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The pH dependent phase transfer of an organometallic complex: synthesis, characterization, and crystal structure of a W(0) tetracarbonyl with an acidic pyridine–imine ligand

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Abstract

Reaction of the asymmetrical pyridine–imine ligand **L** (where **L** = benzoic acid, 3-[(2-pyridinylmethylene)amino]) with $W(CO)_3(EtCN)_3$ and CO (g) affords a W(0) tetracarbonyl in which the Schiff-base ligand coordinates in a bidentate fashion. The complex was characterized by IR, NMR, and UV–visible spectroscopy and elemental analysis. The solid-state structure of $W(CO)_4$(**L**), which crystallized in the orthorhombic space group *Pbca* with unit cell parameters $a = 22.497(4)$ Å, $b = 14.112(6)$ Å, and $c = 13.675(3)$ Å was established by X-ray crystallography. Deprotonation of the $–CO_2H$ group on the ligand with base results in the formation of a water-soluble organometallic complex which can be partitioned between organic and aqueous phases in a biphasic system by pH adjustment.

Keywords: Pyridinylimine ligand; Tungsten(0) complex; Water-soluble complex; Phase transfer

Research in the area of aqueous organometallic chemistry has primarily focused on complexes in which a hydrophilic phosphine ligand is used for the promotion of water solubility [1]. Recently we communicated our success at forming stable water-soluble Pt(0) and Pd(0) complexes with nitrogen-based pyridinylimine and diazabutadiene ligands [2] as well as our ability to extend this chemistry into higher valent Group 10 metal complexes [3,4]. Despite a growing interest in water-soluble organometallic compounds as recoverable "green" catalysts [5,6], the use of nitrogen ligands in this area of research has remained relatively unexplored. One of the major drawbacks to aqueous-phase catalysis is the diminished activity that often results from the limited mass transfer of hydrophobic organic substrates into the catalyst phase [1]. Herein we describe the synthesis and characterization of a stable metal carbonyl with an acidic pyridine–imine ligand and the ability to transfer this complex between organic and aqueous phases via simple pH adjustment, a protocol that may prove useful for catalyst partitioning in other systems.

The pyridinylimine ligand **L** (Fig. 1) was prepared via the condensation of 3-aminobenzoic acid with 2-pyridinecarboxaldehyde in refluxing ethanol, with benzene added to promote the azeotropic removal of water by-product, and isolated as an air-stable pale yellow solid in 79% yield [4]. The observation of signals at 8.62 ppm and 162.5 ppm in the ^1H and ^{13}C NMR spectra of **L**, respectively, are consistent with formation of the imine. Addition of water to **L** results in the immediate hydrolysis of the imine bond as evidenced by the appearance of an aldehyde signal in the ^1H NMR data.

A deep blue–green solution was formed upon addition of Tetrahydrofuran (THF) to a 1:1 mixture of **L** and $W(CO)_3(EtCN)_3$, suggesting displacement of two labile propionitrile molecules and coordination of the ligand as a bidentate nitrogen donor [7]. The resulting air-sensitive mononitrile compound, $W(CO)_3(EtCN)$(**L**), steadily scavenged CO from decomposition products to afford

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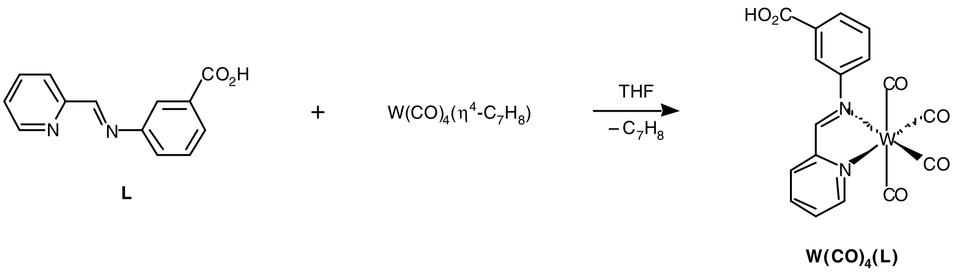

Fig. 1. Synthetic scheme for the preparation of $W(CO)_4$(**L**).

the tetracarbonyl product $W(CO)_4$(**L**) (Fig. 1). Addition of CO to a solution of the tricarbonyl mononitrile species or utilization of $W(CO)_4(C_7H_8)$ (where C_7H_8 = norbornadiene) as the tungsten starting material provided a more convenient synthesis of $W(CO)_4$(**L**) [8]. The deep purple color of $W(CO)_4$(**L**), with a lowest energy metal-to-ligand charge transfer (MLTC) absorption of λ_{max} $(CH_2Cl_2) = 548$ nm in the electronic spectrum, is consistent with literature precedent for the coordination of conjugated pyridine–imine ligands to low valent metals [9–11]. $W(CO)_4$(**L**) was fully characterized by IR and NMR spectroscopic methods, elemental analysis, and the molecular structure in the solid state was determined via X-ray diffraction. Diagnostic of ligand coordination in the tetracarbonyl compound is an overall downfield shift of signals in the ^1H NMR data. The imine proton and the *ortho*-proton of the pyridine ring are most influenced by ligand coordination to the $W(CO)_4$ center, experiencing downfield shifts of 0.75 and 0.58 ppm, respectively. Similar resonance shifts have been observed in related compounds [7]. The three band pattern in the carbonyl region of the IR spectrum of $W(CO)_4$(**L**) ($\nu_{CO} = 2009$ (m), 1901 (s), 1851 (m) cm^{-1}) is consistent with a pseudo C_{2v} symmetry for the *cis*-tetracarbonyl complex.

The molecular structure of $W(CO)_4$(**L**) with the associated atom-numbering scheme are depicted in Fig. 2 with selected bond lengths and angles given in the figure caption [12]. The geometry around the W(0) d^6 metal center in $W(CO)_4$(**L**) is a distorted octahedron, where the relatively small N(1)–W(1)–N(2) bond angle of 72.5(3)° is a result of chelating ligand steric constraints. Consistent with a planar arrangement of the pyridine–imine ligand, the bond angles around the metal center which includes the ligand nitrogen atoms and the carbonyl groups containing C(15) and C(17) sum to 360.1(9)°. A least-squares plane analysis of the 8 non-hydrogen atoms comprising the pyridine–imine ligand and the W atom reveals a planar chelation of the ligand to the metal, with a mean and maximum deviation from planarity of 0.037 and 0.07(1) Å for C(4), respectively. The phenyl ring of the pyridine–imine ligand containing C(7)–C(12) is tilted relative to the metal-chelate ring with a calculated dihedral angle of 45.06° between the two. When bulkier non-hydrogen atoms are located in the *ortho*-position(s), the phenyl ring has been shown to adopt a position perpendicular to that of the metal-chelate in related compounds [13,14]. The relatively short C = N bond length of 1.30(1) Å for C(6)–N(2), when compared to the C(7)–N(2) bond length of 1.42(1) Å and the C(5)–N(1) length of 1.37(1) Å in the pyridine ring, is consistent with a high degree of double bond character in the imine bond and a lack of electron delocalization in the metal-chelate of $W(CO)_4$(**L**). All of the bond lengths and angles are similar to those in related compounds [15]. The hydrogen atom attached to O(2) could not be located, but is inferred from the relatively long C(13)–O(2) bond length of 1.30(1) Å. Analysis of the molecular packing in the unit cell reveals

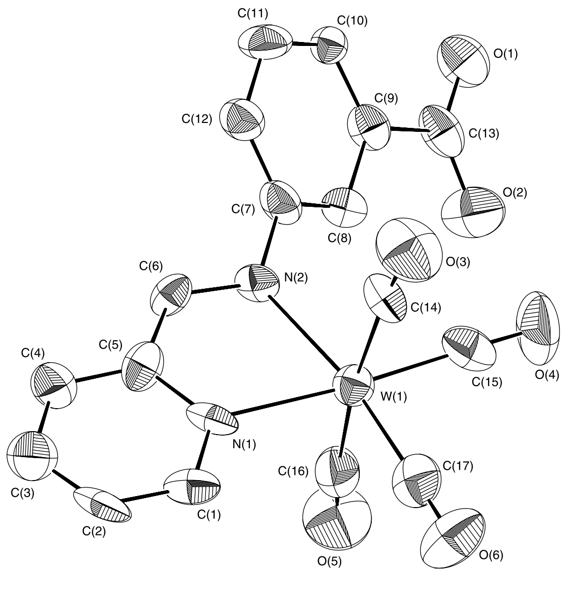

Fig. 2. ORTEP representation of the molecular structure of $W(CO)_4$(**L**) with 50% probability ellipsoids (H atoms and the THF solvent molecule omitted for clarity). Selected bond distances (Å) and angles (°): W(1)–N(1) = 2.252(9), W(1)–N(2) = 2.238(9), W(1)–C(14) = 2.03(1), W(1)–C(15) = 1.95(1), W(1)–C(16) = 2.05(1), W(1)–C(17) = 1.95(1), N(1)–C(5) = 1.37(1), N(2)–C(6) = 1.30(1), N(2)–C(7) = 1.42(1), C(6)–C(5) = 1.43(2), O(1)–C(13) = 1.21(1), O(2)–C(13) = 1.30(1), N(1)–W(1)–N(2) = 72.5(3), N(1)–W(1)–C(14) = 95.7(4), N(1)–W(1)–C(15) = 173.5(5), N(1)–W(1)–C(16) = 91.1(4), N(1)–W(1)–C(17) = 96.1(5), N(2)–W(1)–C(14) = 90.9(4), N(2)–W(1)–C(15) = 101.4(5), N(2)–W(1)–C(16) = 92.1(4), N(2)–W(1)–C(17) = 168.3(4), O(1)–C(13)–O(2) = 126(1).

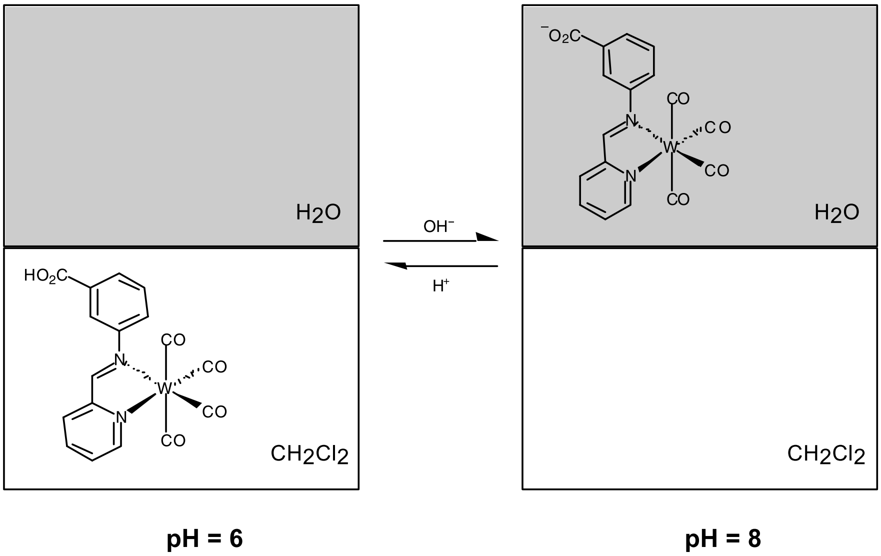

Fig. 3. pH-dependent phase transfer of $W(CO)_4$(**L**).

no tendency for the –COOH groups in adjacent molecules to hydrogen bond. Individual molecules do not appear to be facing each other, and there are no O–O contacts involving O(1) and O(2) out to 3.2 Å. This is in marked contrast to Group 6 metal carbonyls with a related pyridine–imine ligand containing a hydroxyl group in a position *para* to the imine nitrogen, where a range of hydrogen-bonding motifs have been observed in the solid state [15,16].

$W(CO)_4$(**L**) is soluble in a variety of organic solvents including methanol, ethanol, THF, CH_2Cl_2, DMF and DMSO but is insoluble in non-polar hydrocarbon solvents. Although the complex is water insoluble, addition of NaOH base to a suspension of the complex in water results in its immediate dissolution through deprotonation of the acidic $-CO_2H$ group and formation of the charged species, $W(CO)_4(\mathbf{L})^-Na^+$. An independent synthesis of $W(CO)_4(\mathbf{L})^-Na^+$ from L^- and $W(CO)_4(C_7H_8)$ confirmed the identity of the water-soluble species. Thus, the reactive imine group of the ligand has been effectively stabilized towards hydrolysis through coordination to W(0). The MLCT band in the electronic spectrum of $W(CO)_4$(**L**) undergoes a blue shift of 48 nm ($\lambda_{max} = 500$ nm) upon transfer to aqueous solution. This solvatochromism is comparable to that observed in related water-soluble compounds [17,18]. Protonation of the carboxylate ion results in a partitioning of the organometallic complex into the organic phase in a biphasic system. For example, addition of HCl to an aqueous solution of $W(CO)_4(\mathbf{L})^-Na^+$ in a CH_2Cl_2–H_2O biphase results in formation of $W(CO)_4$(**L**) as a neutral species and a complete transfer into the CH_2Cl_2 phase, as monitored by UV–visible, IR and NMR spectroscopy (Fig. 3). Regeneration of the anionic complex by the addition of base results in transfer back into the aqueous phase. This pH dependent phase transfer was accomplished over 20 times with no evidence of complex decomposition. Protonation of the $W(CO)_4(\mathbf{L})^-$ anion in the aqueous phase was also accomplished by addition of acetic acid ($pK_a = 4.76$), bubbling of CO_2 (g) (carbonic acid, $pK_a = 6.35$), and with dihydrogenphosphate ion ($pK_a = 7.20$). *m*-Nitrophenol is not a strong enough acid ($pK_a = 8.39$) to bring about complex protonation and transfer to the organic phase. The reaction chemistry of this metal complex and the ability to promote the pH dependent phase transfer of active catalytic species is currently under investigation.

Supplementary material

Crystallographic data for the structural analysis of $W(CO)_4$(**L**) in CIF format has been deposited with the Cambridge Crystallographic Data Center under CCDC no. 217828. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis, Wiley–VCH, Weinheim, Germany, 1998.
[2] A. Kundu, B.P. Buffin, Organometallics 20 (2001) 3635.

[3] B.P. Buffin, A. Kundu, Inorg. Chem. Commun. 6 (2003) 680.

[4] B.P. Buffin, E.B. Fonger, A. Kundu, Inorg. Chim. Acta (2003), in press; doi:10.1016/S0020-1693(03)00304-9.

[5] P.T. Anastas, R.L. Lankey, in: P.T. Anastas, R.L. Lankey (Eds.), Advancing Sustainability Through Green Chemistry and Engineering, American Chemical Society, Washington, DC, 2002, p. 1.

[6] P.T. Anastas, M.M. Kirchhoff, Accounts Chem. Res. 35 (2002) 686.

[7] B.P. Buffin, T.G. Richmond, Polyhedron 9 (1990) 2887.

[8] Synthesis of $W(CO)_4$(**L**). A 125-ml Schlenk flask equipped with a magnetic stir bar was charged with 1.00 g (2.3 mmol) of $W(CO)_3(EtCN)_3$ and 0.52 g (2.3 mmol) of **L** and then flushed with nitrogen. Tetrahydrofuran (THF, 30 ml) was added by syringe, producing a dark blue–green solution. Carbon monoxide gas was subsequently bubbled through the solution for 15 min to afford an intense purple color reminiscent of the aqueous permanganate ion, and the solution was sealed under an atmosphere of CO (g) for 16 h to complete the transformation to the tetracarbonyl product. The resulting solution was filtered through Celite® to remove insoluble tungsten byproducts, and hexane (30 ml) was layered on top of the THF filtrate. After allowing the solvents to diffuse for approximately 16 h, solvents were partially removed under reduced pressure, and precipitation of product was accomplished by cooling to −10 °C. Isolation of the precipitated solid by filtration and washing with pentane gave 0.95 g (1.8 mmol, 79%) of a dark purple, air-stable solid after vacuum drying. ^{1}H NMR (acetone–d_6): δ 13.5 (br, 1H), 9.37 (s, 1H), 9.32 (d, 1H), 8.40 (d, 1H), 8.27 (m, 1H), 8.24 (m, 1H), 8.11 (m, 1H), 7.91 (m, 1H), 7.74 (m, 2H). $^{13}C\{^1H\}$ NMR (acetone–d_6): δ 216.8, 213.6, 198.8 (2 CO), 167.3, 165.9, 156.1, 152.9, 152.7, 138.1, 131.9, 130.1, 129.6, 129.4, 128.2, 127.4, 123.2. IR (CH_3OH): $\nu_{CO} = 2009$ (m), 1901 (s), 1851 (m) cm^{-1}. Anal. calc. for $C_{17}H_{10}N_2O_6W$: C, 39.11; H, 1.93; N, 5.37%. Found: C, 38.90; H, 1.79; N, 5.43%.

[9] D.P. Drolet, L. Chan, A.J. Lees, Organometallics 7 (1988) 2502.

[10] R.W. Balk, D.J. Stufkens, A. Oskam, Inorg. Chim. Acta 34 (1979) 267.

[11] H. Brunner, W.A. Herrmann, Chem. Ber. 105 (1972) 770.

[12] Crystal data for $W(CO)_4$(**L**): $C_{17}H_{10}N_2O_6W \cdot C_4H_8O$, $M = 594.23$, orthorhombic, *Pbca* (No. 61), $a = 22.497(4)$ Å, $b = 14.112(6)$ Å, $c = 13.675(3)$ Å, $V = 4342(3)$ Å^3, $Z = 8$, $d_{calc} = 1.82$ g cm^{-3}, $\mu = 5.48$ mm^{-1}, $\lambda = 0.71073$ Å, $T = 295$ K, transmission factors = 0.232–0.334, 2θ range for data = 3°–50°, data collected = $+h, +k, -l$, $F000 = 2304e$, total no. of reflections = 3836, no. of reflections $[I > 3\sigma(I)] = 2001$, structural parameters = 280, data/parameter ratio = 7.1, $R(F_o) = 0.037$, $R_w(F_o) = 0.034$, GOF = 1.88, max and min peaks in final $\Delta F = 1.27$ and $-1.18e$ Å^{-3}.

[13] A. Bacchi, M. Carcelli, C. Pelizzi, G. Pelizzi, P. Pelagatti, S. Ugolotti, Eur. J. Inorg. Chem. (2002) 2179.

[14] T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskelä, J. Organomet. Chem. 606 (2000) 112.

[15] K. Heinze, V. Jacob, J. Chem. Soc., Dalton Trans. (2002) 2379.

[16] K. Heinze, J. Chem. Soc., Dalton Trans. (2002) 540.

[17] P. Banerjee, J. Burgess, Inorg. Chim. Acta 146 (1988) 227.

[18] B.A. Razak, P. Banerjee, J. Burgess, A.E. Smith, Transition Met. Chem. 13 (1988) 107.