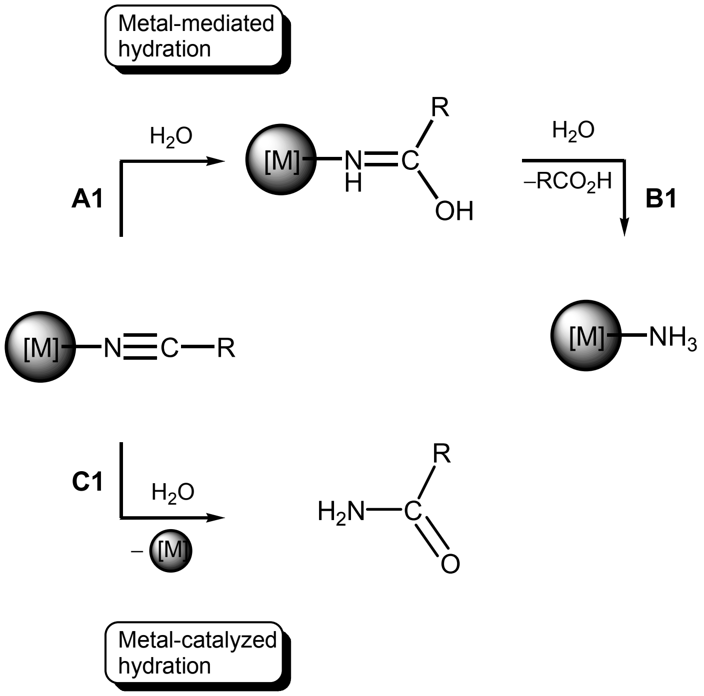
Metal-mediated and Metal-catalyzed Hydration: a Brief Review of Recent Works

After publication of three surveys[1-3] on reaction of metal-activated RCN substrates and, in particular, a review specifically focused on hydration of nitrile ligands,[3] a number of works on addition of water to nitrile species in metal complexes has rapidly expanded.[4-14,15-41] The major part of reports, which were not covered in the reviews[1,1,2] is devoted to metal-catalyzed[4,15-35,38] and metal-mediated[5-11,36-41] hydration of nitriles producing free or complexed amides, respectively, and in some instances ammonia complexes and carboxylic acids[22,42,43] (Scheme S1, Routes A1–C1).



Scheme S1

Within these works, metal-catalyzed conversion of nitriles to amides was reported for a range of transition metals (group 6: Mo^{IV},[23,24] 8: Ru^{II},[15-21] Os^{II},[20,22-24] 9: Ir^{III},[25] Rh^{I},[26] 10: Ni^{0},[27-30] Pd^{II},[31,32] Pt^{II},[33-35] 11: Au^{I} [4]) (Scheme S1, Route C1). Metal-mediated processes involve group 6 (Mo^{IV} [36]), 8 (Fe^{II},[8] Ru^{II},[37-40] Ru^{III} [37,38]), 9 (Co$^{II}_{2}$[11]), 10 (Pd^{II},[5] Pt^{II} [9,36,41]), and 12 (Zn^{II} [10]) metals (Scheme S1, Route A1). It is worthwhile mentioning that hydrolysis of acetonitrile ligated to bimetallic sulfur core $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ is accelerated by the oxygen-containing anions XO$^-$

(X = NO, NO_2, ClO_3), and this reaction involves intermediate derived from an intramolecular nucleophilic addition, which was detected by cyclic voltammetry.[36]

Characterization of $[PtCl_2(NCNR_2)(Me_2\textit{S}O)]$

The IR spectra of *cis*-**1** and *trans*-**1**, *cis*- and *trans*-**2**, and *cis*-**3**, exhibit one strong band each in the range 2276−2300 cm^{-1} due to the C≡N stretching vibrations. Values of these vibrations are higher than those for the corresponding free $NCNR_2$ species (ca. 2215 cm^{-1}) indicating some degree of electrophilic activation of the C≡N bond in the ligated state.[44] The IR spectra also exhibit the medium-to-strong absorption band in the range 1136−1150 cm^{-1}, which is attributed to ν(S=O).[45] These values are higher than those for the corresponding free Me_2SO species (ca. 1055 cm^{-1} [46]) favoring *S*-coordination of dimethyl sulfoxide in all isolated complexes. In the ^1H NMR spectra of **1**−**3**, the $PtSCH_3$ group was detected as a singlet in the range 3.47−3.49 ppm and this peak is flanked with satellites, specific for *S*-coordinated Me_2SO,[46] with $^3J_{PtH}$ varying from 21.5 to 24.0 Hz, and $PtSCH_3$ resonance gives expected integration with the amido protons. In the $^{13}C\{^1H\}$ NMR spectra of **1**−**3**, the carbons of the NR_2 group were observed in the ranges 40.0−49.9, 22.9−25.0, and at 65.6 ppm, while the nitrile carbon was not detected. The SCH_3 resonances were found in the range 43.2−45.1 ppm ($^2J_{PtC}$ 58−64 Hz). The characteristic feature of **1**−**3** is their dimerization under the ESI^+-MS conditions (MeCN or MeCN/H_2O, 70V). In the ESI^+ spectra, $[2M + Na]^+$, $[2M - Cl]^+$, and $[2M - 3Cl]^+$ ions were observed.

The *cis*- and *trans*-isomers for **1** and **2** have no significant differences in IR, ^1H and $^{13}C\{^1H\}$ NMR spectra but these isomers have two distinct spots on TLC.

The molecular structures of complexes *cis*-**1** and *cis*-**3** indicate that both coordination polyhedra have one dialkylcyanamide and one dimethyl sulfoxide ligand in the *cis* orientation and two Cl^- ligands, resulting in a typical square planar conformation. All bond angles around the Pt^{II} center are close to 90°, varying from 87.53(3) to 93.57(7)° (Table 2). The Pt−Cl distances

(2.2775(15)–2.3213(7) Å) are typical for the Pt−Cl bonds,[47-49] the Pt−Cl bond in the *trans* position to any of the dialkylcyanamide ligands [2.2775(15) and 2.2827(7) Å for **1** and **3**, correspondingly] is slightly shorter than the other one [2.306(2) and 2.3213(7) Å for **1** and **3**, respectively] thus reflecting a higher ground-state *trans*-influence of Me$_2$*S*O ligand than that of the R$_2$NCN ligands. Bond lengths and angles of the dimethyl sulfoxide ligands agree well with those for other (sulfoxide)Pt^{II} complexes[50,51] The Pt−N1−C1−N2 arrangement is almost linear [Pt−N1−C1 178.8(6) and 177.4(3)°, N1−C1−N2 179.7(8) and 178.1(3)° for **1** and **3**, correspondingly] and the piperidine ring in *cis*-**3** has a chair conformation. All C−C distances in this ring are the typical C−C single bonds,[52] ranging from 1.514(4) to 1.530(4) Å. The Pt−N1 distance [1.970(6) and 1.978(3) Å for **1** and **3**, respectively] agrees well with the corresponding value observed in *trans*-[PtCl$_2$(NCNMe$_2$)$_2$] [1.973(8) Å].[47] The C1−N1 distance is the normal C≡N triple bond[52] [1.137(9) and 1.150(4) Å for **1** and **3**, respectively] and comparable with those reported for the dialkylcyanamide complex *trans*-[PtCl$_2$(NCNMe$_2$)$_2$] (1.129(14) Å).[48]

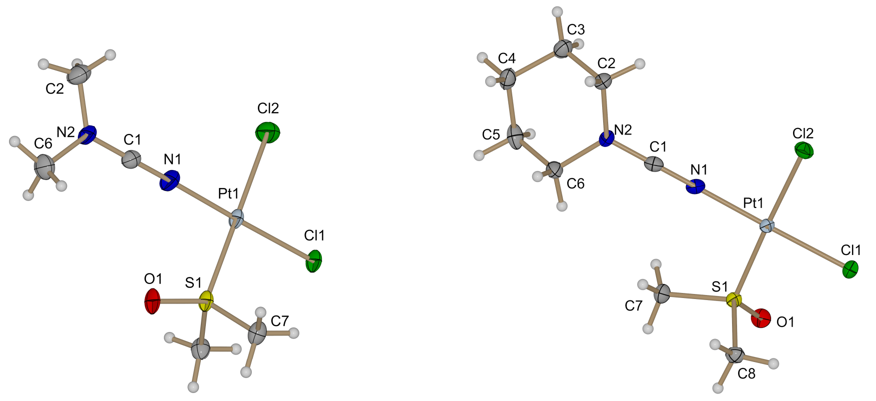


Figure S1. View of *cis*-**1** (left) and *cis*-**3** (right) with atomic numbering schemes. Thermal ellipsoids are drawn at the 50% probability level.

Table S1. Crystal Data for *cis*-**1** and *cis*-**3**.

	cis-**1**	*cis*-**3**
empirical formula	$C_5H_{12}Cl_2N_2OPtS$	$C_8H_{16}Cl_2N_2OPtS$
fw	414.22	454.28
temp (K)	120(2)	120(2)
λ(Å)	0.71073	0.71073
cryst syst	Orthorhombic	Triclinic
space group	*P*bcm	$P\bar{1}$
a (Å)	8.5581(8)	7.9021(6)
b (Å)	18.0603(9)	8.3489(5)
c (Å)	7.4262(6)	9.9116(7)
α (deg)	90	85.659(5)
β (deg)	90	87.383(7)
γ(deg)	90	81.935(7)
V (Å^3)	1147.81(15)	645.17(8)
Z	4	2
ρ_{calc} (Mg/m^3)	2.397	2.338
μ(Mo Kα) (mm^{-1})	12.833	11.427
No. reflns.	19315	10663
Unique reflns.	1426	2949
GOOF (F^2)	1.090	1.048
R_{int}	0.0549	0.0303
R1^a ($I \geq 2\sigma$)	0.0249	0.0169
wR2^b ($I \geq 2\sigma$)	0.0538	0.0350

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

Table S2. Selected bond lengths (Å) and angles (°) for *cis*-**1** and *cis*-**3**.

	cis-**1**	*cis*-**3**
Pt(1)–N(1)	1.970(6)	1.978(3)
Pt(1)–S(1)	2.202(2)	2.2133(7)
Pt(1)–Cl(1)	2.2775(15)	2.2827(7)
Pt(1)–Cl(2)	2.306(2)	2.3213(7)
N(1)–C(1)	1.137(9)	1.150(4)
C(1)–N(2)	1.293(8)	1.298(4)
Cl(1)–Pt(1)–Cl(2)	90.18(7)	90.53(3)
S(1)–Pt(1)–N(1)	91.3(2)	93.57(7)
Pt(1)–N(1)–C(1)	178.8(6)	177.4(3)
N(1)–C(1)–N(2)	179.7(8)	178.1(3)

1. A. J. L. Pombeiro and V. Y. Kukushkin, *Comprehensive Coordination Chemistry II*, 2004, **1**, 639–660.
2. V. Y. Kukushkin and A. J. L. Pombeiro, *Chem. Rev.*, 2002, **102**, 1771–1802.
3. V. Y. Kukushkin and A. J. L. Pombeiro, *Inorg. Chim. Acta*, 2005, **358**, 1–21.
4. R. S. Ramon, N. Marion and S. P. Nolan, *Chem. Eur. J.*, 2009, **15**, 8695–8697.
5. C. Borriello, R. Centore and G. Roviello, *Inorg.Chem. Commun.*, 2005, **8**, 755–758.
6. M. Dequeant, J. L. Eglin, M. K. Graves-Brook and L. T. Smith, *Inorg. Chim. Acta*, 2003, **351**, 141–149.
7. H. Nagao, T. Hirano, N. Tsuboya, S. Shiota, M. Mukaida, T. Oi and M. Yamasaki, *Inorg. Chem.*, 2002, **41**, 6267–6273.
8. N. K. Thallaj, J. Przybilla, R. Welter and D. Mandon, *J. Amer. Chem. Soc.*, 2008, **130**, 2414–2415.
9. K. M. C. Wong, N. Y. Zhu and V. W. W. Yam, *Chem. Commun.*, 2006, 3441–3443.
10. Z. Zhang, Y. He, Q. Zhao, W. Xu, Y. Z. Li and Z. L. Wang, *Inorg. Chem. Commun.*, 2006, **9**, 269–272.
11. P. J. Zinn, T. N. Sorrell, D. R. Powell, V. W. Day and A. S. Borovik, *Inorg. Chem.*, 2007, **46**, 10120–10132.
12. S. N. Greene and N. G. J. Richards, *Inorg. Chem.*, 2006, **45**, 17–36.
13. K. H. Hopmann, J. D. Guo and F. Himo, *Inorg. Chem.*, 2007, **46**, 4850–4856.
14. J. N. Moorthy and N. Singhal, *J. Org. Chem.*, 2005, **70**, 1926–1929.
15. M. Martin, H. Horvath, E. Sola, A. Katho and F. Joo, *Organometallics*, 2009, **28**, 561–566.
16. T. Smejkal and B. Breit, *Organometallics*, 2007, **26**, 2461–2464.
17. T. Oshiki, H. Yamashita, K. Sawada, M. Utsunomiya, K. Takahashi and K. Takai, *Organometallics*, 2005, **24**, 6287–6290.
18. V. Cadierno, J. Francos and J. Gimeno, *Chem. Eur. J.*, 2008, **14**, 6601–6605.
19. C. S. Yi, T. N. Zeczycki and S. V. Lindeman, *Organometallics*, 2008, **27**, 2030–2035.
20. S. M. Ashraf, W. Kandioller, M. G. Mendoza-Ferri, A. A. Nazarov, C. G. Hartinger and B. K. Keppler, *Chemistry & Biodiversity*, 2008, **5**, 2060–2066.

21. A. J. M. van Dijk, T. Heyligen, R. Duchateau, J. Meuldijk and C. E. Koning, *Chem. Eur. J.*, 2007, **13**, 7664–7672.

22. I. N. Stepanenko, B. Cebrian-Losantos, V. B. Arion, A. A. Krokhin, A. A. Nazarov and B. K. Keppler, *Eur. J. Inorg. Chem.*, 2007, 400–411.

23. K. L. Breno, T. J. Ahmed, M. D. Pluth, C. Balzarek and D. R. Tyler, *Coord. Chem. Rev.*, 2006, **250**, 1141–1151.

24. K. L. Breno, M. D. Pluth, C. W. Landorf and D. R. Tyler, *Organometallics*, 2004, **23**, 1738–1746.

25. M. G. Crestani, A. Steffen, A. M. Kenwright, A. S. Batsanov, J. A. K. Howard and T. B. Marder, *Organometallics*, 2009, **28**, 2904–2914.

26. A. Goto, K. Endo and S. Saito, *Angew. Chem.–Int. Ed.*, 2008, **47**, 3607–3609.

27. M. G. Crestani, A. Arevalo and J. J. Garcia, *Adv. Synth. Catal.*, 2006, **348**, 732–742.

28. M. G. Crestani and J. J. Garcia, *J. Mol. Catal.–Chemical*, 2009, **299**, 26–36.

29. P. Zerecero-Silva, I. Jimenez-Solar, M. G. Crestani, A. Arevalo, R. Barrios-Francisco and J. J. Garcia, *Appl. Catal.–General*, 2009, **363**, 230–234.

30. C. Crisostomo, M. G. Crestani and J. J. Garcia, *J. Mol. Catal.–Chem.*, 2007, **266**, 139–148.

31. E. S. Kim, H. S. Lee and J. N. Kim, *Tetrahedron Lett.*, 2009, **50**, 6286–6289.

32. E. S. Kim, H. S. Kim and J. N. Kim, *Tetrahedron Lett.*, 2009, **50**, 2973–2975.

33. M. North, A. W. Parkins and A. N. Shariff, *Tetrahedron Lett.*, 2004, **45**, 7625–7627.

34. T. J. Ahmed, B. R. Fox, S. M. M. Knapp, R. B. Yelle, J. J. Juliette and D. R. Tyler, *Inorg. Chem.*, 2009, **48**, 7828–7837.

35. X. B. Jiang, A. J. Minnaard, B. L. Feringa and J. G. de Vries, *J. Org. Chem.*, 2004, **69**, 2327–2331.

36. M. Le Henanf, C. Le Roy, F. Y. Petillon, P. Schollhammer and J. Talarmin, *Eur. J. Inorg. Chem.*, 2005, 3875–3883.

37. E. Tfouni, K. Q. Ferreira, F. G. Doro, R. S. da Silva and Z. N. da Rocha, *Coord. Chem. Rev.*, 2005, **249**, 405–418.

38. E. Tfouni, A. M. D. Macedo, L. N. Cardoso, K. Q. Ferreira, T. C. de Oliveira and Z. N. N. da Rocha, *Inorg. Chim. Acta*, 2005, **358**, 2909–2920.

39. N. E. Katz, F. Fagalde, N. D. L. de Katz, M. G. Mellace, I. Romero, A. Llobet and J. Benet-Buchholz, *Eur. J. Inorg. Chem.*, 2005, 3019–3023.

40. J. Mola, D. Pujol, M. Rodriguez, I. Romero, X. Sala, N. Katz, T. Parella, J. Benet-Buchholz, X. Fontrodona and A. Llobet, *Austr. J. Chem.*, 2009, **62**, 1675–1683.

41. F. H. Liu and W. Z. Chen, *Eur. J. Inorg. Chem.*, 2006, 1168–1173.

42. G. R. Lee and J. A. Crayston, *Polyhedron*, 1996, **15**, 1817–1821.

43. M. L. Kuznetsov, N. A. Bokach, V. Y. Kukushkin, T. Pakkanen, G. Wagner and A. J. L. Pombeiro, *J. Chem. Soc.–Dalton Trans.*, 2000, 4683–4693.

44. R. A. Michelin, M. Mozzon and R. Bertani, *Coord. Chem. Rev.*, 1996, **147**, 299–338.

45. J. A. Davies, in *Advances in inorganic chemistry and radiochemistry*, Editon edn., 1981, vol. 24.

46. Y. N. Kukushkin, *Russ. J. Coord. Chem.*, 1997, **23**, 169.

47. N. A. Bokach, T. B. Pakhomova, V. Y. Kukushkin, M. Haukka and A. J. L. Pombeiro, *Inorg. Chem.*, 2003, **42**, 7560–7568.

48. P. V. Gushchin, N. A. Bokach, M. Haukka, E. S. Dmitrieva and V. Y. Kukushkin, *Acta Cryst. Sect. E*, 2006, **62**, M244–M246.

49. P. B. Viossat, P. Khodadad and N. Rodier, *Acta Cryst. Sect. C*, 1991, **47**, 1316–1317.

50. M. Calligaris, *Coord. Chem. Rev.*, 2004, **248**, 351–375.

51. M. Calligaris and O. Carugo, *Coord. Chem. Rev.*, 1996, **153**, 83–154.

52. F. H. Allen, O. Kennard and D. G. Watson, *J. Chem. Soc. Perkin Trans. II*, 1987, S2.