Organometallics **2001,** *20,* 3635−3637

Aqueous Organometallic Chemistry with Nitrogen Ligands: Synthesis of Hydrophilic Platinum(0) Olefin Complexes

Abhijit Kundu and Brian P. Buffin*

Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008

Received March 16, 2001

Summary: Reactions of hydrophilic unsymmetrical pyridine−imine chelating ligands with Pt(η^2-norbornene)$_3$ in the presence of olefins that contain electron-withdrawing substituents afford water-soluble three-coordinate Pt(0) complexes. The stability of these organometallic complexes in aqueous solution is dependent on the position of the hydrophilic charged substituents in the chelating ligand and the electronic nature of the coordinated olefin.

Homogeneous catalysis by transition-metal organometallic complexes offers many advantages over traditional heterogeneous systems, including higher activity and selectivity, milder reaction conditions, and the ability to control the steric and electronic properties of the catalyst by ligand modification.[1] The major disadvantage of homogeneous catalysis is the immense difficulty of catalyst recycling. One method used to achieve catalyst separation has been to perform the chemistry in an aqueous biphasic system where an ancillary tertiary phosphine ligand with a charged or polar group (e.g., $-SO_3Na$, $-PO_3Na_2$, −COOH, −OH) imparts aqueous solubility to the organometallic species.[2] The considerable utility of water-soluble organometallic transition-metal complexes employing these ligands is evidenced by their ability to catalyze a very large variety of chemical transformations in aqueous solution, the chemistry of which has been extensively studied.[3]

Despite a growing interest in the use of nitrogen-donor ligands in homogeneous organometallic chemistry and catalysis,[4] the use of hydrophilic nitrogen ligands in aqueous organometallic chemistry has remained relatively unexplored.[5] Competition from water molecules for metal coordination as well as the rapid hydrolysis of imine-based ligands in aqueous solution has likely contributed to the lack of research effort in this field. A systematic attempt to determine relevant factors that govern the potential use of nitrogen-donor ligands in aqueous organometallic systems has not been performed. Aqueous phase catalysis continues to attract research attention due to potential “green” or environmentally benign benefits.[6] Thus, the use of organometallic catalysts with hydrophilic nitrogen-donor ligands, which possess electronic and steric properties different from those of their well-studied phosphine counterparts, may provide new alternatives to processes currently performed in organic solvents. Transition-metal complexes with nitrogen-donor ligands have recently been employed as aqueous phase catalysts for alcohol oxidation,[7] coordination polymerization,[8] the production of hydrogen peroxide,[9] and many other chemical transformations,[10] which suggests a growing importance of this area of chemistry. In this report we communicate initial results from our research aimed at forming aqueous-stable transition-metal organometallic complexes with unsymmetrical hydrophilic pyridine−imine ligands.

Recognizing that bidentate ligand coordination represents a potential means of stabilizing nitrogen ligands toward displacement in water, we focused our efforts on the synthesis of a series of unsymmetrical phenylimino−pyridine-based ligands as depicted in Scheme 1. Condensation of 2-pyridinecarboxaldehyde or 6-methyl-2-pyridinecarboxaldehyde with substituted anilines affords the potentially chelating ligands **1**−**3** in high isolated yields.[11] Ligand syntheses were performed in anhydrous alcohol (methanol or ethanol) solvent either at ambient temperature with formic acid catalyst or at elevated temperatures with azeotropic removal of water by benzene. The symmetrical 1,4-diaza-1,3-butadiene ligand **4** was formed by condensation of *p*-aminobenzoic acid with 2,3-butanedione. All ligands were characterized by ^{1}H and ^{13}C NMR and IR spectra. It is of importance to note that these ligands are soluble in methanol and other highly polar organic solvents but

---

[1] Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley: New York, 1992.

[2] (a) Cornils, B. *J. Mol. Catal. A: Chem.* **1999**, *143*, 1. (b) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177. (c) Cornils, B.; Wiebus, E. *CHEMTECH* **1995**, *25*, 33.

[3] Cornils, B., Herrmann, W. A., Eds. *Aqueous-Phase Organometallic Catalysis*; Wiley-VCH: Weinheim, Germany, 1998.

[4] (a) Fache, F.; Schulz, E.; Tommasino, M. L.; Lemaire, M. *Chem. Rev.* **2000**, *100*, 2159. (b) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497. (c) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (d) Albietz, P. J.; Yang, K.; Lachicotte, R. J.; Eisenberg, R. *Organometallics* **2000**, *19*, 3543. (e) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831. (f) Laine, T. V.; Piironen, U.; Lappalainen, K.; Klinga, M.; Aitola, E.; Leskelä, M. *J. Organomet. Chem.* **2000**, *606*, 112.

[5] (a) Borriello, C.; Ferrara, M. L.; Orabona, I.; Panunzi, A.; Ruffo, F. *J. Chem. Soc., Dalton Trans.* **2000**, 2545. (b) Ferrara, M. L.; Giordano, F.; Orabona, I.; Panunzi, A.; Ruffo, F. *Eur. J. Inorg. Chem.* **1999**, 1939. (c) Ferrara, M. L.; Orabona, I.; Ruffo, F.; Funicello, M.; Panunzi, A. *Organometallics* **1998**, *17*, 3832.

[6] (a) Anastas, P. T.; Bartlett, L. B.; Kirchhoff, M. M.; Williamson, T. C. *Catal. Today* **2000**, *55*, 11. (b) Armor, J. N. *Appl. Catal. A: Gen.* **1999**, *189*, 153. (c) Anastas, P. T., Williamson, T. C. Eds. *Green Chemistry, Frontiers in Benign Chemical Syntheses and Processes*; Oxford University Press: Oxford, U.K., 1998.

[7] ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000**, *287*, 1636.

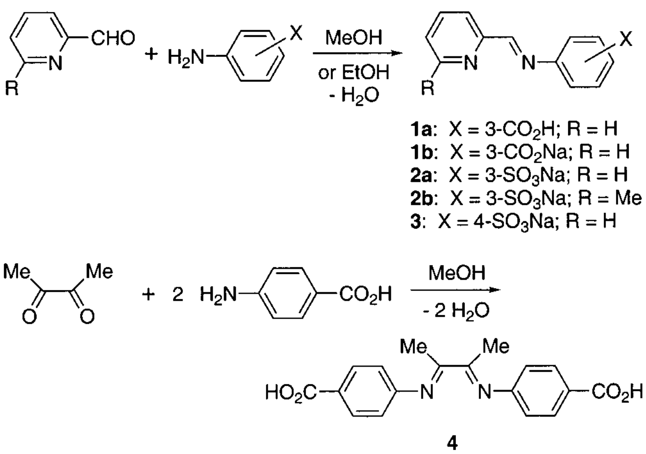
[8] (a) Held, A.; Mecking, S. *Chem. Eur. J.* **2000**, *6*, 4623. (b) Held, A.; Bauers, F. M.; Mecking, S. *Chem. Commun.* **2000**, 301.

[9] (a) Bortolo, R.; Bianchi, D.; D'Aloisio, R.; Querci, C.; Ricci, M. *J. Mol. Catal. A: Chem.* **2000**, *153*, 25. (b) Bianchi, D.; Bortolo, R.; D'Aloisio, R.; Ricci, M. *J. Mol. Catal. A: Chem.* **1999**, *150*, 87.

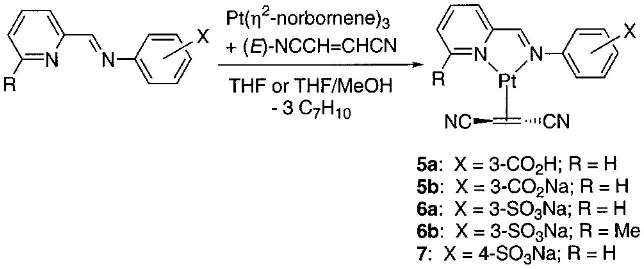
[10] See for example: (a) ten Brink, G.-J.; Arends, I. W. C. E.; Papadogianakis, G.; Sheldon, R. A. *Chem. Commun.* **1998**, 2359. (b) Pénicaud, V.; Maillet, C.; Janvier, P.; Pipelier, M.; Bujoli, B. *Eur. J. Org. Chem.* **1999**, 1745.

10.1021/om010212k CCC: $20.00
Publication on Web 07/19/2001

Scheme 1



Scheme 2



are readily hydrolyzed in the presence of small amounts of water, as evidenced by ^{1}H NMR spectroscopy.

Three-coordinate platinum(0) olefin complexes of all ligands were formed by reaction of Pt(η^2-norbornene)$_3$ in the presence of fumaronitrile ((*E*)-NCCH=CHCN), as illustrated in Scheme 2.[12] These platinum compounds were isolated as air-stable red to orange solids in good yield and characterized by NMR and IR spectroscopy and elemental analysis.[13] In marked contrast to the free ligands, complexes **5b**, **6a**,**b**, and **7** are stable in water for prolonged periods of time.[14] Complexes **6a**,**b**, which contain 3-SO$_3$Na-substituted ligands, were found to be the most stable, with very little decomposition evident even after several days in aqueous solution. Interestingly, complex **7**, with the 4-SO$_3$Na moiety, slowly decomposed after several hours. Stable water-soluble Pt(0) compounds are uncommon,[5,15] and to our knowledge, only the homoleptic complex Pt(TPPTS)$_4$ (where TPPTS = P(C$_6$H$_4$-*m*-SO$_3$Na)$_3$) contains a charged sulfonate ion as the hydrophilic moiety.[16] In addition, zerovalent platinum compounds with direct carbon–platinum bonds that are stable in aqueous solution are exceedingly rare.[5] Diagnostic of chelating ligand coordination in these complexes is the downfield shift in the ^{1}H NMR spectra of the imine proton signal by 0.5–1.0 ppm upon coordination to the Pt(0) center. Olefin coordination is evidenced by a dramatic high-field shift in both the ^{1}H and ^{13}C NMR spectra. For example, the olefinic carbons of coordinated fumaronitrile are observed approximately 100–120 ppm upfield relative to the unbound species. ^{195}Pt satellites on the imine proton ($^3J_{\mathrm{Pt-H}}$ ca. 50 Hz), the ortho proton of the pyridine ring ($^3J_{\mathrm{Pt-H}}$ ca. 25 Hz), and the olefinic protons ($^2J_{\mathrm{Pt-H}}$ ca. 80 Hz) provide further evidence that both the chelating nitrogen ligands and fumaronitrile retain coordination to platinum in both water and polar organic solvents on the NMR time scale. For all complexes **5b**, **6a**,**b**, and **7**, signals in the ^{1}H NMR that could be attributed to free fumaronitrile or 2-pyridinecarboxaldehyde were either not observed or were observed only after several hours, which indicates that both the metal–olefin bond and the imine bond in the coordinated ligand are stable in neutral aqueous solution. This is in contrast to related Pt(0) complexes with ligands based on α-D-mannose, which have been shown to slowly decompose through olefin dissociation.[5c] For comparison with the Pt(0) olefin complexes, the Pd(0) fumaronitrile complex Pd(**2b**)(η^2-(*E*)-NCCH=CHCN) was synthesized from bis(dibenzylideneacetone)palladium(0) and was likewise found to be stable in aqueous solution.

Complex **5a**, which contains the 3-CO$_2$H-functionalized ligand **1a**, is soluble in polar organic solvents, including THF and dimethylformamide, but is water insoluble. Previous work in our group has shown that W(0) carbonyl complexes of similar ligands can be transferred into an aqueous phase by deprotonation of the acidic form of the ligand with base.[17] Surprisingly, attempts to generate a water-soluble form of **5a** by addition of NaOH to an aqueous suspension of the solid resulted in decomposition of the organometallic complex, as evidenced in the ^{1}H NMR data. Believing that the addition of highly nucleophilic hydroxide ion may be responsible for complex breakdown, we independently synthesized the related anionic ligand **1b**. Complex **5b**

---

(11) **Synthesis of 2b.** Metanilic acid, sodium salt (1 g, 5.13 mmol), was dissolved in dry methanol (8 mL). Formic acid (3 drops) was added, followed by the addition of 6-methyl-2-pyridinecarboxaldehyde (1 equiv). After the mixture was stirred for 18 h at ambient temperature, anhydrous MgSO$_4$ was added to remove water. Stirring was continued for another 3 h. The desired pyridine–imine ligand **2b** was obtained quantitatively after separation of the MgSO$_4$ desiccant and the removal of methanol under reduced pressure. ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 8.52 (s, 1H, CH=N), 7.98 (d, 1H), 7.86 (t, 1H), 7.52 (d, 1H), 7.48 (s, 1H), 7.40 (m, 2H), 7.28 (d, 1H), 2.56 (s, 3H, Me-py). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, δ): 161.1 (CH=N), 158.2, 153.3, 150.0, 149.5, 137.3, 128.8, 125.1, 123.8, 120.8, 118.6, 118.4, 23.9 (Me-py). Synthetic details and ^{1}H and ^{13}C NMR spectroscopic data for all ligands are contained in the Supporting Information.

(12) Stereocenters on coordinated olefins are shown to depict the relative trans position of –CN and –CO$_2$Me groups in fumaronitrile and dimethyl fumarate, respectively, and do not imply a preferential coordination of one diastereotopic face over the other.

(13) **Synthesis of Pt(2a)(η^2-(*E*)-NCCH=CHCN) (6a).** To a stirred solution of fumaronitrile (9 mg, 0.12 mmol) and Pt(η^2-norbornene)$_3$ (48 mg, 0.10 mmol) in dry THF (20 mL) was added solid ligand **2a** (29 mg, 0.10 mmol) under nitrogen. The reaction medium became clear upon addition of dry MeOH (5 mL). After the mixture was stirred for 14 h at ambient temperature, the resulting yellow solid was separated by filtration, washed with THF, and dried under vacuum. The isolated yield of product **6a** is 38 mg (70%). ^{1}H NMR (D$_2$O, 400 MHz, δ): 9.35 (s, 1H, CH=N), 8.50 (d, 1H, J = 5.2 Hz, *o*-py), 7.90 (m, 3H), 7.62 (d, 1H, J = 7.7 Hz), 7.56 (d, 1H, J = 8.1 Hz), 7.33 (t, 1H, J = 8.1 Hz), 7.16 (t, 1H, J = 5.8 Hz), 2.83 (d, 1H, J = 7.7 Hz, $^2J_{\mathrm{Pt-H}}$ = 79 Hz), 2.74 (d, 1H, J = 7.7 Hz, $^2J_{\mathrm{Pt-H}}$ = 80 Hz). ^{13}C{^{1}H} NMR (D$_2$O, 100 MHz, δ): 163.1 (CH=N), 154.5, 153.4, 144.1, 139.7, 130.5, 130.4, 129.4, 127.4, 125.7 (NC–), 125.6 (NC–), 125.4, 123.0, 0.26 (HC=CH), –0.72 (HC=CH). IR (solid, cm^{-1}): 2214, 1222. Anal. Calcd for C$_{16}$H$_{11}$N$_4$O$_3$SNaPt: C, 34.47; H, 1.99; N, 10.05. Found: C, 34.24; H, 1.94; N, 9.86. It should be noted that in the case of ligands containing sodium salts (**1b**, **2a**,**b**, and **3**), reaction with Pt(η^2-norbornene)$_3$ and olefin does not proceed cleanly either in THF or in MeOH alone and a combination of THF and MeOH (4:1) is recommended. Synthetic details and characterization data for all metal–olefin complexes are contained in the Supporting Information.

(14) The duration of complex stability ranges from 4 h to >3 days in aqueous solution. The solubility of these Pt(0) complexes is estimated at >2.5 g/100 mL of H$_2$O as determined for **6a**.

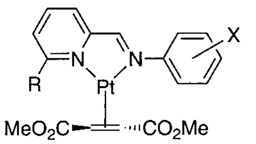
(15) (a) Darensbourg, D. J.; Decuir, T. J.; Stafford, N. W.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *Inorg. Chem.* **1997**, *36*, 4218. (b) Ellis, J. W.; Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *Inorg. Chem.* **1992**, *31*, 3026.

(16) Herrmann, W. A.; Kellner, J.; Riepl, H. *J. Organomet. Chem.* **1990**, *389*, 103.

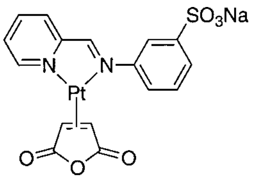
(17) Buffin, B. P. Unpublished results.

formed from this ligand is water-soluble and stable in neutral aqueous solution, which suggests a limited stability of these organometallic species in alkaline solution.

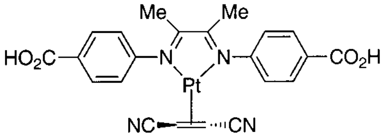
To determine the potential for forming aqueous stable Pt(0) complexes with other electron-withdrawing olefins, the analogous dimethyl fumarate ((*E*)-$MeO_2CCH{=}CHCO_2Me$) complexes **8** and **9**, with ligands **2a**,**b** and **3**, respectively, and the maleic anhydride Pt(0) derivative **10** were formed in a manner similar to the fumaronitrile derivatives. All four complexes are stable in aqueous solution. However, the dimethyl fumarate complexes were found to be the least stable and started to slowly decompose to untraceable products after 1 h. However, even after 24 h significant amounts of the complexes remained in solution. In agreement with previous reports,[5] the maleic anhydride complex displayed stability comparable to that of the fumaronitrile derivatives. Reaction of the symmetrical ligand **4** with Pt(η^2-norbornene)$_3$ in the presence of fumaronitrile gave complex **11** in high yield. Complex **11** is water-insoluble, and attempts to promote aqueous dissolution by addition of NaOH resulted in product decomposition, as was the case for complex **5a**.



8a: X = 3-SO_3Na; R = H
8b: X = 3-SO_3Na; R = Me
9: X = 4-SO_3Na; R = H



10

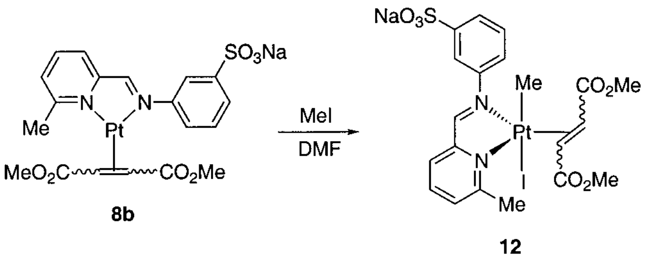


11

Olefinic signals in the ^1H NMR spectra of complexes **5**–**10**, which contain unsymmetrical pyridine–imine ligands, appear as separated doublets or as AB quartets. The corresponding alkene carbon signals in the ^{13}C NMR data are also nonequivalent. It is therefore reasoned that at ambient temperatures rotation about the Pt–olefin bond is slow on the NMR time scale, as a faster rotation would equilibrate the signals. This is true for all complexes regardless of olefin identity. As expected, the fumaronitrile protons in complex **11**, with the symmetrical diazabutadiene ligand, are observed as a single resonance with ^{195}Pt satellites. Spectral evidence for a fluxional process is only found in the ^1H NMR data of complex **5b**, where the fumaronitrile protons appear as an AB quartet at low complex concentration, which collapses to a singlet with coupling to ^{195}Pt as the amount of complex is increased. An intermolecular olefin exchange process thought to be responsible for this behavior is being examined.[18]

Preliminary results on the reactivity of these water-soluble Pt(0) olefin species have been obtained. Addition of methyl iodide to a solution of the dimethyl fumarate complex **8b** results in oxidative addition of the carbon–iodine bond to afford the five-coordinate Pt(II) complex **12**, as depicted in Scheme 3. Interestingly, a near 1:1 mixture of isomers is observed in both the ^1H and ^{13}C NMR spectra. This distribution of isomeric products is likely a result of random olefin coordination in the parent Pt(0) complex **8b**, which lacks the ability to direct preferential coordination of one diastereotopic olefin face over the other (*re* vs *si*). Similar oxidative addition reactions to Pt(0) olefin complexes that contain a variety of N–N′ chelating ligands have been investigated previously.[19] The stability of **12** is attributed to the electron-withdrawing nature of the dimethyl fumarate ligand as well as the in-plane steric hindrance imposed by the methyl group in the 6-position of the pyridine ring. The presence of sterically demanding groups around the metal center in related complexes has been shown to stabilize five-coordinate species through a relative destabilization of the four-coordinate square-planar (N–N′)PtMeX species which would be formed upon olefin dissociation.[19b] Formation of four-coordinate Pt(**2b**)MeI from **12** is not observed in DMF solution; however, dissociation of the dimethyl fumarate ligand is evident after several hours in D_2O at ambient temperature. In addition, these Pt(0) and Pd(0) complexes have recently been found to be active catalysts for the aqueous phase hydrogenation of olefins, though a heterogeneous mechanism involving precipitated metal cannot be ruled out at this time.

Scheme 3



In summary, we have synthesized novel platinum(0) olefin complexes with hydrophilic pyridine–imine ligands. Although the free ligands containing the imine bonds are extremely unstable in water and undergo rapid hydrolysis, the organometallic complexes containing these chelating ligands are stable in aqueous medium. The influence of ligand substituents on complex stability and reactivity as well as the ability of these water-soluble complexes to participate in aqueous biphasic oxidative addition processes are currently being investigated.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (PRF No. 32973-GB3) and to Western Michigan University for start-up funds awarded to B.P.B.

Supporting Information Available: Text giving details of syntheses and complete spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010212K

---

[18] For recent studies of olefin exchange in similar systems see: (a) Canovese, L.; Visentin, F.; Chessa, G.; Uguagliati, P.; Dolmella, A. *J. Organomet. Chem.* **2000**, *601*, 1. (b) Van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Speck, A. L. *Inorg. Chem.* **1994**, *33*, 1521. (c) Van Asselt, R.; Elsevier, C. J. *Tetrahedron* **1994**, *50*, 323.

[19] (a) De Felice, V.; Funicello, M.; Panunzi, A.; Ruffo, F. *J. Organomet. Chem.* **1991**, *403*, 243. (b) Cucciolito, M. E.; De Felice, V.; Panunzi, A.; Vitagliano, A. *Organometallics* **1989**, *8*, 1180.