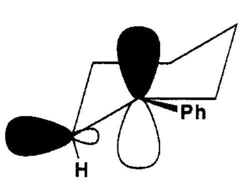

Further computational studies of SOC in substituted olefins are underway, as are experimental studies of constrained olefins which the present calculations point out as good tests. In particular the role of pyramidalizations deserves more scrutiny than it has hitherto received.

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Transition-Metal-Based Reagents for Molecular Recognition: Hydrogen-Bonding Properties of Tungsten(II) *cis*-Amino Halides

Carolyn E. Osterberg, Atta M. Arif, and
Thomas G. Richmond*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

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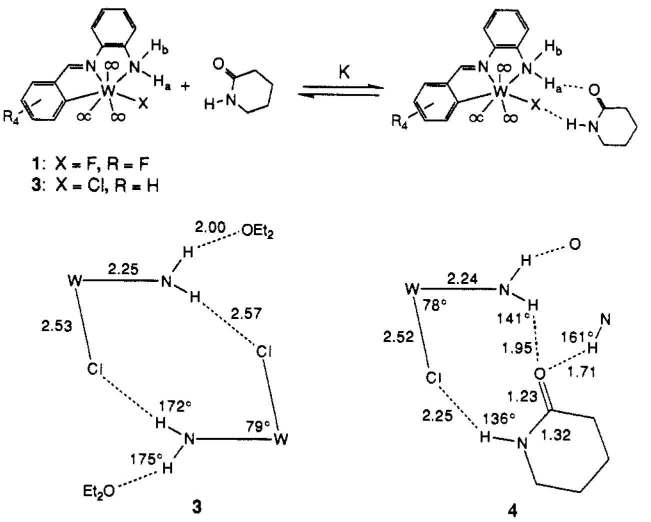
Hydrogen bonding frequently plays a central role in the process of molecular recognition. This is evidenced in numerous biochemical systems as well as in attempts by synthetic chemists to elucidate the molecular basis for recognition.[1] The design of new types of receptors has largely involved organic molecules[2] although literature reports noting the occurrence of hydrogen bonding in transition-metal coordination[3] and organometallic compounds[4] have appeared. Herein we report that the bifunctional hydrogen bonding capabilities of a series of tungsten(II) *cis*-amino halides provide a binding site for complementary organic substrates such as lactams and nucleosides. The interactions of metal complexes with biological molecules are important in the design and elucidation of the chemotherapeutic action of selective metal-based drugs.[5]

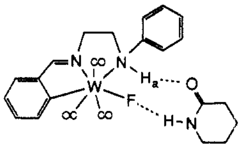
We have previously reported the preparation of seven-coordinate tungsten(II) complexes by chelate assisted oxidative addition of aromatic C–X (X = F, Cl, Br, I) bonds to tungsten(0).[6] Spectroscopic and crystallographic analysis of **1** suggested that the coordinated fluoride could function as a hydrogen bond acceptor and that the relatively acidic hydrogens on the primary amine could act as hydrogen bond donors. This is evidenced in the head-to-tail dimerization observed in the solid-state structure of **1**·THF.[6a]

Scheme I



3 **4**

We have investigated the ability of **1** to bind complementary organic substrates in solution by recording ^{1}H and ^{19}F NMR spectra as a function of substrate concentration. For solubility reasons, experiments were conducted in the relatively polar solvent acetone. The concentration independent chemical shifts of **1** in acetone indicate that **1** is monomeric in solution. Upon addition of δ-valerolactam (val),[7] the NH protons of **1** and val shift downfield and the ^{19}F NMR resonance of the fluoride bound to tungsten shifts upfield as the val concentration is increased and **1**·val is formed (Scheme I). Binding constants were calculated from ^{19}F NMR titration data by using an iterative nonlinear least-squares procedure.[8] Linear Scatchard plots[9] for the fluorine resonance and for the proton resonance H$_a$ covering the observable (ca. 80%) portion of the binding isotherm are consistent with the formation of a 1:1 adduct with $K_1 = 4.5$ M^{-1} at 25 °C. Variable temperature equilibrium measurements[9e] gave $\Delta H = -2.1 \pm 0.4$ kcal/mol and $\Delta S = -3.9 \pm 0.2$ eu. This simple model is undoubtedly perturbed by interaction of free val with H$_b$ and by val self-association.[7] However, the related *N*-phenyl-substituted complex **2**[10] shown below exhibits similar binding parameters. The



2 • val

K_2 (25 °C) = 2.1 M^{-1}
$\Delta H = -1.8 \pm 0.1$ kcal/mole
$\Delta S = -4.6 \pm 0.1$ eu

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(1) (a) Rebek, J., Jr. *Science (Washington, D. C.)* **1987**, *235*, 1478. (b) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (c) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039. (d) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 487.

(2) (a) Kilburn, J. D.; MacKenzie, A. R.; Still, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 1307. (b) Chang, S. K.; Hamilton, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 1318. (c) Wilcox, C. S.; Greer, L. M.; Lynch, V. *J. Am. Chem. Soc.* **1987**, *109*, 1865.

(3) (a) Chatt, J.; Duncanson, L. A.; Venanzi, L. M. *J. Inorg. Nucl. Chem.* **1958**, *8*, 67. (b) Massa, W.; Babel, D. *Chem. Rev.* **1988**, *88*, 275. (c) Perry, D. L.; Ruben, H.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1980**, *19*, 1067. (d) Strauss, S. H.; Abney, K. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 2806. (e) van Driel, G. J.; Driessen, W. L.; Reedijk, J. *Inorg. Chem.* **1985**, *24*, 2919. (f) Hughes, D. L. *Acta Crystallogr., Sect. B* **1981**, *37*, 557. (g) Aoyama, Y.; Yamagishi, A.; Asagawa, M.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1988**, *110*, 4076. (h) Antolini, L.; Benedetti, A.; Fabretti, A. C.; Giusti, A. *Inorg. Chem.* **1988**, *27*, 2192. (i) van Staveren, C. J.; van Eerden, J.; van Veggel, F. C. J. M.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4994.

(4) (a) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 6563. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803. (c) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7238. (d) Andrews, M. A.; van Buskirk, G.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7245. (e) Sartorelli, U.; Garlaschelli, L.; Ciani, G.; Bonora, G. *Inorg. Chem. Acta* **1971**, *5*, 1971. (f) Fawzi, R.; Hiller, W.; Lorenz, I. P.; Mohyla, J.; Zeiher, C. *J. Organomet. Chem.* **1984**, *262*, C43.

(5) (a) Kopf-Maier, P.; Kopf, H. *Chem.* Rev. **1987**, *87*, 1137. (b) Sherman, S. E.; Lippard, S. J. *Chem. Rev.* **1987**, *87*, 1153. (c) Dervan, P. B. *Science (Washington, D. C.)* **1986**, *232*, 464. (d) Barton, J. K. *Science (Washington, D. C.)* **1986**, *232*, 727. (e) Basile, L. A.; Barton, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7548.

(6) (a) Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091. (b) Richmond, T. G.; King, M. A.; Kelson, E. P.; Arif, A. M. *Organometallics* **1987**, *6*, 1995. (c) Poss, M. J.; Arif, A. M.; Richmond, T. G. *Organometallics*, **1988**, *7*, 1669.

(7) Self-association of δ-valerolactam has been investigated in nonpolar solvents: (a) Tsuboi, M. *Bull. Chem. Soc. Jpn.* **1951**, *24*, 75. (b) Purcell, J. M.; Susi, H.; Cavanaugh, J. R. *Can. J. Chem.* **1969**, *47*, 3655. (c) Klemperer, W.; Cronyn, M. W.; Maki, A. H.; Pimentel, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 5846. (d) Krikorian, S. E. *Spectrochimica Acta* **1981**, *37A*, 745.

(8) (a) Shepodd, T. J.; Petti, M. A.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1983. (d) Barrans, R. E., Jr.; Dougherty, D. A., personal communication, **1988**.

(9) (a) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044. (b) Scatchard, G. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 660. (c) Connors, K. A. *Binding Constants*; Wiley: New York, 1987. (d) Binding isotherms and Scatchard plots are included as Supplementary Material. We report equilibrium constants obtained from ^{19}F NMR measurements since the NH resonances of **1**–**3** in the ^{1}H NMR are broad and at times obscured by the large excess of val present. (e) Determined over the temperature range –40 to 25 °C; uncertainty limits quoted are three standard deviations.

(10) Prepared by Dr. M. A. King, University of Utah, unpublished results, 1988.

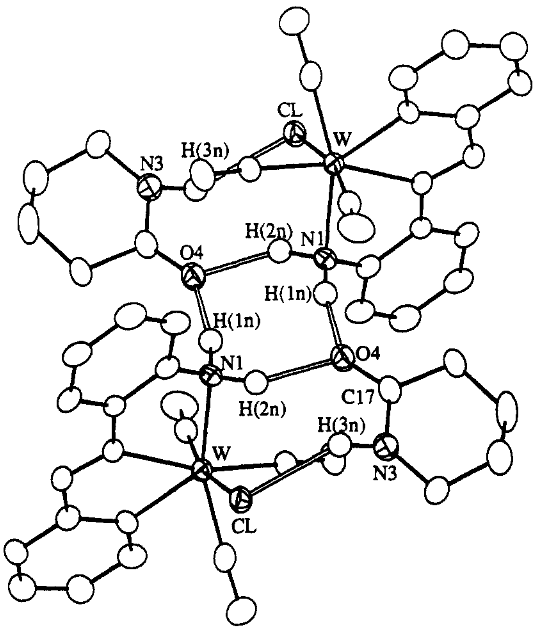

Figure 1. ORTEP representation of **3**. Hydrogen bonds are indicated by open bonds, and the disordered THF solvate which is not involved in the hydrogen bonding is omitted.

^1H NMR shifts for a titration of **3**,[11] which contains a chloride bound to tungsten, with val were similar although the binding constant ($K_3 = 1.3 \pm 0.5$ M^{-1}) is smaller. The more electronegative fluoride appears to be a better hydrogen bond acceptor than chloride when coordinated to tungsten(II).

The solution NMR data for the interaction of **1–3** with val suggest the chelating structure depicted in Scheme I. Solid-state structural studies of **3** provide support for this formulation.[12] Like the tungsten fluoride **1**, the chloride **3** crystallizes as a head-to-tail dimer. Relevant metrical parameters are given in Scheme I; the NH···Cl distance is consistent with hydrogen bonding in the solid state.[13] The Et_2O solvate is tightly bound to H(1n).

Cocrystallization of **3**·Et_2O with 5 equiv of val in THF by vapor diffusion of Et_2O affords single crystals of the adduct **4** as illustrated in Figure 1.[14] Dimers of **4** related by a center of inversion generate the tetrameric structure. Hydrogen bonding between **3** and val is clearly evident as depicted in Scheme I (lower half). Note that the NH(3n)···Cl distance in **4** is shorter than the related interval in the homomolecular dimer **3**. This suggests that stronger hydrogen-bonding interactions exist in the heterodimer **4** relative to the parent compound **3**. Solid-state IR spectra show that the amide carbonyl stretching frequency of val is reduced by 42 cm^{-1} upon complex formation; the NH bands broaden and shift to lower frequency (ν_{NH} = 3278 (m), 3235 (m), 3125 (m) cm^{-1}) compared to free val.[7]

Preliminary experiments show that **1** also interacts with protected nucleosides in nonaqueous solution. The binding constant for 2′,3′-*O*-isopropylidene-5′-*O*-acetyl uridine[15] in acetone is 3.6 M^{-1} at 25 °C. Although the strength of the binding is modest, these studies show that transition-metal complexes possessing *cis*-amino halide ligands can act as ditopic molecular receptors for biologically relevant molecules. This property should be general and most evident for coordination complexes containing fluoride. Elimination of HF[16] from hydrogen-bonded complexes such as these may enable a covalent host–guest linkage to be formed. We are continuing to investigate the chemistry of this new class of receptors.

Acknowledgment. We thank Professor D. A. Dougherty (California Institute of Technology) for a copy of the NMRFIT program, Professor C. D. Poulter for helpful discussions, and the referees for cogent comments. T.G.R. is the recipient of a Distinguished New Faculty Grant from the Camille and Henry Dreyfus Foundation Inc. We are grateful for support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Utah Research Committee. High field NMR spectrometers employed in this work were obtained through departmental grants from the National Science Foundation.

Supplementary Material Available: Titration data for complexes **1–3** and full crystallographic data for **3**·Et_2O and **4**·THF including tables of bond distances and angles and final positional and thermal parameters (39 pages); a listing of calculated and observed structure factors (39 pages). Ordering information is given on any current masthead page.

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[11] (a) Preparation of **2** is analogous to our published procedure for **1**:[6a] IR (Nujol mull, cm^{-1}) 3160, 3052 (m, ν_{NH}), 2009, 1934, 1893 (s, ν_{CO}); nonaromatic ^1H NMR δ 9.596 ($^3J_{WH}$ = 7.7 Hz), δ 6.60 (d, J = 11.8 Hz), δ 6.15 (d, J = 11.8 Hz). Anal for **2**·Et_2O. Calcd $C_{20}H_{21}N_2ClO_4W$: C, 41.95; H, 3.70; N, 4.89. Found: C, 42.05; H, 3.55; N, 5.02. (b) Binding constant determined by averaging K_3 for each proton.

[12] Crystal data for **2**·Et_2O: $WClO_4N_2C_{20}H_{21}$, red-orange, triclinic, $P\bar{1}$, a = 10.172 (3) Å, b = 10.524 (4) Å, c = 11.117 (4) Å, α = 115.52 (2)°, β = 101.24 (3)°, γ = 84.04 (3)°, V = 1053.2 Å^3, Z = 2, Mo Kα. Of 3751 reflections collected at ambient temperature (Syntex P1, $2° < 2\theta < 49°$) 3305 were unique of which 3118 had $I > 3\sigma(I)$ and were used in the solution and refinement (SDP PLUS Software). Final refinement included all non-hydrogen atoms as anisotropic and hydrogen atoms as idealized isotropic contributions. All hydrogens were located on a difference map but not refined. For 253 parameters, R = 0.022 and R_w = 0.025, GOF = 1.3, and highest peak in the final map of 1.1 e/Å approximately 1.1 Å from W.

[13] (a) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, 1968. (b) Bronty, C.; Spinat, P.; Whuler, A. *Acta Crystallogr., Sect. B* **1980**, *36*, 1967. (c) Novak, A. *Struct. Bonding* **1974**, *18*, 177.

[14] (a) Anal for **3**·THF. Calcd $C_{25}H_{28}N_3ClO_5W$: C, 44.83; H, 4.21; N, 6.27. Found: C, 44.73; H, 4.22; N, 6.27. (b) Crystal data for **3**·THF: $WClO_5N_3C_{25}H_{28}$, red-orange, monoclinic, $C2/c$, a = 19.939 (5) Å, b = 14.025 (4) Å, c = 19.411 (4) Å, β = 99.44 (2)°, V = 5354.5 Å^3, Z = 8, Mo Kα. Of 4319 reflections collected at ambient temperature (Syntex P1, $2° < 2\theta < 48°$) 4049 were unique of which 2750 had $I > 3\sigma(I)$ and were used in the solution and refinement (SDP PLUS Software). Final refinement included all non-hydrogen atoms as anisotropic and hydrogen atoms as idealized isotropic contributions. H(1n), H(2n), and H(3n) were located on a difference map, and remaining hydrogens were placed in calculated positions but not refined. For 271 parameters, R = 0.054 and R_w = 0.074, GOF = 1.7, and highest peak in the final map of 1.3 e/Å^3 approximately 0.80 Å from W.

[15] (a) Iwahashi, H.; Kyogoku, Y. *J. Am. Chem. Soc.* **1977**, *99*, 7761. (b) Reuben, J. *J. Am. Chem. Soc.* **1987**, *109*, 316. (c) Gmeiner, W. H.; Poulter, C. D. *J. Am. Chem. Soc.*, in press.

[16] (a) Basolo, F.; Matoush, W. R.; Pearson, R. G. *J. Am. Chem. Soc.* **1956**, *78*, 4833.

Photochemical Activation of CO_2. Transient Absorbance Kinetic Studies of the Addition of CO_2 to a Metal-to-Bridging Ligand Charge-Transfer State of a Binuclear Ni(0) Complex

Frederick R. Lemke, Dru L. DeLaet, Jiali Gao, and Clifford P. Kubiak*,[1]

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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We report the photochemical activation of CO_2 by a ligand-centered charge-transfer excited state of a binuclear Ni(0) complex. The activation and reduction of carbon dioxide are areas of considerable interest and potential importance for artificially recycling the products of combustion and respiration.[2–16] Among

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[1] Research Fellow of the Alfred P. Sloan Foundation, 1987–1989.

[2] Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79.

[3] Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651.

[4] Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

[5] Inoue, S.; Koinuma, H.; *Rev. Inorg. Chem.* **1984**, *6*, 291.

[6] Lundquist, E. G.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1986**, *108*, 8309.

[7] Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1467.

[8] DeLaet, D. L.; del Rosario, R.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1987**, *109*, 754.

0002-7863/88/1510-6904$01.50/0