molecular second-order susceptibility. This optimization of molecular nonlinear optical properties will be of value in the fabrication of bulk nonlinear optical materials.[13]

Acknowledgment. We thank E. A. Chandross, M. L. Kaplan, and R. D. Small for helpful discussions, H. Zahn for his assistance in the laboratory, and A. M. Mujsce for obtaining mass spectra.

Supplementary Material Available: Syntheses of **4**, **5**, and **7** (2 pages). Ordering information is given on any current masthead page.

(13) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248-250.

Rhodium Alkoxide Complexes: Formation of an Unusually Strong Intermolecular Hydrogen Bond in $(PMe_3)_3Rh$-Otol(HOtol)

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Received June 15, 1987

Hydrogen bonding has been the subject of frequent study by physical, organic, and biological chemists.[1] In inorganic and organometallic chemistry, hydrogen bonds have been observed in many crystalline solids by X-ray diffraction; however, little information is available on the occurrence and energetics of intermolecular hydrogen bonding of metal complexes in solution.

We wish to report the synthesis and characterization of several electron-rich rhodium alkoxide and aryloxide complexes of the type $(L)_3RhOR$ and their reaction with hydroxy compounds to form organometallic hydrogen-bonded species $(L)_3Rh$-OR(HOR). We have measured accurate association heats and equilibrium constants for two of these adducts: they have surprisingly large values (e.g., $\Delta H = -14.5$ kcal/mol for one system in cyclohexane solution).

Reaction of $(PPh_3)_3Rh$-R complexes with phenols has been reported to lead to both σ- and π-bound rhodium phenoxides.[2] In contrast, treatment of a toluene solution of $(PMe_3)_3Rh$-Me (**1**)[3] with 1 equiv of the appropriate alcohol at room temperature results in immediate evolution of methane and formation of bright yellow σ-alkoxide complexes in good yield; none of the corresponding π-phenoxide complexes (whose formation would presumably require loss of a strongly bound PMe_3 ligand) were detected.[4,5] Four $(PMe_3)_3Rh$-OAr complexes have been prepared in this way, having *p*-methylphenoxy (**2a**) *p*-(trifluoromethyl)-phenoxy (**2b**), trifluoroethoxy (**2c**), and hexafluoroisopropoxy (**2d**) groups (Scheme I). Alternate synthetic pathways to the alkoxide complexes include reaction of $(PMe_3)_3Rh^+PF_6^-$ (**3**)[6] with K^+RO^- ($R = p$-CH_3-C_6H_4, CH_2CF_3) and reaction of $[(COD)Rh(Otol)]_2$ (**4**)[7] with phosphine (COD = 1,5-cyclooctadiene; tol = *p*-CH_3-C_6H_4). $(PPhMe_2)_3$Rh-Otol (**2e**) has been prepared in 86% yield by using the latter method. Spectral and analytical data are consistent with the formation of **2** as typical square planar Rh(I) complexes (see Supplementary Material). The structure of **2c** was confirmed by single-crystal X-ray diffraction; an ORTEP diagram is included in Scheme I.[8] The geometry about the Rh atom is slightly distorted square planar (P-Rh-P bond angles 93-96°), with the distortion presumably due to the steric bulk of the PMe_3 ligands. The Rh-O-C bond angle of 117.9° is indicative of little or no π-interaction of the lone pair of the trifluoroethoxide ligand with the Rh atom.

Treatment of **1** with 2 equiv of alcohol or *p*-cresol (or reaction of **2** with a single equivalent) leads to the formation of the hydrogen-bonded species **5a-e**. The second molecule of alcohol is strongly associated with the alkoxide complex even in solution, and the chemical shift of the hydrogen-bonded proton in the ^1H NMR spectrum occurs at unusually low field (9-14 ppm). As expected for hydrogen-bonded systems,[9] these chemical shifts are concentration and temperature dependent, reflecting changes in the position of the equilibrium in eq 2. For example, in the NMR spectrum of **5a**, it was not possible to observe absorptions due to free *p*-cresol at any temperature down to -80 °C, the ortho protons of the free and hydrogen-bonded *p*-cresol appearing as a single averaged resonance at all temperatures. In contrast, the ^1H NMR resonances due to the free/complexed *p*-cresol and the rhodium-bound aryloxide ligand are distinguishable below 45 °C. Thus, the ortho protons of the two moieties are distinct at temperatures below 45 °C; above that, temperature coalescence occurs, and at 70 °C these resonances appear as a single averaged doublet. We conclude from those observations that exchange of free and hydogen-bonded cresol is rapid on the NMR time scale at room temperature, but that incorporation of the hydrogen-bonded aromatic compound into the rhodium-bound alkoxy position (eq 3) occurs somewhat more slowly.[10]

Recrystallization of **5a** from a toluene/pentane mixture gave blocky yellow crystals that were analyzed by single crystal X-ray diffraction[11]; an ORTEP diagram is included in Scheme I. In analogy to the structure of **2c**, the geometry about the Rh atom is approximately square planar (P-Rh-P bond angles 94-95°), and the Rh-O-C bond angle is 121.5°. The O1-O2 bond distance of 2.62 Å falls in the range of other H-bonded structures,[12] and further refinement permitted location of the hydrogen atom. The O1-H-O2 linkage is markedly asymmetric, although essentially linear, the hydrogen atom being more closely associated with the molecule of *p*-cresol than with the alkoxide ligand (O1-H, 1.4 ± 0.1 A; O2-H, 1.2 ± 0.1 A).[11b]

(1) See, for example: (a) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, 1960. (b) Rochester, C. H. "Acidity and Inter- and Intramolecular H-Bonds", In *Chemistry of the Hydroxyl Group: Part 1*; Patai, S., Ed.; Interscience: London, 1971; Chapter 7. (c) *The Hydrogen Bond*; Schuster, P.; Zundel, G.; Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Vol. 1-3. (d) Joesten, M. D. *J. Chem. Ed.* **1982**, *59*, 362.

(2) (a) Keim, W. *J. Organomet. Chem.* **1968**, *14*, 179. (b) Cole-Hamilton, D. J.; Young, R. Y.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1995.

(3) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 126.

(4) Yields are quantitative by NMR spectrometry. Isolated yields are as follows: $R = p$-CH_3-C_6H_4, 80%; *p*-CF_3-C_6H_4, 82%; CH_2CF_3, 42%; $CH(CF_3)_2$, 70%. Analytical and spectral data are provided as Supplementary Material.

(5) No reaction was observed between **1** and less acidic alcohols or amines such as EtOH, *t*-BuOH, $PhNH_2$, or $PhCH_2NH_2$.

(6) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511.

(7) $[(COD)Rh(Otol)]_2$ was prepared from $[(COD)Rh(OMe)]_2$ (ref 7a), by using a procedure similar to that described in ref 7b. (a) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *25*, 127. (b) Pannetier, G.; Fougeroux, P.; Bonnaire, R.; Platzer, N. *J. Less-Common Met.* **1971**, *24*, 83.

(8) Crystal data for **2c**: space group $P2_1/n$, $a = 12.01$ (9) Å, $b = 11.88$ (8) Å, $c = 13.87$ (7) Å, $\alpha = 90.00°$, $\beta = 109.8$ (7)°, $\gamma = 90.00°$, $V = 1862.5$ (7) A^3, $Z = 4$, $T = -70$ °C. The structure of **2e** has also been determined by X-ray diffraction; details will be reported at a later date.

(9) (a) Davis, J. C., Jr; Deb, K. K. *Adv. Magn. Reson.* **1970**, *4*, 201. (b) Murthy, A. S. N.; Rao, C. N. R. *Appl. Spec. Revs.* **1968**, *2*, 69. (c) Tucker, E. E.; Lippert, E., in ref 1c.

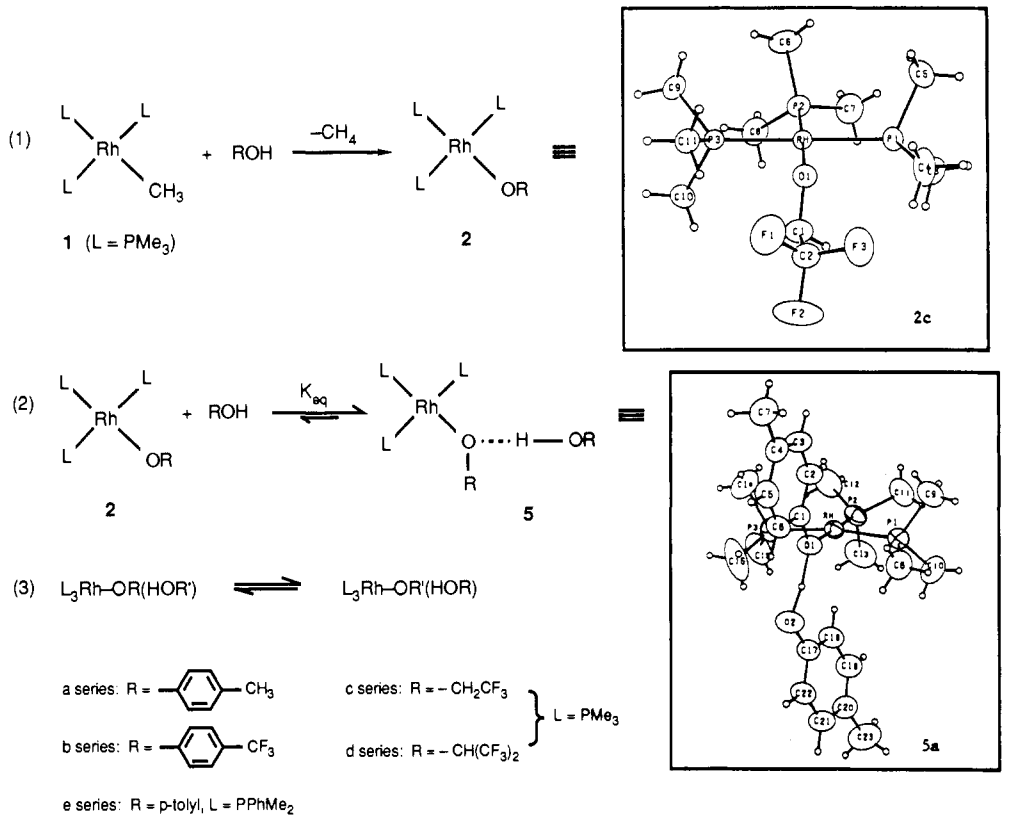
(10) Similar alkoxide exchange has been observed for $Cp^*(PPh_3)Ir(OR)H$ systems, with the exchange reaction proceeding through a spectroscopically characterized hydrogen bonded intermedate, $Cp^*(PPh_3)Ir(H)(OR)(HOR')$, presumably analogous to the ones described here. Newman, L. J. Ph.D. Thesis, University of California, Berkeley, 1986. Newman, L. J.; Bergman, R. G., unpublished results.

(11) (a) Crystal data for **5a**: space group $P2_1/n$, $a = 13.97$ (8) Å, $b = 12.38$ (8) Å, $c = 17.20$ (6) Å, $\alpha = 90.00°$, $\beta = 110.1$ (7)°, $\gamma = 90.00°$, $V = 2794.4$ (7) A^3, $Z = 4$, $T = 20$ °C. (b) The hydrogen atom in the O—H···O linkage was located in a difference Fourier map, but its position was not refined.

(12) Strauss, S. H.; Abney, K. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 2806 and references therein.

0002-7863/87/1509-6563$01.50/0

Scheme I



From the spectroscopic data, it is clear that the equilibrium in eq 2 lies far to the right, which suggests that the hydrogen bond in **5a** is unusually strong. In order to determine equilibrium constants for adduct formation as accurately as possible, we employed NMR spectrometry with use of the Scatchard method[13] for complexes **5a** and **5e**. Excellent linear Scatchard plots were obtained for both the PMe_3 and $PPhMe_2$ complexes; these gave association constants of $1.56 \pm 0.03 \times 10^3$ and $1.14 \pm 0.03 \times 10^3$ for **5a** and **5e**, respectively.

In order to obtain accurate measurement of ΔH for reaction 2, a calorimetric determination of the heat evolved in the conversions of **2a** to **5a** and **2e** to **5e** were carried out. For **5a**, ΔH was found to be -14.0 ± 0.4 kcal/mol in cyclohexane and -11.4 ± 0.5 kcal/mol in benzene; ΔH is -9.7 ± 0.5 kcal/mol for **5e** in benzene.

Conventional enthalpies for intermolecular hydrogen bonding between phenols and uncharged electron pair donors normally lie in the -3 to -6 kcal/mol range.[14] In CCl_4, for example, ΔH for association of phenol with acetone is -3.3 kcal/mol; for phenol plus acetonitrile it is -5.22 kcal/mol. The phenol/anisole hydrogen bond (perhaps the most reasonable organic model for **5**) is also weak, estimated to be about 3.5 kcal/mol. Stronger association occurs when the acceptor is relatively basic (e.g., ΔH for phenol/pyridine has recently been measured as -6.88 kcal/mol in CCl_4 and -7.8 kcal/mol in cyclohexane[15]). However, the strongest interactions occur between hydroxy compounds and *charged* electron pair donors. Quantitative ΔH's for most of these have been measured only in the gas phase: e.g., the strongest known hydrogen bond, HF_2^- (39 kcal/mol[16]); PhO^-/HOEt, 19.3 kcal/mol.[17,18] Thus, ΔH for our rhodium complex **5a** appears to be more comparable to those measured for hydrogen bonds between proton donors and *anionic*, rather than neutral, electron pair donors.

We conclude from these comparisons that the hydrogen-bonded *p*-cresol group in **5** sees the oxygen atom in the rhodium-bound alkoxide as a site of unusually high electron density.[19] This suggests that the Rh–O aryloxide bond is strongly polarized, having excess negative charge at oxygen and excess positive charge at the rhodium atom. Our results may have important implications for the catalytic carbalkoxylation of olefins, where a proposed step in one possible mechanism involves insertion of CO into an M–O bond.[20] These reactions are generally carried out in alcoholic solvents, and hydrogen bonding to the alkoxide ligand could play an important role in this process. Stoichiometric organometallic reactions have also recently been reported in which hydrogen bonding has been postulated as a critical mechanistic step, although the hydrogen bonded species have not been observed directly.[21] The availability of isolable free and hydrogen-bonded alkoxides such as **2** and **5** will allow us to investigate directly the effect of the hydrogen-bonded hydroxy compound on the reactivity of the alkoxide ligand. Such studies are under way.

Acknowledgment. We thank Dr. Fred Hollander, staff crystallographer of the UC Berkeley X-ray crystallographic facility (CHEXRAY), for performing the crystal structure analyses. This work was supported by NIH Grant No. GM-25459 (to R.G.B.), NSF Grant No. CHE8618753 (to C.D.H.), and an NSF-ROA award to S.E.K. We are grateful to Dr. Steven Fine and Prof. W. Keim for helpful discussions and to Prof. Keim for disclosure

(13) (a) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044. (b) Scatchard, G. *Ann. N. Y. Acad. Sci.* **1949**, *51*, 660.
(14) See ref 1a, pp 340–350.
(15) Spencer, J. N.; Andrefsky, J. C.; Grushow, A.; Naghdi, J.; Patti, L. M.; Trader, J. F. *J. Phys. Chem.* **1987**, *91*, 1673.
(16) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 5848.
(17) Meot-Ner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525.
(18) A very strong solution hydrogen bond has also been found in the $[H(OTeF_5)_2]^-$ dimer (ref 12), although ΔH could not be measured quantitatively in this case.
(19) Additional evidence for this hypothesis is the observation of a similar downfield shift in the ^1H NMR (9–10 ppm) of the O*H* proton of *p*-cresol for a mixture of *p*-cresol and K^+-Otol in toluene.
(20) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.
(21) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5473.

of results prior to publication. We also acknowledge a NATO postdoctoral fellowship to C.J.S., a postdoctoral fellowship from the Miller Research Foundation at the University of California, Berkeley, to J.H.F., and a generous loan of $RhCl_3.3H_2O$ from Johnson-Matthey, Inc.

Supplementary Material Available: Spectroscopic and analytical data for complexes **2a–e** and **5a–e** and details of the structure determination of complexes **2c** and **5a**, including experimental description, ORTEP drawings showing full atomic numbering scheme, crystal and data collection parameters, general temperature factor expressions (B's), positional parameters and their estimated standard deviations, and intramolecular distances and angles (34 pages); tables of calculated and observed structure factors for **1** (37 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Magnetic Properties of Manganese in the Photosynthetic O_2-Evolving Complex. 2. Evidence for a Manganese Tetramer [*J. Am. Chem. Soc.* **1986**, *108*, 4002–4009]. JULIO C. DE PAULA, WARREN F. BECK, and GARY W. BRUDVIG*

Page 4007: In the fourth row of Table I, following (NH_4Cl treated), the exchange coupling constants should be $J = 16$ cm^{-1} and $J' = -42$ cm^{-1} instead of $J = 23$ cm^{-1} and $J' = -53.5$ cm^{-1} and $\Delta_2 = 8.1$ cm^{-1} instead of 48.6 cm^{-1}.

Page 4007: In Table II, the headings should read Δc_1, Δc_2, Δc_D, Δc_3, and Δc_4 rather than c_1, c_2, c_D c_3, c_4, where Δc_i represents the difference of the c_i's (as given in the text) of the two levels of the Kramer's doublet. The corrected Table II is given below.

Table II. Hyperfine Reduction Constants for a $3Mn^{III}$–Mn^{IV} Tetramer

state of OEC	illumination (K)	Δc_1	Δc_2	Δc_D	Δc_3	Δc_4
resting	200	−0.006	−0.006	−0.989	1.978	0.989
(NH_4Cl treated)	273	−0.085	−0.085	−0.830	−1.660	0.830
active	245	−0.071	−0.071	−0.859	−1.718	0.859
	160	−0.029	−0.029	−0.941	−1.882	0.941

*Book Reviews**

Mechanisms of Inorganic and Organometallic Reactions. Volume 4. Edited by M. V. Twigg. Plenum Press: New York and London. 1986. xviii + 536 pp. $79.50. ISBN 0-306-42332-4

Reviews of previous volumes have described the antecedents, scope, organization, usefulness, and limitations of this continuing series (*J. Am. Chem. Soc.* **1985**, *107*, 1091; **1986**, *108*, 2496). In this volume, the text continues to be organized into the three main sections: Electron Transfer Reactions (3 chapters), Substitution and Related Reactions (6 chapters), and Reactions of Organometallic Compounds (5 chapters). A fourth section is a 13-page Table of Volumes of Activation. The literature is covered for the period January 1984 through June 1985. To hold down the length of the book and its price, the Author Index has been eliminated. While the user can still turn to a particular subject, one can no longer quickly review the publications of a particular research group. This series belongs in research libraries and is useful to specialists in the field and those writing reviews.

John T. Yoke, *Oregon State University*

The Peptides: Analysis, Synthesis, Biology. Volume 7: Conformation in Biology and Drug Design. Edited by Victor J. Hruby. Academic Press: Orlando. 1985. xx + 495 pp. $99.00. ISBN 0-12-304207-0

This is the seventh volume of the very successful, *The Peptides*. As expected from the title, the book describes the present state of conformational analysis of peptides in biology and drug design. There is a balance between chapters describing experimental methods and theoretical analysis with two of the nine chapters devoted to energetic calculations. The critical utility of NMR in the field is borne out by the fact that four chapters introduce different aspects of the applications of NMR. Chapters on the use of fluorescence and circular dichroism as well as a brief introduction to conformational analysis complete the book.

The two chapters on energetic calculations provide a well-referenced, detailed introduction into the field. The chapter by S. Zimmerman represents a clear and concise overview of the development of energy calculations. He begins with a description of the hard-sphere approximations used early in the development of the field and continues with the determination of parameters and methods of minimization. Although most of the examples and applications used are drawn from the program ECEPP (Empirical Conformational Energy Program for Peptides) the chapter is quite thorough in its coverage. A more general description of the methods employed in energetic calculations can be found in the chapter written by A. Hagler. There is an historical description of the different methods and analysis of what can be gained from the use of them. The chapter concludes with what can be expected in the future with the advent of faster and larger computers.

The use of NMR in conformational analysis begins with a description of the use of paramagnetic ions as a conformational probe. The chapter written by R. E. Lenkinski and J. D. Glickson examines the utilization of the binding of paramagnetic ions by monitoring variance in chemical shift and relaxation rates in conformational analysis. The next topic covered is the NMR examination of peptide–macromolecule interaction. The chapter by M. Blumenstein is a well-written, detailed presentation with many timely examples. S. J. Opella and L. M. Gierasch have examined the use of solid-state NMR in the study of peptide conformations. Solid-state NMR is growing in importance. This chapter should serve as a basic and focused reference on the subject. Finally, H. Kessler et al. have the formidable task of describing the use of NMR studies of solutions in the conformational analysis of peptides. Realizing that a complete introduction of NMR studies in solution would require many monographs of this size the chapter concentrates on the use of 2D techniques. There is a description, with adequate references and examples, of the most common homo- and heteronuclear techniques used in the assigning of proton, carbon, and nitrogen resonances.

Chapters on circular dichroism and fluorescence complete the book. As the contributors note both of these techniques are powerful tools, especially when used in conjunction with NMR and energetic calculations. The chapter written by R. W. Woody is a detailed description of the theoretical and experimental aspects of CD and optical rotary dispersion, ORD. There are many well-referenced examples of applications of these techniques. The use of fluorescence in conformational studies is described by P. W. Schiller. Again there are many referenced examples with an emphasis on the practical concerns of the utilization of fluorescence. The presentation of the theoretical details and the many applications are very timely.

*Unsigned book reviews are by the Book Review Editor.