, 1085.

(38) (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1. (b) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(39) Glocker, M. O.; Shrestha-Davadi, P. B.; Küchler-Krischun, J.; Hofmann, J.; Fischer, H.; Jochims, J. J. *Chem. Ber.* **1993**, *136*, 1859.

(40) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(41) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, U.K., 1986.

(42) (a) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(43) (a) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Shaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 1. (b) Branden, C.; Tooze, J. *Introduction to Protein Structure*; Garland Publishing: New York, London, 1991; p 262 f. (c) Kyte, J. *Structure in Protein Chemistry*, Garland Publishing: New York, London, **1995**; p 159 ff.

and $H_2C{=}NH\cdots CH_2{=}NH_2^+$) is 6.5 kcal/mol, indicating a strong hydrogen bond compared with the low value of 1.1 kcal/mol of the compound modeling the platinum complexes. Of course, these values have to be interpreted with care since the calculations are for the gas phase, not including any solvent effects. Despite this limitation, the value of 6.5 kcal/mol for an ideal hydrogen bond compares well with experimental values determined for simple amine dimers and in proteins (generally nonideal geometries), e.g. 3.7−4 kcal/mol for hydrogen bonds in charged species.[43b,c]

The above calculations indicate that the hydrogen bond is weak and hardly responsible for stabilization of the one-end coordination of iminoacyls. We believe that another reason for the stabilization is the expected instability of cationic Pt(IV) complexes which should be formed in the case of *N*,*N*-ligation of $NH{=}C(R)ON{=}CR_1R_2$ to the central atom. Indeed, cationic species with sp^2-*N*-donors are quite rare in the platinum(IV) chemistry.[44]

Concluding Remarks. Newly formed iminoacyl ligands in the platinum(IV) complexes exhibit an exceptional stability toward hydrolysis. All syntheses were done in nondried solvents, and products were isolated in high yields. In addition, the complexes remain intact in acetone-d_6 and methanol-d_4 containing 5% deuterium oxide for 1 week at room temperature and only then slowly start to decompose giving acetic acid and 2-propanone oxime among other unidentified hydrolysis products. In our opinion, such a resistance of the platinum(IV) complexes *trans*-$[PtCl_4(NH{=}C(R)ON{=}CR_1R_2)_2]$ to hydrolysis is surprising from at least three viewpoints: (i) Quadruple charged platinum(IV) ion provides electrophilic activation of the nitrile carbon expressed in its enhanced reactivity toward nucleophiles in general and toward water−hydroxide in particular.[24,34,45] It would be perhaps reasonable to assume a similar high susceptibility of (imine)platinum(IV) species in the hydrolysis. Indeed, imines as, for example, $N(Ph){=}CHR$ are subject to fast hydrolysis that occurs *even in platinum(II) complexes* in mild reaction conditions.[46] (ii) Imine ligands, especially those that contain donor groups, for example $N(H){=}CMe_2$, exhibit high reactivity in both hydrolysis and polymerization.[47,48] Stability of such species can be reached by introducing acceptor substituents to the carbon, for instance $N(H){=}CPh_2$.[47] In our case, imines $NH{=}C(Me)ON{=}CR_1R_2$ with the two donor substituents at the carbon represent a distinctive subclass of stable imines. Previously only alkoxy-, $NH{=}C(OR')R$,[49] and amino-, $NH{=}C(NH_2)R$,[50] substituted imines formed fairly stable platinum(II) complexes which were isolated and characterized. In addition, amidine complexes of platinum(IV) are stable although the ligand coordination mode in those complexes is yet unclear.[50] (iii) It has recently become known[39] that purely organic materials, e.g. the nitrilium salts $R_1{-}C{\equiv}N^+{-}R_2$, react with 2-propanone oxime to furnish the adducts $R_2(H)N^+{=}C(R_1)ON{=}CMe_2$ as temperature- and moisture-sensitive compounds. Furthermore, treatment of the nitrilium salt $[MeC{\equiv}N^+Et][BF_4]$[51] or trichloroacetonitrile,[52] which contains a strong acceptor CCl_3 group, with aldoximes $RCH{=}NOH$ brings about easy conversion of the parent materials to $RC{\equiv}N$ and $MeC({=}O)NHEt$ and $Cl_3CC({=}O)NH_2$, respectively.[51] These reactions proceed via intermediate formation of unstable addition products, e.g. $EtN{=}C(Me)ON{=}C(H)R$ or $HN{=}C(CCl_3)ON{=}C(H)R$.[53]

Comparison of our results with those indicated in cases *i*−*iii* shows that coordination of the iminoacyl ligands to platinum(IV) ion leads to stabilization of potentially unstable species. We hope that the discovery of platinum(IV)-stabilized iminoacylated oximes might be interesting for *coordination chemistry* in modeling elusive monodentate imine ligands[49,54] and for *organic chemistry* as models of highly unstable intermediates in a nitrilium ion catalyzed Beckmann rearrangement.[39,55] Factors determining stability of $[Pt^{IV}]{-}NH{=}C(Me)ON{=}CR_1R_2$ and similar species, biological investigations of the iminoacyl complexes,[56] extending the reaction described here to other metal nitrile complexes, to other hydroxylamine derivatives,[57] and also to other nucleophiles are under way in our group.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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(44) (a) Cotton, S. *Chemistry of Precious Metals*; Chapman & Hall: London, 1997. (b) Greenwood, N. N.; Earnshow, A. *Chemistry of the Elements*, Pergamon Press: Oxford, 1994; p 1339. (c) Davies, J. A.; Hockensmith, C. M.; Kukushkin, V. Yu.; Kukushkin, Yu. N. *Synthetic Coordination Chemistry: Theory and Practice*; World Scientific: Singapore, 1996. (d) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science Publishers: London, 1973. (e) Belluco, U. *Organometallic and Coordination Chemsitry of Platinum*; Academic Press: London, 1974.

(45) Paul, P.; Nag, K. *Inorg. Chem.* **1987**, *26*, 1586.

(46) Cross, R. J.; Davidson, M. F.; Rocamora, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1147.

(47) Nitta, M.; Sasaki, I.; Miyano H.; Koboyashi, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 7, 3357.

(48) Langenbahn, M.; Stoeckli-Evans, H.; Süss-Fink, G. *Helv. Chim. Acta* **1991**, *74*, 549.

(49) Prenzler, P. D.; Hockless, D. C. R.; Heath G. A. *Inorg. Chem.* **1997**, *36*, 5845.

(50) Kukushkin, V. Yu.; Aleksandrova, E. A.; Kukushkin, Yu. N. *Zh. Obshch. Khim.* **1995**, *65*, 1937.

(51) (a) Ho, T.-L.; Wong, C. M. *J. Org. Chem.* **1973**, *38*, 2241. (b) Ho, T.-L. *Synthesis* **1975**, 401.

(52) Rosini, G.; Baccolini, G.; Cacchi, S. *J. Org. Chem.* **1973**, *38*, 1060.

(53) Fatiadi, A. J. In *The Chemsitry of Triple-bonded Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K. 1983; Part 2, p 1066.

(54) (a) Diamond, S. E.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 2661. (b) Adcock, P. A.; Keene, F. R.; Smythe, R. S.; Snow, M. R. *Inorg. Chem.* **1984**, *23*, 2336.

(55) Meerwein, H. *Angew. Chem.* **1955**, *67*, 374.

(56) Keppler, B. K. Work in progress.

(57) Kukushkin, Yu. N.; Pakhomova, T. B.; Wagner, G.; Pombeiro, A. J. L.; Kukushkin, V. Yu. Manuscript in preparation.