Inorg. Chem. **2003**, *42*, 7560–7568

Hydrolytic Metal-Mediated Coupling of Dialkylcyanamides at a Pt(IV) Center Giving a New Family of Diimino Ligands

Nadezhda A. Bokach,[†] Tatyana B. Pakhomova,[‡] Vadim Yu. Kukushkin,*[,†] Matti Haukka,[§] and Armando J. L. Pombeiro*[,||]

Department of Chemistry, St. Petersburg State University, 198504 Stary Petergof, Russian Federation, Inorganic Chemistry, St. Petersburg State Technological Institute, 198013 St. Petersburg, Russian Federation, Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101, Joensuu, Finland, Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

Received July 10, 2003

Addition of excess R_2NCN to an aqueous solution of $K_2[PtCl_4]$ led to the precipitation of $[PtCl_2(NCNR_2)_2]$ (R_2 = Me_2 **1**; Et_2 **2**; C_5H_{10} **3**; C_4H_8O, **4**) in a *cis*/*trans* isomeric ratio which depends on temperature. Pure isomers *cis*-**1**–**3** and *trans*-**1**–**3** were separated by column chromatography on SiO_2, while *trans*-**4** was obtained by recrystallization. Complexes *cis*-**1**–**3** isomerize to *trans*-**1**–**3** on heating in the solid phase at 110 °C; *trans*-**1** has been characterized by X-ray crystallography. Chlorination of the platinum(II) complexes *cis*-**1**–**3** and *trans*-**1**–**4** gives the appropriate platinum(IV) complexes $[PtCl_4(NCNR_2)_2]$ (*cis*-**5**–**7** and *trans*-**5**–**8**). The compound *cis*-**6** was also obtained by treatment of $[PtCl_4(NCMe)_2]$ with neat Et_2NCN. The platinum(IV) complex *trans*-$[PtCl_4(NCNMe_2)_2]$ (*trans*-**5**) in a mixture of undried Et_2O and CH_2Cl_2 undergoes facile hydrolysis to give *trans*-$[PtCl_4\{N(H)=C(NMe_2)OH\}_2]$ (**9**; X-ray structure has been determined). The hydrolysis went to another direction with the *cis*-$[PtCl_4(NCNR_2)_2]$ (*cis*-**5**–**7**) which were converted to the metallacycles $[PtCl_4\{NH=C(NR_2)OC(NR_2)=NH\}]$ (**11**–**13**) due to the unprecedented hydrolytic coupling of the two adjacent dialkylcyanamide ligands giving a novel (for both coordination and organic chemistry) diimino linkage. Compounds **11**–**13** and also **14** (R_2 = C_4H_8O) were alternatively obtained by the reaction between *cis*-$[PtCl_4(MeCN)_2]$ and neat undried $NCNR_2$. The structures of complexes **11**, **13**, and **14** were determined by X-ray single-crystal diffraction. All the platinum compounds were additionally characterized by elemental analyses, FAB mass-spectrometry, and IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopies.

Introduction

The hydrolysis of organonitriles involving metal complexes is a field with highly recognized synthetic significance (recently reviewed by two of us[1] and also by others[2−6]), in particular toward the laboratory and industrial preparation of amides, e.g., for kiloton production of acrylamide and nicotineamide, and also in view of the pharmacological interest of $RC(=O)NH_2$ species. Typically, metal centers behave as extremely strong activators of the C≡N group toward nucleophilic attack by OH^-/H_2O, and they facilitate the first step of the hydrolysis of nitriles (further hydrolysis to ammino complexes and carboxylic acids is a rare phenomenon[7,8]) giving either free or metal-bound carboxamides in iminol (R(HO)C=N(H)−[M]) or amide ($RC(NH_2)$=O−

* Corresponding authors. E-mail: kukushkin@VK2100.spb.edu (V.Yu.K.); pombeiro@ist.utl.pt (A.J.L.P.).
[†] St. Petersburg State University.
[‡] St. Petersburg State Technological Institute.
[§] University of Joensuu.
[||] Centro de Química Estrutural.

(1) Kukushkin, V. Yu.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771 and references therein. Pombeiro, A. J. L.; Kukushkin, V. Yu. In *Comprehensive Coordination Chemistry*, 2nd ed.; Lever, A. B. P. ; Elsevier: New York, in press.
(2) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299.
(3) Eglin, J. L. *Comments Inorg. Chem.* **2002**, *23*, 23.
(4) Kuznetsov, M. L. *Russ. Chem. Rev.* **2002**, *71*, 265.
(5) da Rocha, Z. N.; Chiericato, G., Jr.; Tfouni, E. *Adv. Chem. Ser.* **1997**, 297.
(6) Parkins, A. W. *Platinum Met. Rev.* **1996**, *40*, 169. Ghaffar, T.; Parkins, A. W. *J. Mol. Catal. A: Chem.* **2000**, *160*, 249 and references therein.
(7) Bennett, B. K.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 4336. Lee, G. R.; Crayston, J. A. *Polyhedron* **1996**, *15*, 1817.
(8) Kuznetsov, M. L.; Bokach, N. A.; Kukushkin, V. Yu.; Pakkanen, T.; Wagner, G.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2000**, 4683. Kukushkin, V. Yu.; Zenkevich, I. G.; Belsky, V. K.; Konovalov, V. E.; Moiseev, A. I.; Sidorov, E. O. *Inorg. Chim. Acta* **1989**, *166*, 79.

10.1021/ic034800x CCC: $25.00
Published on Web 10/14/2003

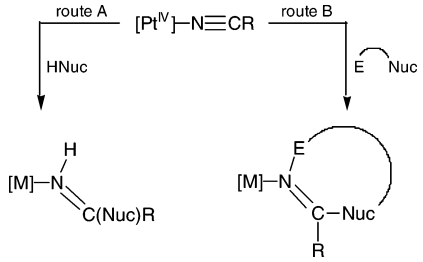
[M]) forms. The overwhelming fraction of works on the hydrolysis of metal-activated nitrile ligands is devoted to (i) the homogeneous catalytic hydrolysis when the formed amides are expelled from the coordination sphere of the metal ions, e.g., our recent finding of the hydrolysis catalyzed by a simple, cheap, and environmentally benign Zn(II)/ketoxime system[9] (this area also involves studies on nitrile hydratases[2,10] and on complexes that mimic or are relevant to these enzymes[2,11]); (ii) the stoichiometric metal-mediated hydrolysis giving amides which remain ligated (recent works include hydrolysis at Ru,[12,13] Cu,[14,15] Ni,[15,16] Co,[17] Re,[3] Pd,[18] and Pt[19] centers) or can be liberated from the coordination sphere in secondary displacement reactions (e.g., at a Ru center[13]).

Data emerged in the past few years that indicate that the hydrolytic transformation of RCN involving metal complexes is far from being restricted to only the two already mentioned types. Thus, recent and not yet systematically investigated examples include the hydrolytic conversion of nitriles into amidines RC(═NH)NH_2,[20,21] imidoylamidines RC(═NH)NHC(═NH)R,[22] and acyl amides $(RCO)_2NH$;[23] although these species are well-known in organic chemistry, the metal-mediated reactions opened up new attractive routes for their preparation. Here we describe a novel reactivity mode for organonitriles, i.e., their metal-mediated hydrolytic coupling giving the previously unknown oxadiimine linkage.

Results and Discussion

Although a great amount of works dealt with the nucleophilic additions to organonitriles bound to Pt(II) ions,[1] it has only recently been established that a Pt(IV) center provides a substantially stronger activation of RCN species, thus making feasible reactions that cannot occur not only at Pt(II) but also at a great variety of other metal centers. In fact, platinum(IV) is currently recognized as one of the strongest electrophilic activators of RCN substrates which allow the performance of the facile coupling (e.g., with hydroxamic acids,[24] oximes,[25,26] *vic*-dioximes,[27] dione monoximes,[28] alcohols,[29] amino alcohols,[30] imines,[23,31] and suflimides[32]) (route A, Scheme 1) or [2 + 3] cycloadditions of both allyl- and propargyl/allenyl anion type dipoles (e.g., nitrones[33−36] or nitrile oxides[37]) (route B). All the reactions listed here were performed with the ordinary organonitriles, i.e., bearing alkyl, benzyl, or aryl group R.

Scheme 1



Being interested in the amplification of these works to other (more complicated) nitrile systems, we focused our attention on so-called push−pull nitriles[38,39] such as cyanamides (i.e., cyanamide, $H_2NC{\equiv}N$, and dialkylcyanamides, $R_2NC{\equiv}N$), and we observed some unusual reactivity patterns[26,40] unknown for RCN species. Moreover, literature

(9) Kopylovich, M. N.; Kukushkin, V. Yu.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Inorg. Chem.* **2002**, *41*, 4798. Pombeiro, A. J. L.; Kukushkin, V. Yu.; Kopylovich, M. N.; Fraústo da Silva, J. J. R. PCT Int. Appl., WO 2001-102618, 2002; *Chem. Abstr.* **2002**, *138*, 13921.

(10) For recent reviews see: Endo, I.; Odaka, M. *Prog. Biotechnol.* **2002**, *22*, 159. Martinkova, L.; Kren, V. *Biocatal. Biotransform.* **2002**, *20*, 73. Yamada, H.; Shimizu, S.; Kobayashi, M. *Chem Rec.* **2001**, *1*, 152. Endo, I.; Nojiri, M.; Tsujimura, M.; Nakasako, M.; Nagashima, S.; Yohda, M.; Odaka, M. *J. Inorg. Biochem.* **2001**, *83*, 247.

(11) For recent review see: Mascharak, P. K. *Coord. Chem. Rev.* **2002**, *225*, 201.

(12) Novais da Rocha, Z.; Ferreira, K. Q.; Silva, M.; Cristina de Oliveira, E.; Chiericato, G., Jr.; Tfouni, E. *Inorg. Chem.* **2001**, *40*, 5385. Mori, K.; Yamaguchi, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Commun.* **2001**, 461.

(13) Fagalde, F.; Lis De Katz, N. D.; Katz, N. E. *J. Coord. Chem.* **2002**, *55*, 587.

(14) Siegfried, L.; Kowallick, R.; Kaden, T. A. *Supramol. Chem.* **2001**, *13*, 357.

(15) Kang, S.-G.; Song, J.; Jeong, J. H. *Bull. Korean Chem. Soc.* **2002**, *23*, 824.

(16) Eisch, J. J.; Ma, X.; Han, K. I.; Gitua, J. N.; Kruger, C. *Eur. J. Inorg. Chem.* **2001**, 77.

(17) Angus, P. M.; Jackson, W. G. *Inorg. Chim. Acta* **2003**, *343*, 95.

(18) Ghammami, S.; Derakhshan, S.; Mahjoub, A. R.; Soudi, A. *Indian J. Chem., Sect. B* **2001**, *40B*, 625.

(19) Luzyanin, K. V.; Haukka, M.; Bokach, N. A.; Kuznetsov, M. L.; Kukushkin, V. Yu.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2002**, 1882.

(20) Kopylovich, M. N.; Kukushkin, V. Yu.; Guedes da Silva, M. F. C.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1569.

(21) Longato, B.; Bandoli, G.; Mucci, A.; Schenetti, L. *Eur. J. Inorg. Chem.* **2001**, 3021. Emirdag-Eanes, M.; Ibers, J. A. *Inorg. Chem.* **2002**, *41*, 6170.

(22) Kryatov, S. V.; Nazarenko, A. Y.; Smith, M. B.; Rybak-Akimova, E. V. *Chem. Commun.* **2001**, 1174.

(23) Bokach, N. A.; Kukushkin, V. Yu.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 3602.

(24) Luzyanin, K. V.; Kukushkin, V. Yu.; Kuznetsov, M. L.; Garnovskii, D. A.; Haukka, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2002**, *41*, 2981.

(25) Kukushkin, V. Yu.; Pakhomova, T. B.; Kukushkin, Yu. N.; Herrmann, R.; Wagner, G.; Pombeiro, A. J. L. *Inorg. Chem.* **1998**, *37*, 6511.

(26) Ferreira, C. M. P.; Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Kukushkin, V. Yu.; Michelin, R. A. *Inorg. Chem.* **2001**, *40*, 1134.

(27) Kukushkin, V. Yu.; Pakhomova, T. B.; Bokach, N. A.; Wagner, G.; Kuznetsov, M. L.; Galanski, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2000**, *39*, 216.

(28) Makarycheva-Mikhailova, A. V.; Haukka, M.; Bokach, N. A.; Garnovskii, D. A.; Galanski, M.; Keppler, B. K.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *New J. Chem.* **2002**, *26*, 1085.

(29) Bokach, N. A.; Kukushkin, V. Yu.; Kuznetsov, M. L.; Garnovskii, D. A.; Natile, G.; Pombeiro, A. J. L. *Inorg. Chem.* **2002**, *41*, 2041.

(30) Makarycheva-Mikhailova, A. V.; Kukushkin, V. Yu.; Nazarov, A. A.; Garnovskii, D. A.; Pombeiro, A. J. L.; Haukka, M.; Keppler, B. K.; Galanski, M. *Inorg. Chem.* **2003**, *42*, 2805.

(31) Garnovskii, D. A.; Kukushkin, V. Yu.; Haukka, M.; Wagner, G.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2001**, 560.

(32) Makarycheva-Mikhailova, A. V.; Bokach, N. A.; Kukushkin, V. Yu.; Kelly, P. F.; Gilby, L. M.; Kuznetsov, M. L.; Holmes, K. E.; Haukka, M.; Parr, J.; Stonehouse, J. M.; Elsegood, M. R. J.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 301.

(33) Wagner, G.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *J. Am. Chem. Soc.* **2000**, *122*, 3106.

(34) Wagner, G.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chem.* **2001**, *40*, 264.

(35) Kuznetsov, M. L.; Kukushkin, V. Yu.; Dement'ev, A. I.; Pombeiro, A. J. L. *J. Phys. Chem. A* **2003**, *107*, 6108.

(36) Kukushkin, V. Yu.; Pombeiro, A. J. L.; Wagner, G.; Fraústo da Silva, J. J. R. Patent Portugal WO 01/98283 A1, 2000.

(37) Bokach, N. A.; Khripoun, A. V.; Kukushkin, V. Yu.; Haukka, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 836.

(38) Ziao, N.; Graton, J.; Laurence, C.; Le Questel, J. Y. *Acta Crystallogr., Sect. B* **2001**, *B57*, 850.

(39) Le Questel, J.-Y.; Berthelot, M.; Laurence, C. *J. Phys. Org. Chem.* **2000**, *13*, 347.

data[41] also give nice examples of exciting chemistry for cyanamides at various metal centers.

In the current work, we attempted to combine two directions of our research, i.e., the chemistries of Pt(IV) and cyanamides, and to synthesize and study (dialkylcyanamide)-Pt(IV) complexes, namely searching for novel types of reactions, and our results are presented in sections that follow.

Synthesis of Dialkylcyanamide Pt(II) and Pt(IV) Complexes. The nitrile complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = alkyl, benzyl or aryl) are convenient starting materials for the synthesis of different platinum compounds by substitution reactions of RCN[42] or reactions with coordinated nitriles.[1] Synthesis of these Pt compounds is usually performed either by reacting solid $PtCl_2$ upon heating in neat RCN[43] or by treatment of $K_2[PtCl_4]$ with RCN in water.[44,45] The former method usually yields *trans*-isomers, but the latter brings about a mixture of *cis*- and *trans*-forms favoring the *cis*-isomer at lower temperatures.[45] In addition, complexes $[PtCl_2(NCR)_2]$ can be obtained by heating of $[PtCl_2(NCMe)_2]$ in RCN at temperatures higher than the boiling point of acetonitrile.[46]

The reaction between $PtCl_2$ and RCN has recently been applied, by some of us,[47] to the preparation of isomerically pure *trans*-$[PtCl_2(NCNR_2)_2]$ (R = Me, Et). The method with $K_2[PtCl_4]$[44,45] was employed in this work for preparation of *cis*- and *trans*-$[PtCl_2(NCNR_2)_2]$ (R_2 = Me_2, **1**; Et_2, **2**; C_5H_{10}, **3**; C_4H_8O, **4**) insofar as we endeavored to obtain both isomeric forms for these complexes. In accord with our expectations, addition of excess R_2NCN to an aqueous solution of $K_2[PtCl_4]$ led to the precipitation of *cis*/*trans*-$[PtCl_2(NCNR_2)_2]$, where the ratio of isomers depends on temperature; e.g., for **1** it is ca. 2:3 at 20−25 °C, while at 5 °C the ratio is 2:1. The isomers of **1**−**3** show two distinct spots and good separation on TLC, but their ^1H and $^{13}C\{^1H\}$ NMR spectra are very similar, and the difference in chemical shifts, although clearly visible when the mixtures of isomers are measured, is small. Pure isomers of **1**−**3** were separated by column chromatography on SiO_2. The complex *cis*-**4** is formed in small amounts, and it possesses a solubility in the most common solvents at 20−25 °C that is too low for it to be dissolved and then to be separated on the column. Therefore, we were able to obtain only *trans*-**4**. It is worthwhile to mention that the samples of *trans*-**1** and *trans*-**2** are authentic as compared to those prepared by treatment of $PtCl_2$ with $NCNR_2$ (R = Me, Et).[47] We also established that *cis*-**1**−**3** isomerize to *trans*-**1**−**3** on heating in the solid phase at 110 °C and the direction of isomerization corresponds to the previously reported *cis*-to-*trans* transformation for $[PtCl_2(NCR)_2]$.[48] This also explains why heating $PtCl_2$ in Et_2NCN[47] furnishes solely the *trans*-isomer.

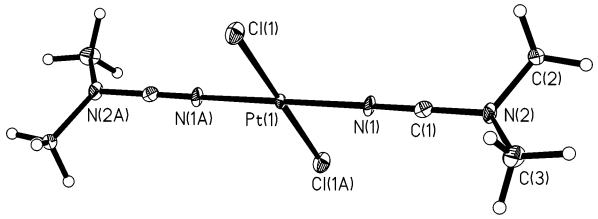


Figure 1. Thermal ellipsoid view of complex *trans*-**1** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 1.973(8), Pt(1)−Cl(1) 2.292(3), N(1)−C(1) 1.129(14), N(2)−C(1) 1.302(14), N(2)−C(3) 1.469(13), N(2)−C(2) 1.473(13), N(1)−Pt(1)−N(1A) 180.0, N(1)−Pt(1)−Cl(1) 90.5(3), N(1)−Pt(1)−Cl(1A) 89.5(3), C(1)−N(1)−Pt(1) 177.6(9), N(1)−C(1)−N(2) 175.6(11), C(3)−N(2)−C(2) 117.6(8).

The complex *trans*-**1** has been characterized by X-ray crystallography (Figure 1). In the structure, all bond lengths are of normal values, the C≡N bond distance agrees with those in other platinum(II) nitrile complexes,[48,49] and the $CN(2)C_2$ fragment is almost planar (the maximum deviation is 0.1242 Å for N(2) atom), thus indicating the amide character of the NMe_2 group.

Chlorination of the platinum(II) complexes *cis*-**1**−**3** and *trans*-**1**−**4** gives the appropriate platinum(IV) complexes $[PtCl_4(NCNR_2)_2]$ (*cis*-**5**−**7** and *trans*-**5**−**8**). Another possible, although less straightforward, route to obtain the platinum(IV) complexes consists of treatment of $[PtCl_4(NCMe)_2]$ with the appropriate neat R_2NCN, and this synthetic route was illustrated for the complex *cis*-**6** (see Experimental Section).

(40) Cunha, S. M. P. R. M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans*. **2001**, 1791. 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. Pombeiro, A. J. L.; Guedes da Silva, M. F. C.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem*. **1989**, *371*, C45.

(41) Cunha, S. M. P. R. M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 2157. Tsai, Y.-C.; Stephens, F. H.; Meyer, K.; Mendiratta, A.; Gheorghiu, M. D.; Cummins, C. C. *Organometallics* **2003**, *22*, 2902. Fisher, H.; Troll, C.; Schleu, J. In *Transition Metal Complexes*; Kreissl, F. R., Ed.; NATO ASI Series; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; p 79 and references therein.

(42) Davies, J. A.; Hockensmith, C. M.; Kukushkin, V. Yu.; Kukushkin, Yu. N. *Synthetic Coordination Chemistry: Principles and Practice*; World Scientific: River Edge, NJ, 1996; p 58. Dunbar, K. R. *Comments Inorg. Chem*. **1992**, *13*, 313. Davies, J. A.; Hartley, F. R. *Chem. Rev*. **1981**, *81*, 79.

(43) Fraccarollo, D.; Bertani, R.; Mozzon, M.; Belluco, U.; Michelin, R. A. *Inorg. Chim. Acta* **1992**, *201*, 15. Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science: London, 1973; p 462. Hartley, F. R.; Murray, S.; McAuliffe, C. A. *Inorg. Chem*. **1979**, *18*, 1394. Kharasch, M. R.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc*. **1938**, *60*, 882.

(44) Kukushkin, V. Yu.; Oskarsson, Å.; Elding, L. I. *Inorg. Synth.* **1997**, *31*, 279. Kukushkin, V. Yu.; Oskarsson, Å.; Elding, L. I. *Zh. Obsch. Khim*. **1994**, *64*, 881; *Russ. J. Gen. Chem. (Engl. Transl.)* **1994**, *64*, 793. Kukushkin, V. Yu.; Tkachuk, V. M. *Z. Anorg. Allg. Chem*. **1992**, *613*, 123.

(45) Fanizzi, F. P.; Intini, F. P.; Maresca, L. Natile, G. *J. Chem. Soc., Dalton Trans*. **1990**, 199.

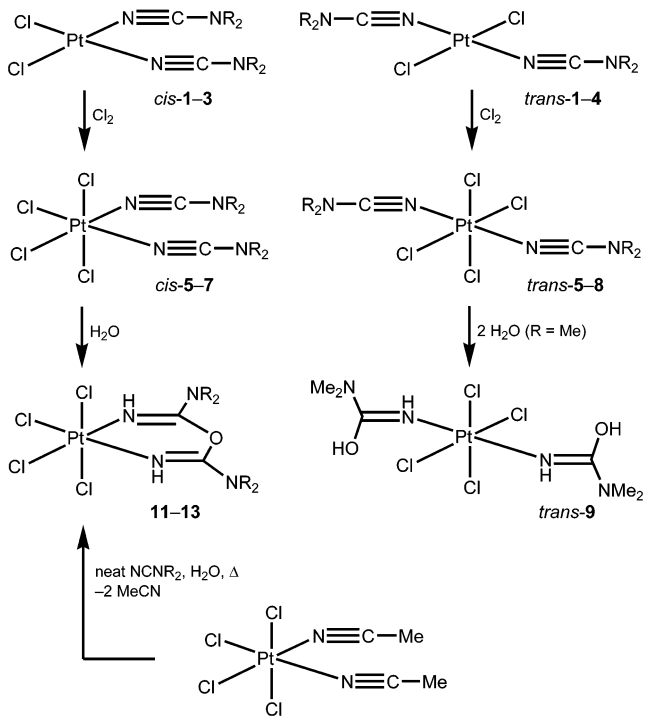
(46) Kukushkin, Yu. N.; Pakhomova, T. B. *Zh. Obshch. Khim*. **1995**, *65*, 330.

(47) Ferreira, C. M. P.; Guedes da Silva, M. F. C.; Michelin, R. A.; Kukushkin, V. Yu.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2003**, 3751.

(48) Svensson, P.; Lövqvist, K.; Kukushkin, V. Yu.; Oskarsson, Å. *Acta Chem. Scand*. **1995**, *49*, 72.

(49) Belluco, U.; Benetollo, F.; Bertani, R.; Bombieri, G.; Michelin, R. A.; Mozzon, M.; Pombeiro, A. J. L.; Guedes da Silva, F. C. *Inorg. Chim. Acta* **2002**, *330*, 229. Sun, J.-S.; Uzelmeier, C. E.; Ward, D. L.; Dunbar, K. R. *Polyhedron* **1998**, *17*, 2049. Steenwinkel, P.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1998**, *17*, 5411. Belsky, V. K.; Konovalov, V. E.; Kukushkin, V. Yu.; Moiseev, A. I. *Inorg. Chim. Acta* **1990**, *169*, 101. Chan, C.-W.; Lai, T.-F.; Che, C.-M.; Peng, S.-M. *J. Am. Chem. Soc*. **1993**, *115*, 11245. Kritzenberger, J.; Yersin, H.; Range, K.-J.; Zabel, M. *Z. Naturforsch., B: Chem. Sci*. **1994**, *49*, 297. Buchner, R.; Field, J. S.; Haines, R. J.; Cunningham, C. T.; McMillin, D. R. *Inorg. Chem*. **1997**, *36*, 3952.

Scheme 2



In the IR spectra, the Pt(II)-bound dialkylcyanamides exhibit a strong band in the range 2284−2294 cm^{-1} due to C≡N stretching vibrations. These values are higher (by 70−75 cm^{-1}) than those for the corresponding free R_2NCN species (ca. 2215 cm^{-1}). IR spectra of the Pt(IV) complexes display strong bands, in the range 2170−2200 cm^{-1}, that are lower than those for the free cyanamides (20−40 cm^{-1}) and for the Pt(II) ligated cyanamides (100−110 cm^{-1}). Moreover, these values are lower than those for the corresponding (RCN)Pt(IV) complexes (2330−2340 cm^{-1}).[25,27,44] Increasing ν(C≡N) values on going from free to Pt(II)-bound forms demonstrate that R_2NCN has the same tendency as RCN and can be explained similarly, i.e., by σ-donation from the ligand and electrostatic effects.[4] Decreasing ν(C≡N) values in (R_2NCN)Pt(IV) complexes versus those in the free dialkylcyanamides reflect the opposite effect from that of the corresponding (RCN)Pt(IV) species, probably due to a strong contribution of the bipolar structure as $[Pt]^-\leftarrow N{=}C{=}N^+R_2$ and $[Pt]{-}N^-{=}C{=}N^+R_2$ in the resonance hybrid of the push−pull ligand.

In the ^{13}C NMR spectra of the platinum(II) complexes, the carbon from the nitrile group emerges at 113−115 ppm, and these values lie almost in the same range as those for both free R_2NCN and RCN. The NCN groups were not detected for Pt(IV) species because of their low solubility. The *cis*- and *trans*-isomers for both Pt(II) and Pt(IV) complexes have no significant differences in IR and ^1H and $^{13}C\{^1H\}$ NMR spectra, but the isomers have two distinct spots on TLC and can be easily separated by chromatography.

Hydrolytic Coupling and Hydrolysis of Dialkylcyanamide Ligands. In our previous work on the hydrolysis of Pt(IV)-bound nitriles, it has been shown that the complexes *trans*-$[PtCl_4(NCR)_2]$ (R = alkyl) react smoothly and under mild conditions in acetone with traces of water to afford

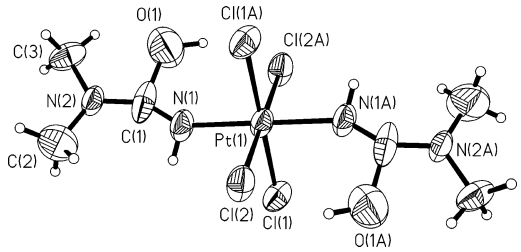


Figure 2. Thermal ellipsoid view of complex **9** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Cl(1)−Pt(1) 2.315(2), Cl(2)−Pt(1) 2.316(2), N(1)−Pt(1) 2.015(6), C(1)−N(1) 1.146(9), C(1)−O(1) 1.651(13), C(1)−N(2) 1.286(9), C(2)−N(2) 1.439(11), C(3)−N(2) 1.436(9), N(1)−Pt(1)−Cl(1) 90.4(2), N(1)−Pt(1)−Cl(2) 87.5(2), C(1)−N(1)−Pt(1) 147.7(7), N(1)−C(1)−N(2) 149.7(11), C(3)−N(2)−C(2) 118.2(7).

trans-$[PtCl_4\{N(H){=}C(OH)R\}_2]$; no hydroxide is required, in contrast to relevant Pt(II) systems, to furnish the metal-bound carboxamides which stabilize in the iminol form.[19] We found in this work that this reactivity mode observed for (nitrile)Pt(IV) complexes is also specific for dialkylcyanamides as illustrated by the hydrolysis of *trans*-$[PtCl_4(NCNMe_2)_2]$ (*trans*-**5**) in a mixture of undried Et_2O and CH_2Cl_2 to give *trans*-$[PtCl_4\{N(H){=}C(NMe_2)OH\}_2]$ (**9**; Scheme 2); the latter compound was characterized by X-ray crystallography (Figure 2). All bond lengths and angles are normal.[50,51] Although the C(1)−N(1) double bond is rather short [1.146(9) Å] to be purely a double bond, this value corresponds to that observed previously by us[19] in *trans*-$[PtCl_4\{N(H){=}C(OH)Et\}_2]$ [1.169(10) Å].

The complexes derived from hydrolysis of *trans*-**6**−**8** are unstable, easily decomposing to give mixtures of yet unidentified compounds, and this instability precluded characterization of the hydrolysis products.

Interestingly, the hydrolysis went to another direction with the *cis*-isomers of $[PtCl_4(NCNR_2)_2]$ which were studied. Thus, when *cis*-**5**−**7** were dissolved in undried CH_2Cl_2 and left to stand for 1 day at 40 °C, the metallacycles **11**−**13** (Scheme 2) were formed and isolated in 30−35% yields; the reaction mixture also contained other products which contaminated **11**−**13**, and to achieve satisfactory analytic data, these compounds should be recrystallized. More pure metallacycles can be obtained by the reaction between *cis*-$[PtCl_4(MeCN)_2]$ and neat undried $NCNR_2$, and we succeeded in obtaining by this route (also in a higher yield, 40%) complexes **11**−**14**. We also found at least some other products from the reaction; i.e., in the case of **12**, it is $(Et_2NH_2)_2[PtCl_6]$ (**15**; characterized by X-ray crystallography and C, H, N elemental analyses), while in the case of **14** a half molecule of HNC_4H_8O was observed in the crystal structure (see later). These amines are presumably formed upon the known[52] degradation of the dialkylcyanamides.

In the IR spectra, all the metallacycles exhibit a medium-to-strong band at 3300−3260 cm^{-1} which corresponds to

(50) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
(51) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.
(52) Meyer, F.; Kaifer, E.; Kircher, P.; Heinze, K.; Pritzkow, H. *Chem. Eur. J.* **1999**, *5*, 1617. Meyer, F.; Hyla-Kryspin, I.; Kaifer, E.; Kircher, P. *Eur. J. Inorg. Chem.* **2000**, 771.

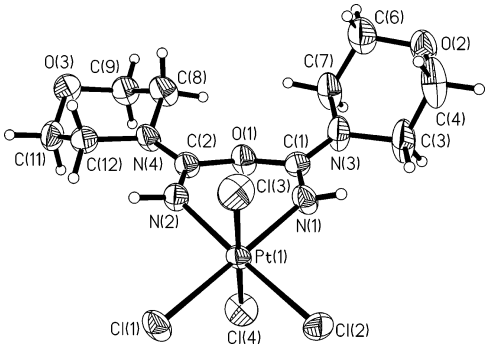


Figure 3. Thermal ellipsoid view of complex **14** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. The same numbering scheme was applied also to structures **11** and **13**. Selected bond lengths (Å) and angles (deg) are shown in Table 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **11**, **13**, and **14**

	11	**13**	**14**
Pt(1)−Cl(1)	2.312(2)	2.3155(11)	2.297(2)
Pt(1)−Cl(2)	2.317(2)	2.3150(10)	2.299(2)
Pt(1)−Cl(3)	2.321(2)	2.3187(9)	2.321(2)
Pt(1)−Cl(4)	2.3258(15)	2.3231(10)	2.301(2)
Pt(1)−N(1)	2.015(5)	2.008(3)	1.991(6)
Pt(1)−N(2)	2.011(6)	2.004(3)	2.011(6)
N(1)−C(1)	1.288(8)	1.298(4)	1.287(10)
C(1)−O(1)	1.357(8)	1.366(4)	1.364(10)
C(1)−N(3)	1.353(8)	1.322(5)	1.309(10)
O(1)−C(2)	1.368(8)	1.374(4)	1.378(9)
C(2)−N(2)	1.344(8)	1.299(4)	1.284(10)
Cl(1)−Pt(1)−Cl(2)	93.54(6)	94.03(4)	89.84(7)
Cl(3)−Pt(1)−Cl(4)	178.19(6)	179.34(3)	177.58(9)
Cl(1)−Pt(1)−N(1)	175.5(2)	175.73(9)	178.8(2)
Cl(2)−Pt(1)−N(2)	175.9(2)	175.21(9)	177.6(2)
Pt(1)−N(1)−C(1)	123.0(5)	121.2(2)	125.8(6)
N(1)−C(1)−O(1)	123.3(6)	121.6(3)	121.5(7)
C(1)−O(1)−C(2)	122.7(5)	125.7(3)	126.3(6)
C(2)−N(2)−Pt(1)	123.0(5)	125.4(2)	125.4(6)

ν(N−H) and strong bands at ca. 1670 and 1630 cm^{-1} due to ν(C═N). In the ^{1}H NMR spectra, only signals from the alkyl groups and the newly formed NH were detected. The coupling constants $^2J_{Pt-H}$ (17.5 and 15.9 Hz) were found for the NH group of two compounds (**11** and **12**) in dmso-d_6, while **13** and **14** in acetone-d_6 do not display this coupling. The carbon from the N═*C*−N group for **11** and **12** was detected in the ^{13}C{^{1}H} NMR spectra at 152.30 and 151.45 ppm, correspondingly, and it was not observed for **13** and **14** even at a long acquisition time.

The structures of complexes **11**, **13**, and **14**, derived from the hydrolytic coupling, were determined by X-ray single-crystal diffraction (Figure 3). In all three cases, the corresponding bond lengths and angles agree with each other (Table 1); the C═N and N−O bonds are typical double and single bonds,[50,51] respectively, and CNC_2 groups are planar and have the amide character.

The hydrolytic coupling reported here is a novel reactivity mode which has never been observed in the past at any metal center. In particular, the hydrolysis of organonitriles at Pt centers has been known since the discovery of platinum blues,[53] and examples accumulated in the literature include generation of ammino,[8] carboxamide in the iminol form,[19,54,55] and terminal[56,57] and bridged[58] carboxamidato complexes.

In the context of the hydrolytic coupling, it is worthwhile to mention two studies which are relevant to the observed transformation. In the first, it was reported that heating of [RuCl(H)(CO)(PPh_3)$_3$] and the nondried *p*-tolunitrile led to the formation of [Ru]−N(H)═C(C_6H_4Me)−N═C(C_6H_4Me)−O metallacycle. The authors[59] argue that the formation of the metallacycle proceeds via initial hydrolysis of the nitrile to give the carboxamide species followed by the coupling of the latter with one more molecule of the nitrile. The described carboxamide−nitrile integration proceeds via the N atom of the carboxamide rather that the O atom, in contrast to our experiments. In the second study,[60,61] it was found that the 2-cyanobenzamide complex [Co(NH_3)$_5${*o*-(*N*HCO)(C≡N)C_6H_4}]$^{2+}$ rapidly rearranges to form the nitrile-bonded isomer [Co(NH_3)$_5${*o*-(NHCO)(C≡N)-C_6H_4}]$^{2+}$, and the mechanism of this isomerization was suggested to involve ligand cyclization to give the [Co(NH_3)$_5$-{N(H)═C−O−C(C_6H_4))═NH}]$^{2+}$ intermediate with subsequent ring opening. In this intermediate, the formation of the HN═C(R)−O−C(R)═NH linkage due to the intramolecular carboxamide−nitrile coupling was postulated on the basis of kinetic data, but these species were neither isolated nor characterized in situ. Our observation gives further arguments favoring this functionality.

Final Remarks

The hydrolytic coupling described in this article appears to be specific for dialkylcyanamides since this reaction has never been observed for alkyl and aryl nitriles despite a large amount of work devoted to their hydrolytic conversions. Differences in reactivity modes for R_2NCN and RCN species were indicated previously, in particular by us.[26,40] However, in the present case the different behaviors can hardly be regarded as resulting only from the difference between the

(53) For reviews see: Matsumoto, K.; Sakai, K. *Adv. Inorg. Chem.* **2000**, *49*, 375. Lippert, B. In *Cisplatin*; Lippert, B., Ed.; Verlag Helvetica Chimica Acta: Zurich, 1999; p 379. Tejel, C.; Ciriano, M. A.; Oro, L. A. *Chem. Eur. J.* **1999**, *5*, 1131.

(54) Cini, R.; Fanizzi, F. P.; Intini, F. P.; Pacifico, C.; Natile, G. *Inorg. Chim. Acta* **1997**, *264*, 279. Cini, R.; Cavaglioni, A.; Intini, F. P.; Fanizzi, F. P.; Pacifico, C.; Natile, G. *Polyhedron* **1999**, *18*, 1863. Cini, R.; Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Am. Chem. Soc.* **1993**, *115*, 5123.

(55) Fairlie, D. P.; Jackson, W. G.; Skelton, B. W.; Wen, H.; White, A. H.; Wickramasinghe, W. A.; Woon, T. C.; Taube, H. *Inorg. Chem.* **1997**, *36*, 1020. Lopez, G.; Ruiz, J.; Garcia, G.; Vicente, C.; Martí, J. M.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 53.

(56) Maresca, L.; Natile, G.; Intini, F. P.; Gasparrini, F.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Am. Chem. Soc.* **1986**, *108*, 1180.

(57) Erxleben, A.; Mutikainen, I.; Lippert, B. *J. Chem. Soc., Dalton Trans.* **1994**, 3667.

(58) Rochon, F. D.; Kong, P. C.; Melanson, R. *Inorg. Chem.* **1990**, *29*, 1352. Rochon, F. D.; Boughzala, R.; Melanson, R. *Can. J. Chem.* **1992**, *70*, 2476. Rochon, F. D.; Boutin, S.; Kong, P.-C.; Melanson, R. *Inorg. Chim. Acta* **1997**, *264*, 89.

(59) Hiraki, K.; Kinoshita, Y.; Kinoshita-Kawashima, J.; Kawano, H. *J. Chem. Soc., Dalton Trans.* **1996**, 291.

(60) Balahura, R. J.; Purcell, W. L. *Inorg. Chem.* **1981**, *20*, 4159. Balahura, R. J.; Purcell, W. L. *Inorg. Chem.* **1979**, *18*, 937. Balahura, R. J.; Purcell, W. L. *Inorg. Chim. Acta* **1978**, *31*, L383.

(61) Angus, P. M.; Jackson, W. G. *Inorg. Chem.* **1996**, *35*, 7196. Angus, P. M.; Jackson, W. G. *Inorg. Chem.* **1994**, *33*, 1569.

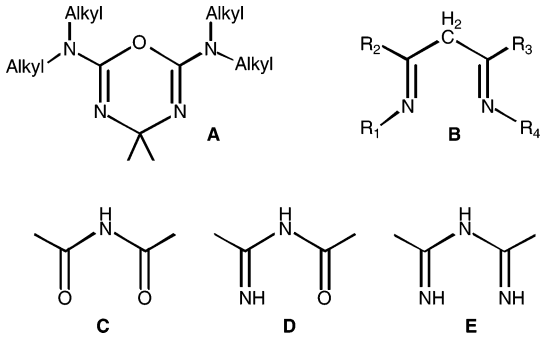


Figure 4.

push−pull and ordinary nitriles in substituent electronic effects because, for example, it was established that the rates for hydration of the Co-bound nitrile and cyanamide in $[Co(NH_3)_5(NCR)]^{3+}$ (R = Me, NMe_2) are very similar.[62] The difference can be explained by the basic character of the R_2N group (vs Me group in MeCN) and/or the availability of R_2NH in the reaction mixture; the latter formed upon degradation of R_2NCN, as was observed in the current work. The basicity of the system might promote the deprotonation of the initially formed Pt(IV) ligated iminol ([Pt]−N(H)═C(OH)NR_2) to achieve the [Pt]−N(H)═C(O^-)NR_2 species (related deprotonated ligands have been described[63]), where the iminolato moiety exhibits an increased nucleophilicity and might easily attack the adjacent nitrile in the *cis*-position. The easier formation of the iminolato species in the cyanamide systems relative to the nitrile one, i.e., [Pt]−N(H)═C(O^-)NR_2 vs [Pt]−N(H)═C(O^-)R, can also be accounted for by electronic factors, i.e., the inductive electron acceptance of the NR_2 group (which promoted the deprotonation of the corresponding parent iminol form) and the stronger electron-donor character by resonance (with a stabilizing effect of the iminolato form), in comparison with the organo R group in the nitrile case.

Interestingly, a somewhat similar distinction in reactivity between R_2NCN and RCN nitriles was observed in pure organic chemistry when dialkylcyanamides, upon their interaction with electron deficient ketones, form 4*H*-1,3,5-oxadiazine heterocycles[64] depicted in Figure 4A, while RCN species do not exhibit this reactivity mode.

The obtained results can be considered from one more viewpoint. In general, there is an increasing interest in the chemistry of diimine ligands such as ketimines (Figure 4B) which, as diaza analogues of acetylacetone, ligate a variety of metal ions.[65] Their complexes serve as useful models for synthetic, reactivity, and structural investigations[66−68] and also as models for active sites of metalloenzymes.[69] In addition, ketiminates of labile metal ions have intrinsic practical applications, e.g., as polymerization catalysts.[70−73] The current work is a continuation of our efforts directed, on one hand, to the development of the chemistry of metal-activated nitriles[1] and, on the other hand, to the synthesis of new chelating ligands from nitriles, e.g., monoaza (C),[74] diaza (D),[23] and triaza (E)[74] analogues of acetylacetone (Figure 4). From the latter perspective, one should notice that the obtained metallacycles (Scheme 1) represent a novel diimine linkage in coordination chemistry, and in addition, such diimines are unknown in organic chemistry. In fact, they form a new family of diimine ligands which can be considered as diaza analogues of $(RCO)_2O$ anhydrides. We anticipate the development of synthetic routes to these oxodiimines by using more labile metals and the study of the catalytic properties of these systems, in particular in aqueous media, in view of the hydrophilic properties of such oxadiimino moieties.

Experimental Section

Materials and Instrumentation. The nitriles were purchased from Lancaster ($NCNMe_2$), Aldrich ($NCNEt_2$ and $NCNC_4H_8O$), and Acros Organics ($NCNC_5H_{10}$). Solvents were obtained from commercial sources and used as received. C, H, and N elemental analyses were carried out by the Microanalytical Service of the University of Joensuu and the Instituto Superior Técnico. For TLC, Merck UV 254 SiO_2-plates have been used. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding

(62) Dixon, N. E.; Fairlie, D. P.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 4038.
(63) Nagao, H.; Hirano, T.; Tsuboya, N.; Shiota, S.; Mukaida, M.; Oi, T.; Yamasaki, M. *Inorg. Chem.* **2002**, *41*, 6267.
(64) Sokolov, V. B.; Aksinenko, A. Yu. *Russ. Chem. Bull. (Engl. Transl.)* **1998**, *47*, 727. Kennard, C. H. L.; Byriel, K. A.; Woon, T. C.; Fairlie, D. P. *Chem. Commun.* **1996**, 1731. Burger, K.; Simmerl, R. *Leibigs Ann. Chem.* **1984**, 982. Burger, K.; Simmerl, R. *Synthesis* **1983**, 237.
(65) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031.
(66) Andres, H.; Bominaar, E. L.; Smith, J. M.; Eckert, N. A.; Holland, P. L.; Muneck, E. *J. Am. Chem. Soc.* **2002**, *124*, 3012. Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416. Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Organometallics* **2002**, *21*, 4808.
(67) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le Pape, L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307. Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108. Aboelella, N. W.; Lewis, E. A.; Reynolds, A. M.; Brennessel, W. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 10660. Panda, A.; Stender, M.; Wright, R. J.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909.
(68) Yao, Y.; Zhang, Y.; Shen, Q.; Yu, K. *Organometallics* **2002**, *21*, 819. Yokota, S.; Tachi, Y.; Itoh, S. *Inorg. Chem.* **2002**, *41*, 1342. Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S.; Sablong, R. *Chem. Commun.* **2002**, 1920. Avent, A. G.; Khvostov, A. V.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **2002**, 1410. Farwell, J. D.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **2002**, 456.
(69) Lee, W.-Z.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 5656. Randall, D. W.; DeBeer, G. S.; Holland, P. L.; Hedman, B.; Hodgson, K. O.; Tolman, W. B.; Solomon, E. I. *J. Am. Chem. Soc.* **2000**, *122*, 11632.
(70) For review see: Shen, Q.; Yao, Y. *J. Organomet. Chem.* **2002**, *647*, 180.
(71) Zhou, M.-S.; Huang, S.-P.; Weng, L.-H.; Sun, W.-H.; Liu, D.-S. *J. Organomet. Chem.* **2003**, *665*, 237. Dove, A. P.; Gibson, V. C.; Hormnirun, P.; Marshall, E. L.; Segal, J. A.; White, A. J. P.; Williams, D. J. *Polym. Mater. Sci. Eng.* **2002**, *87*, 225. Gibson, V. C.; Cameron, P. A.; Dove, A. P.; Graham, A. J.; Marshall, E. L. *Polym. Mater. Sci. Eng.* **2002**, *87*, 91.
(72) Theopold, K. H.; MacAdams, L. A.; Puttnual, C.; Buffone, G. P.; Rheingold, A. L. *Polym. Mater. Sci. Eng.* **2002**, *86*, 310. MacAdams, L. A.; Kim, W.-K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952. Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132.
(73) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895. Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161. Reetz, M. T.; Haderlein, G.; Angermund, K. *J. Am. Chem. Soc.* **2000**, *122*, 996.
(74) Kopylovich, M. N.; Pombeiro, A. J. L.; Fischer, A.; Kloo, L.; Kukushkin, V. Yu. *Inorg. Chem.*, in press.

Table 2. Crystallographic Data for *trans*-**1**, **9**, **11**, **13**, and **14**

	trans-**1**	**9**	**11**	**13**	**14**
empirical formula	$C_6H_{12}Cl_2N_4Pt$	$C_6H_{16}Cl_4N_4O_2Pt$	$C_6H_{14}Cl_4N_4OPt$	$C_{12}H_{22}Cl_4N_4OPt$	$C_{17}H_{30.5}Cl_4N_{6.5}O_{4.5}Pt$
fw	406.19	513.12	495.10	575.23	735.37
temp, K	100(2)	150(2)	150(2)	100(2)	100(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a, Å	5.4171(3)	6.3653(13)	9.2538(3)	11.322(2)	9.7603(14)
b, Å	7.5013(3)	8.0735(16)	11.0170(3)	10.516(2)	16.9136(11)
c, Å	7.5856(5)	8.3994(17)	13.1671(3)	15.596(3)	15.4971(9)
α, deg	115.003(4)	115.72(3)	90	90	90
β, deg	90.654(4)	97.35(3)	90	101.64(3)	94.184(7)
γ, deg	93.277(4)	104.80(3)	90	90	90
V, Å^3	278.68(3)	361.58(13)	1342.37(6)	1818.7(6)	2551.5(4)
Z	1	1	4	4	4
ρ_{calcd}, g/cm^3	2.420	2.356	2.450	2.101	1.914
μ (Mo Kα), mm^{-1}	13.029	10.436	11.234	8.308	5.957
R1[a] ($I \geq 2\sigma$)	0.0304	0.0287	0.0255	0.0223	0.0391
wR2[b] ($I \geq 2\sigma$)	0.0950	0.0723	0.0543	0.0503	0.0935

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

3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. 1.28 10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a JASCO FT/IR-430 instrument in KBr pellets. ^{1}H and ^{13}C{^{1}H} spectra were measured on Varian UNITY 300 and Bruker AMX 300 spectrometers at ambient temperature.

X-ray Crystal Structure Determinations. The crystals were immersed in perfluoropolyether, mounted in a cryo-loops and measured at 100 or 150 K. The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The Denzo-Scalepack[75] or EvalCCD[76] program packages were used for cell refinements and data reductions. All structures were solved by direct methods using the SHELXS-97 or SIR-97 programs with the WinGX graphical user interface.[77−79] An empirical absorption correction was applied to all data using either SADABS (for *trans*-**1** and **14**) or XPREP in SHELXTL v. 6.12 (for all the others)[80,81] programs (T_{max}/T_{min}: 0.5562/0.1172, 0.30755/0.19080, 0.27509/0.22527, 0.14831/0.06340, and 0.5230/0.3704, respectively, for *trans*-**1**, **9**, **11**, **13**, and **14**). Structural refinements were carried out with SHELXL-97.[82] Structure **14** contained one molecule of $NCN(C_2H_4)O$ and half a molecule of HNC_4H_8O per platinum unit. Both of these molecules were disordered. HNC_4H_8O was refined anisotropically with equal U_{ij} in two positions around the center of symmetry. In $NCN(C_2H_4)O$, disordered carbons C93A, C93B, C96A, C96B, C97A, C97B were refined only isotropically with equal U_{iso}. NH and OH hydrogens were located from the difference Fourier map but not refined. All other hydrogens were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data are summarized in Table 2. Selected bond lengths and angles are shown in figure captions. $[PtCl_6]^{2-}$ salts, $[Et_2NH_2]_2[PtCl_6]$ (**15**) and the structurally known $[Me_2NH_2]_2[PtCl_6]$ (**10**),[83] have been presented only as Supporting Information.

Synthetic Work. A. Synthesis of the Platinum(II) Dialkylcyanamide Complexes. Preparation of $[PtCl_2(NCNMe_2)_2]$ (1). $NCNMe_2$ (0.5 mL, 7.2 mmol) was added to $K_2[PtCl_4]$ (0.5 g, 1.2 mmol) in water (5 mL), whereupon a yellow powder began to release almost immediately. The yellow precipitate was filtered off after 6 h, washed by three 3-mL portions of water, and dried in air at room temperature. Overall yield is 80−85%. At room temperature, the complex is released as a mixture of *cis* and *trans* isomers in ca. 2:3 ratio, while at 5 °C the ratio is 2:1 (both by ^{1}H NMR integration). The pure *cis* isomer was obtained from the latter *cis*/*trans* mixture by column chromatography. The complete *cis*-to-*trans* isomerization to achieve the pure *trans*-isomer was performed upon heating of the former mixture at 110 °C for 3 h.

Other dialkylcyanamide complexes were prepared similarly. $[PtCl_2(NCNEt)_2]$ (**2**), $[PtCl_2(NCNC_5H_{10})_2]$ (**3**), and $[PtCl_2(NCNC_4H_8O)_2]$ (**4**) (yields are 82%, 87%, and 51%, respectively) were obtained at 20−25 °C as ca. 2:3, 1:1, and 1:4 *cis*/*trans* isomeric mixtures. Pure isomers of **2** and **3** were separated by column chromatography. The isomeric mixture of *cis*/*trans*-$[PtCl_2(NCNC_4H_8O)_2]$ (**4**) has low solubility in the most common organic solvents at room temperature, and we were unable to separate the isomers by column chromatography. However, on heating the *cis*/*trans* mixtures in the solid phase at 110 °C, *cis*-**1**−**4** convert to the *trans*-forms. After the solid state thermal isomerization, *trans*-**1**, **2**, and **3** were purified by column chromatography on silica gel (type 70−230 mesh, 60 Å, Aldrich, eluent $CH_2Cl_2/Et_2O = 5:1$, first fraction) to get rid of some yet unidentified byproducts. The *trans*-**4** can be more easily obtained by recrystallization of the *cis*/*trans*-**4** mixture from hot CH_2Cl_2.

***trans*-$[PtCl_2(NCNMe_2)_2]$ (*trans*-1).** Anal. Calcd for $C_6H_{12}N_4Cl_2Pt$: C, 17.74; H, 2.98; N, 13.79. Found: C, 17.68; H, 2.99; N, 13.73%. FAB$^+$-MS, *m*/*z*: 406 $[M]^+$, 370 $[M - HCl]^+$, 334 $[M - HCl - Cl]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.64$ (eluent acetone/CH_2Cl_2 = 1:1, v/v). IR spectrum in KBr, selected bands,

(75) Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. *Macromolecular Crystallography*; Carter, C. W., Jr., Sweet, R. M., Eds.; Methods in Enzymology, Vol. 276; Academic Press: New York, 1997; Part A, pp 307−326.

(76) Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. An intensity evaluation method: EVAL-14. *J. Appl. Crystallogr.* **2003**, *36*, 220.

(77) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

(78) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(79) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(80) Sheldrick, G. M. *SADABS—Bruker Nonius scaling and absorption correction*, v 2.06; Bruker AXS Inc.: Madison, WI, 2002.

(81) Sheldrick, G. M. *SHELXTL* v. 6.12; Bruker Analytical X-ray Systems, Bruker AXS Inc.: Madison, WI, 2002.

(82) Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(83) Makitova, D. D.; Krasochka, O. N.; Atovmyan, L. O.; Lavrent'ev, I. P.; Shul'ga, Yu. M.; Revenko, L. V.; Khidekel, M. L. *Koord. Khim.* **1987**, *13*, 383.

cm^{-1}: 2294 vs ν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.06 (s, Me). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 114.79 (NCN), 39.96 (Me).

***cis*-[PtCl$_2$(NCNMe$_2$)$_2$] (*cis*-1).** Anal. Calcd for $C_6H_{12}N_4Cl_2Pt$: C, 17.74; H, 2.98; N, 13.79. Found: C, 17.78; H, 3.07; N, 13.70%. FAB^+-MS, *m*/*z*: 406 $[M]^+$, 370 $[M - HCl]^+$, 334 $[M - HCl - Cl]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.53$ (eluent acetone/CH_2Cl_2 = 1:1, v/v). IR spectrum in KBr, selected bands, cm^{-1}: 2294 vs ν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.08 (s, Me). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 114.79 (NCN), 39.91 (Me).

***trans*-[PtCl$_2$(NCNEt$_2$)$_2$] (*trans*-2).** Anal. Calcd for $C_{10}H_{20}N_4Cl_2Pt$: C, 25.98; H, 4.36; N, 12.12. Found: C, 26.13; H, 4.40; N, 12.00%. FAB^+-MS, *m*/*z*: 485 $[M + Na]^+$, 462 $[M]^+$, 427 $[M - Cl]^+$, 391 $[M - 2Cl]^+$. IR spectrum in KBr, selected bands, cm^{-1}: 2289 vs ν(C≡N). TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.65$ (eluent Et_2O/CH_2Cl_2 = 1:5). ^1H NMR in $CDCl_3$, δ: 3.19 (q, 7.82 Hz, 2*H*, C*H*$_2$CH$_3$), 1.32 (t, 7.82 Hz, 3*H*, CH$_2$C*H*$_3$). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 113.40 (NCN), 45.79 (*C*H$_2$CH$_3$), 12.86 (CH$_2$*C*H$_3$).

***cis*-[PtCl$_2$(NCNEt$_2$)$_2$] (*cis*-2).** Anal. Calcd for $C_{10}H_{20}N_4Cl_2Pt$: C, 25.98; H, 4.36; N, 12.12. Found: C, 25.79; H, 4.32; N, 12.02%. FAB^+-MS, *m*/*z*: 462 $[M]^+$, 427 $[M - Cl]^+$, 391 $[M - 2Cl]^+$. IR spectrum in KBr, selected bands, cm^{-1}: 2289 vs ν(C≡N). TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.44$ (eluent Et_2O/CH_2Cl_2 = 1:5). ^1H NMR in $CDCl_3$, δ: 3.21 (q, 7.82 Hz, 2*H*, C*H*$_2$CH$_3$), 1.32 (t, 7.82 Hz, 3*H*, CH$_2$C*H*$_3$). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 113.40 (NCN), 45.89 (*C*H$_2$CH$_3$), 12.82 (CH$_2$*C*H$_3$).

***trans*-[PtCl$_2$(NCNC$_5$H$_{10}$)$_2$] (*trans*-3).** Anal. Calcd for $C_{12}H_{20}N_4Cl_2Pt$: C, 29.64; H, 4.15; N, 11.52. Found: C, 30.00; H, 4.40; N, 11.39%. FAB^+-MS, *m*/*z*: 486 $[M]^+$, 449 $[M - HCl]^+$, 414 $[M - 2Cl]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.59$ (eluent $Et_2O/CHCl_3$ = 1:9). IR spectrum in KBr, selected bands, cm^{-1}: 2292 s ν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.30 (t, 5.6 Hz, 2*H*, α-CH$_2$), 1.64 (m, 2*H*, β-CH$_2$), 1.57 (m, 1*H*, γ-CH$_2$). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 114.06 (NCN), 49.59 (α-CH$_2$), 24.39 (β-CH$_2$), 22.32 (γ-CH$_2$).

***cis*-[PtCl$_2$(NCNC$_5$H$_{10}$)$_2$] (*cis*-3).** Anal. Calcd for $C_{12}H_{20}N_4Cl_2Pt$: C, 29.64; H, 4.15; N, 11.52. Found: C, 29.47; H, 4.50; N, 11.10%. FAB^+-MS, *m*/*z*: 486 $[M]^+$, 449 $[M - HCl]^+$, 415 $[M - HCl - Cl]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.31$ (eluent $Et_2O/CHCl_3$ = 1:9). IR spectrum in KBr, selected bands, cm^{-1}: 2284 s ν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.36 (t, 5.6 Hz, 2*H*, α-CH$_2$), 1.69 (m, 2*H*, β-CH$_2$), 1.59 (m, 1*H*, γ-CH$_2$). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 114.09 (NCN), 49.58 (α-CH$_2$), 24.54 (β-CH$_2$), 22.40 (γ-CH$_2$).

***trans*-[PtCl$_2$(NCNC$_4$H$_8$O)$_2$] (*trans*-4).** Anal. Calcd for $C_{10}H_{16}N_4Cl_2O_2Pt$: C, 24.50; H, 3.29; N, 11.43. Found: C, 24.73; H, 3.40; N, 11.25%. FAB^+-MS, *m*/*z*: 513 $[M + Na]^+$, 490 $[M]^+$, 455 $[M - Cl]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.52$ (eluent acetone/CH_2Cl_2 = 1:4, v/v). IR spectrum in KBr, selected bands, cm^{-1}: 2300 s ν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.78 (t, 4.89 Hz, 2*H*, OCH$_2$), 3.42 (t, 4.89 Hz, 2*H*, NCH$_2$). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 65.44 (OCH$_2$), 48.05 (NCH$_2$), NCN was not detected. The corresponding *cis*-isomer exists in small amounts in the isomeric *cis*/*trans* mixture, and we could isolate only the dominant *trans*-form.

B. Synthesis of the Platinum(IV) Dialkylcyanamide Complexes. Preparation of [PtCl$_4$(NCNR$_2$)$_2$]. [PtCl$_2$(NCNR$_2$)$_2$] (200 mg) was dissolved in dried CH_2Cl_2 (5 mL), and dried Cl_2 was passed through this solution for 15 min. The reaction mixture was then left to stand for 30 min, and the solvent was evaporated under vacuum. Yield is 80−90%.

***trans*-[PtCl$_4$(NCNMe$_2$)$_2$] (*trans*-5).** Anal. Calcd for $C_6H_{12}N_4Cl_4Pt$: C, 15.11; H, 2.54; N, 11.74. Found: C, 15.23; H, 2.47; N, 11.36%. FAB^+-MS, *m*/*z*: 477 $[M]^+$, 406 $[M - 2Cl]^+$, 369 $[M - 2HCl - H]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.44$ (eluent acetone/CH_2Cl_2 = 1:1). IR spectrum in KBr, selected bands, cm^{-1}: 2192 s ν(C≡N). ^1H NMR in CD_2Cl_2, δ: 3.14 (Me). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, δ: 40.93 (J_{Pt-C} 5.0 Hz, Me), NCN was not observed even at high acquisition time.

***cis*-[PtCl$_4$(NCNMe$_2$)$_2$] (*cis*-5).** Anal. Calcd for $C_6H_{12}N_4Cl_4Pt$: C, 15.11; H, 2.54; N, 11.74. Found: C, 15.09; H, 2.69; N, 11.15%. FAB^+-MS, *m*/*z*: 477 $[M]^+$, 406 $[M - 2Cl]^+$, 369 $[M - 2HCl - H]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.35$ (eluent acetone/CH_2Cl_2 = 1:1). IR spectrum in KBr, selected bands, cm^{-1}: 2191 s ν(C≡N). ^1H NMR in CD_2Cl_2, δ: 3.14 (Me). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, δ: 40.93 (J_{Pt-C} 5.0 Hz, Me), NCN was not observed even at high acquisition time.

***trans*-[PtCl$_4$(NCNEt$_2$)$_2$] (*trans*-6).** Anal. Calcd for $C_{10}H_{20}N_4Cl_4Pt$: C, 22.53; H, 3.78; N, 10.51. Found: C, 22.28; H, 3.74; N, 10.30%. FAB^+-MS, *m*/*z*: 460 $[M - 2HCl]^+$, 425 $[M - Cl - 2HCl]^+$, 390 $[M - 3Cl - HCl]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.64$ (eluent acetone/CH_2Cl_2 = 1:9). IR spectrum in KBr, selected bands, cm^{-1}: 2172 s ν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.34 (q, 2*H*), 1.48 (t, 3*H*)(Et). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 46.99 (CH_2), 12.87 (CH_3), NCN was not observed even at high acquisition time due to low solubility of the compound.

***cis*-[PtCl$_4$(NCNEt$_2$)$_2$]·1/2NCNEt$_2$ (*cis*-6).** The complex was obtained (i) by the dissolution of $[PtCl_4(MeCN)_2]$ (50 mg) in Et_2NCN (0.3 mL; fresh sample should be used) at 40 °C followed by its precipitation with Et_2O (10 mL) from the homogeneous reaction mixture [yield is 60−70% (analyses are given in the following text)]; (ii) by chlorination of the corresponding Pt(II) complex with dry Cl_2 (authenticity of the samples was confirmed by comparison of their IR and ^1H NMR spectra). Calcd for $C_{10}H_{20}N_4Cl_4Pt \cdot 1/2NCNEt_2$: C, 25.79; H, 4.33; N, 12.03. Found: C, 25.79; H, 4.32; N, 12.02%. FAB^+-MS, *m*/*z*: 462 $[M - 2Cl]^+$, 426 $[M - 2Cl - HCl]^+$. TLC on Merck 60 F_{254} SiO_2 plates: R_f = 0.38 (eluent acetone/CH_2Cl_2 = 1:9). IR spectrum in KBr, selected bands, cm^{-1}: 2191 and 2168 sν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.34 (q, 2*H*), 1.46 (t, 3*H*)(Et). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 46.89 (*C*H$_2$), 13.00 (*C*H$_3$), NCN was not observed even at high acquisition time due to low solubility of the compound. Diethylcyanamide of crystallization was detected in the NMR spectra.

***trans*-[PtCl$_4$(NCNC$_5$H$_{10}$)$_2$] (*trans*-7).** Anal. Calcd for $C_{12}H_{20}N_4Cl_4Pt$: C, 25.87; H, 3.62; N, 10.06. Found: C, 25.61; H, 4.01; N, 9.62%. FAB^+-MS, *m*/*z*: 486 $[M - 2Cl]^+$, 449 $[M - 3Cl - 2H]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.70$ (eluent Et_2O/CH_2Cl_2 = 1:10). IR spectrum in KBr, selected bands, cm^{-1}: 2210 and 2166 s ν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.49 (m, br, 2*H*, α-CH$_2$), 1.76 and 1.67 (two s, br, 3*H*, β-CH$_2$ and γ-CH$_2$). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 50.26 (α-CH$_2$), 25.02 and 24.82 (β-CH$_2$), 22.31 (γ-CH$_2$).

***cis*-[PtCl$_4$(NCNC$_5$H$_{10}$)$_2$]·CH$_2$Cl$_2$ (*cis*-7).** Calcd for $C_{12}H_{20}N_4Cl_4Pt \cdot CH_2Cl_2$: C, 24.31; H, 3.45; N, 8.73. Found: C, 24.17; H, 3.82; N, 8.31%. FAB^+-MS, *m*/*z*: 579 $[M + Na - H]^+$, 485 $[M - 2Cl - H]^+$, 450 $[M - 3Cl - H]^+$, 413 $[M - 4Cl - 2H]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.59$ (eluent acetone/CH_2Cl_2 = 1:2). IR spectrum in KBr, selected bands, cm^{-1}: 2210 and 2164 s ν(C≡N).^1H NMR in $CDCl_3$, δ: 3.50 (m, br, 2*H*, α-CH$_2$), 1.77 and 1.67 (two s, br, 3*H*, β-CH$_2$ and γ-CH$_2$). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 50.33 (α-CH$_2$), 25.06 (β-CH$_2$), 22.33 (γ-CH$_2$), NCN was not observed even at high acquisition time.

***trans*-[PtCl$_4$(NCNC$_4$H$_8$O)$_2$]·CH$_2$Cl$_2$ (*trans*-8).** Calcd for $C_{10}H_{16}N_4Cl_4Pt \cdot CH_2Cl_2$: C, 20.45; H, 2.81; N, 8.67. Found: C, 19.93; H, 3.11; N, 8.60%. FAB^+-MS, *m*/*z*: 413 $[M - 4Cl - 6H]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.43$ (eluent acetone/CH_2Cl_2 = 2:1). IR spectrum in KBr, selected bands, cm^{-1}: 2169 s ν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.79 (m, br, 3*H*) and 3.56 (m, br, 1*H*,

OCH_2 and NCH_2). The solubility of the compound is insufficient to measure its ^{13}C NMR spectrum.

C. Pt(IV)-Mediated Hydrolysis of $NCNMe_2$. *trans*-[$PtCl_4${NH=C(NMe_2)OH}$_2$]·$2H_2O$ (9). This complex was obtained as yellow crystals (which were subject to X-ray crystallography) by slow evaporation of the solution of *trans*-[$PtCl_4(NCNMe_2)_2$] (*trans*-**5**) in a mixture of undried Et_2O and CH_2Cl_2. $C_4H_{12}N_4Cl_4Pt·2H_2O$: C, 13.12; H, 3.67; N, 10.20. Found: C, 13.42; H, 3.21; N, 9.84%. FAB^+-MS, *m*/*z*: 477 $[M - Cl]^+$, 443 $[M - 2Cl]^+$, 407 $[M - 3Cl]^+$. IR spectrum in KBr, selected bands, cm^{-1}: 3220 s ν(N—H), 1671 s and 1637 m—s ν(C═N). ^1H NMR in DMSO-d_6, δ: 8.28 (s+d, br, 1*H*, J_{Pt-H} 16.54 Hz, NH), 3.14 (s, 6*H*, Me). The low solubility of the complex does not allow us to measure the $^{13}C\{^1H\}$ NMR in CD_2Cl_2 even with a long acquisition time. The complex exhibits better solubility in DMSO-d_6, but it decomposes in this solvent during acquisition of the ^{13}C NMR spectrum. The two molecules of water were not found in the crystal structure (see later) probably due to the disorder.

trans-[$PtCl_4(NCNMe_2)_2$] (*trans*-**5**; 50 mg) was dissolved in acetone (1 mL) and left at 40 °C overnight. During this time, an orange solution and an orange precipitate were formed. The precipitate was filtered off, washed with acetone (0.3 mL) and with two 1-mL portions of Et_2O, and dried in air. Yield of $[Me_2NH_2]_2$-$[PtCl_6]$ (**10**) is 35%. The filtrate contains a broad mixture of yet unidentified products. Complex **10** was also obtained as orange-yellow crystals by heating [$PtCl_4(NCNMe_2)_2$] in nondried $MeNO_2$ for 3 days, and it was identified by its complete X-ray structural analysis and by comparison of the X-ray data (see Supporting Information) with those available from the literature.[83]

D. Pt(IV)-Mediated Hydrolytic Coupling of $NCNR_2$ (R = Me, Et; $R_2 = C_5H_{10}$, C_4H_8O). Undried $NCNR_2$ (1 mL) was added to [$PtCl_4(MeCN)_2$] (50 mg), and the reaction mixture was heated at 50 °C for 15 min and then left to stand overnight. In the cases of $R_2 = Me_2$ and C_4H_8O, the product was precipitated from the reaction mixture as yellow crystals after 2 ($R_2 = Me_2$) or 1 ($R_2 = C_4H_8O$) days. In the cases of $R_2 = Et_2$ and C_5H_{10}, the product was precipitated from the reaction mixture after 1 ($R_2 = C_5H_{10}$) or 2 ($R_2 = Et_2$) days by addition of Et_2O (10 mL). Yields are ca. 40%. If the reaction mixture (R = Et) was allowed to stand for a longer period (4 days), yellow-orange crystals of $(Et_2NH_2)_2[PtCl_6]$ were released in ca. 40% yield. This method gives sufficiently pure compounds, and their recrystallization is not required.

Alternatively, the metallacycles **11**—**13** were obtained by hydrolysis of *cis*-**5**—**7**, respectively. *cis*-[$PtCl_4(NCNR_2)_2$] (20 mg) was dissolved in CH_2Cl_2 (0.5 mL) and left to stand for 1 day at 40 °C, whereupon the yellow product that formed was separated by filtration and dried in air at room temperature. Yields are 30—35%. To obtain analytically pure samples, complex **11** was recrystallized from $MeNO_2$, and **12** and **13** were purified by dissolution in CH_2Cl_2 followed by addition of Et_2O.

[$PtCl_4${*N*H=C(NMe_2)OC(NMe_2)=*N*H}] (11). Anal. Calcd for $C_6H_{14}N_4Cl_4OPt·0.325NCNMe_2$: C, 16.18; H, 3.10; N, 12.58. Found: C, 16.11; H, 3.26; N, 12.27%. FAB^+MS, *m*/*z*: 447 $[M - 2Cl + Na]^+$, 466 $[M - 2Cl + 2Na - 3H]^+$. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.41$ (eluent acetone/CH_2Cl_2 = 1:1). IR spectrum in KBr, selected bands, cm^{-1}: 3267 s ν(N—H), 1678 and 1637 s ν(C═N). ^1H NMR in DMSO-d_6, δ: 8.31 (s+d, br, 1*H*, J_{Pt-H} 15.93 Hz, NH), 3.15 (s, 6*H*, Me). $^{13}C\{^1H\}$ NMR in DMSO-d_6, δ: 152.30 (J_{Pt-C} 7.86 Hz, NCN), 39.28 (Me). Crystals for X-ray analysis were obtained by slow evaporation of $MeNO_2$ solution.

[$PtCl_4${*N*H=C(NEt_2)OC(NEt_2)=*N*H}]·H_2O (12). Anal. Calcd for $C_{10}H_{24}N_4Cl_4O_2Pt$: C, 21.10; H, 4.25; N, 9.84. Found: C, 20.92; H, 4.00; N, 9.44%. FAB-MS, *m*/*z*: 480 $[M - 2Cl]^+$, 444 $[M - 2Cl - HCl]^+$. IR spectrum in KBr, selected bands, cm^{-1}: 3275 s-m ν(N—H), 1672 and 1628 s-m ν(C═N). ^1H NMR in DMSO-d_6, δ: 8.16 (s+d, br, 1*H*, J_{Pt-H} 17.5 Hz, NH), 3.54 (q, br, 7.0 Hz, 4*H*) and 1.16 (t, br, 7.0 Hz, 6*H*)(Et). $^{13}C\{^1H\}$ NMR in DMSO-d_6, δ: 151.45 (J_{Pt-C} 8.41 Hz, NCN), 44.29 (CH_2), 12.95 (CH_3). The complex $(Et_2NH_2)_2[PtCl_6]$ (**15**) (see Results and Discussion section) was characterized by X-ray diffractometry (see Supporting Information) and by C, H, N elemental analyses. Anal. Calcd for $C_{10}H_{22}N_4$-Cl_4OPt: C, 17.34; H, 4.00; N, 5.06. Found: C, 17.68; H, 4.52; N, 5.63%.

[$PtCl_4${*N*H=C(NC_5H_{10})OC(NC_5H_{10})=*N*H}] (13). Calcd for $C_{12}H_{22}N_4Cl_4OPt·0.125C_5H_{10}NCN$: C, 26.00; H, 3.98; N, 10.11. Found: C, 26.44; H, 4.12; N, 10.05%. FAB-MS, *m*/*z*: 540 $[M - Cl]^+$, 504 $[M - 2Cl]^+$. TLC on Merck 60 F_{254} SiO_2 plates: R_f = 0.64 (eluent acetone/CH_2Cl_2 = 1:2). IR spectrum in KBr, selected bands, cm^{-1}: 3264 m ν(N—H), 1672 vs and 1630 s ν(C═N). ^1H NMR in acetone-d_6, δ: 7.22 (s, br, 1*H*, NH), 3.84 (m, 4*H*, α-CH_2), 1.75 (m, 6*H*, β- and γ-CH_2). $^{13}C\{^1H\}$ NMR in acetone-d_6, δ: 49.05 (α-CH_2), 26.00 (β-CH_2), 23.98 (γ-CH_2), NCN was not detected.

[$PtCl_4${*N*H=C(NC_4H_8O)OC(NC_4H_8O)=*N*H}]·H_2O (14). This complex crystallizes from the reaction mixture as [$PtCl_4${*N*H=C(NC_4H_8O)OC(NC_4H_8O)=*N*H}]·$NCNC_4H_8O$·1/2HNC_4H_8O, and the structure of this solvate was determined by X-ray diffraction. To obtain reproducible microanalyses, the finely powdered complex was carefully washed with diethyl ether and then dried in a vacuum. The thus prepared sample contains no solvent molecules. Anal. Calcd for $C_{10}H_{20}N_4Cl_4O_4Pt$: C, 20.11; H, 3.38; N, 9.38. Found: C, 20.00; H, 3.48; N, 9.09%. FAB-MS, *m*/*z*: 508 $[M - 2Cl]^+$. TLC on Merck 60 F_{254} SiO_2 plates: R_f = 0.62 (eluent acetone/CH_2Cl_2 = 2:1). IR spectrum in KBr, selected bands, cm^{-1}: 3301 m ν(N—H), 1663 and 1627 s ν(C═N). ^1H NMR in acetone-d_6, δ: 7.52 (s, br, 1*H*, NH), 3.86 (m, 8*H*, OCH_2), 3.83 (m, 8*H*, NCH_2). $^{13}C\{^1H\}$ NMR in acetone-d_6, δ: 66.38 (OCH_2), 47.78 (OCH_2).

Acknowledgment. N.A.B. expresses gratitude to the INTAS (Grant YSF 2002-93) and the Center for Natural Sciences (Konkursnii Tsentr Fundamentalnogo Estestvoznaniya), Russia, (Grant PD03-1.3-28) for financial support. V.Yu.K. thanks the Russian Fund for Basic Research for a grant (03-03-32363), the International Science Foundation (Soros Foundation) for a Soros Professorship, and the Academy of Finland for support of the cooperation with the University of Joensuu. A.J.L.P. and V.Yu.K. are grateful to the FCT (Foundation for Science and Technology) (Portugal) and its POCTI (FEDER supported) program (POCTI/QUI/43415/2001 Project) for financial support of these studies.

Supporting Information Available: Crystallographic data in CIF format. Additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034800X