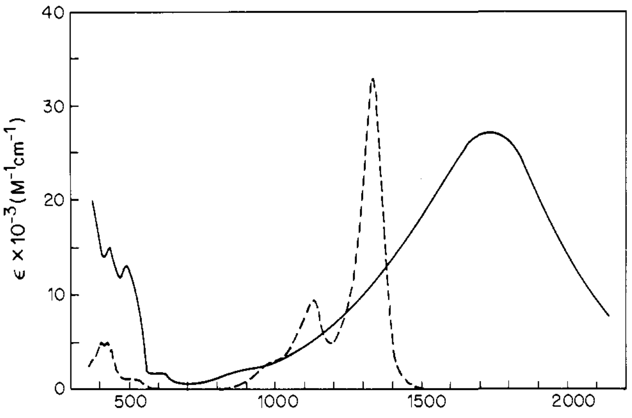


Figure 1. Absorption spectra for $\mathbf{1}^{\bullet-}$ (—) and $\mathbf{2}^{\bullet-}$ (--) in DMF, Bu_4NBF_4.

of $\mathbf{1}^{\bullet-}$ (Figure 1) is quite *unordinary*. It shows a band with λ_{max} at 1730 nm (0.74 eV) ϵ = 27 000.

Few semiquinone spectra are reported in the literature,[4] so in order to understand this observation, a number of model compounds have been prepared and studied by using the above method. Electrochemically, each diquinone showed two reversible, one-electron couples and a third quasi-reversible couple. The monoquinones gave two reversible couples. Preparative scale reduction gave stable semiquinones. The optical spectra are described in Table I. It was found that monoquinone anion-radicals do not exhibit these intense long wavelength bands. Simple di- and triquinone anion-radicals do show such bands. There seems to be a trend to lower transition energies for the diquinone anion radicals as the quinones are spaced farther apart, and it may be that this observation could be capitalized on to push the absorption maximum farther into the IR.

Because the neutral quinones do not have these 1–2 μm bands, it is proposed that the absorption originates from excitation of the odd electron of the anion-radical. In this wavelength region, intramolecular intervalence-transfer transitions of mixed-valence species are commonly observed.[5] Since the radical-anions of diquinones (or triquinones) might be envisaged to have a quinone and a semiquinone site, they could, in principle, qualify as mixed-valence species.[6] As such the spectra of $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ suggest that the two sites are fully delocalized (type III mixed-valence). Thus, the sharpness of the bands and the high absorption intensity at long wavelength indicate that the two mixed-valence sites are very similar in structure and strongly interacting. A second possible interpretation for the band is from intermolecular charge transfer. Evidence against this origin is provided by linear Beer's law behavior for $\mathbf{2}^{\bullet-}$ in DMF over the concentration range 10^{-5}–5×10^{-4} M. Evidence against either intermolecular or intramolecular charge transfer comes from the lack of solvent dependence.[7] With use of $\mathbf{2}^{\bullet-}$ it was shown that the band maximum at 1335 nm was unaffected (±10 nm) as the medium was changed from DMF, Bu_4NBF_4 to DMF, $LiClO_4$; THF, Bu_4NBF_4 and $CHCl_3$, Bu_4NBF_4. With use of $\mathbf{1}^{\bullet-}$ the band maximum was the same in DMF or CH_2Cl_2 containing Bu_4NBF_4.

It is suggested that these transitions involve π^*–π^* excitation of the odd electron, which is initially held in a delocalized orbital. In agreement with this assignment for $\mathbf{2}^{\bullet-}$, $\mathbf{3}^{\bullet-}$, and $\mathbf{4}^{\bullet-}$ are ESR spectra showing the expected symmetry. In addition the IR spectrum of $\mathbf{2}^{\bullet-}$ Bu_4N^+ as a KBr disk shows no quinone carbonyl. Finally, ab initio calculations on $\mathbf{3}^{\bullet-}$, $\mathbf{4}^{\bullet-}$, and $\mathbf{5}^{\bullet-}$ confirm that π^*–π^* transitions are involved.[8] These restricted Hartree–Fock calculations were performed for the ground and excited states of the anion-radicals and gave a satisfactory account of the trends in transition energies.

There is some concern over extrapolating the conclusions from $\mathbf{2}^{\bullet-}$, $\mathbf{3}^{\bullet-}$, and $\mathbf{4}^{\bullet-}$ to $\mathbf{1}^{\bullet-}$ especially in view of the width of the band for $\mathbf{1}^{\bullet-}$ compared to $\mathbf{2}^{\bullet-}$. In this regard we note that the spectrum of $\mathbf{1}^{2-}$ is unusual and entirely different from that of $\mathbf{2}^{2-}$. Most piquant is the $\mathbf{1}^{2-}$ spectrum which shows λ_{max} 1.9 μm (ϵ 75 000). Further explication of the origin of these spectra, a definition to the scope of this phenomenon, and applications to switchable optical devices will be reported.

Acknowledgment. This work was supported by the NSF and ONR. Thomas H. Jozefiak held a fellowship from the Proctor and Gamble Co. Compound **1** was supplied by Dr. W. Christopfel. Data on $\mathbf{7}^{\bullet-}$ were from Stan Rak.

---

(4) 1,4-Benzosemiquinone and derivatives: Iida, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1777. Phenanthrasemiquinone and acenaphthenesemiquinone: Staples, T. L.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 5022. Anthrasemiquinone: Mitzner, R.; Dorst, H.; Frosch, D. *Z. Chem.* **1975**, *15*, 400. (Bands with $\epsilon < 10^3$ near 800 nm are reported.) Other semiquinones: Mikhailov, G.; Trifonov, A. *Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk.* **1971**, *4*, 533.

(5) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. Taube, H. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 481.

(6) For an example of a mixed valence organic anion radical, see: Schroeder, A. H.; Mazur, S. *J. Am. Chem. Soc.* **1978**, *100*, 7339.

(7) Sullivan, B. P.; Curtis, J. C.; Kober, E. M.; Meyer, T. J. *Nouv. J. Chim.* **1980**, *4*, 643.

(8) Performed by Professor Jan Almlof and Martin Feyereisen. Details will be provided in the full paper.

Greatly Enhanced Second-Order Nonlinear Optical Susceptibilities in Donor–Acceptor Organic Molecules

H. E. Katz,*[†] K. D. Singer,*[‡] J. E. Sohn,*[‡] C. W. Dirk,*[†]
L. A. King,[‡] and H. M. Gordon[‡]

AT&T Bell Laboratories
Murray Hill, New Jersey 07974
AT&T Engineering Research Center
Princeton, New Jersey 08540

Received May 28, 1987

It has been generally recognized[1,2] that donor–acceptor substituted organic compounds such as benzenes, stilbenes, and azo dyes possess large molecular second-order nonlinear optical susceptibilities (β). Measurements and calculations of second-order susceptibilities of these organic materials have largely been limited to compounds containing substituents whose donating or accepting abilities do not exceed those of amino or nitro, respectively.[1,2] Herein, we report that β can be increased substantially through the use of dicyanovinyl or tricyanovinyl as acceptor and/or dithiolylidinemethyl as donor groups. The use of cyanovinyl acceptors in compounds for nonlinear optics has been previously suggested.[3]

Table I lists a representative sample of the molecules we have investigated. Compounds **1** and **6** were obtained commercially, while **2**[4] and **3**[5] were synthesized as previously described. The synthesis of **7** had been noted[6] without details. Compounds **4** and

---

[†] AT&T Bell Laboratories.

[‡] AT&T Engineering Research Center.

(1) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; references therein.

(2) Williams, D. J. *Nonlinear Optical Properties of Organic and Polymeric Materials*; ACS Symposium Series 233; American Chemical Society: Washington, DC 1983; references therein.

(3) Stamatoff, J. B.; Buckley, A.; Calundann, G.; Choe, E. W.; DeMartino, R.; Khanarian, G.; Leslie, T.; Nelson, G.; Stuetz, D.; Teng, C. C.; Yoon, H. N. *Proc. SPIE* **1986**, *682*, 85–92.

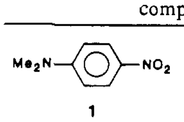
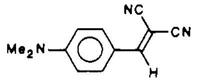
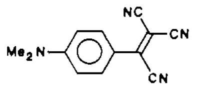
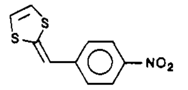
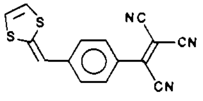
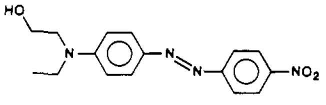
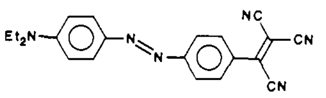
(4) Corson, B. B.; Stoughton, R. W. *J. Am. Chem. Soc.* **1928**, *50*, 2825–2837.

(5) McKusick, B. C.; Heckert, R. E.; Cairns, T. C.; Coffman, D. D.; Mower, H. F. *J. Am. Chem. Soc.* **1958**, *80*, 2806–2815.

(6) Chu, K. Y.; Griffiths, J. *Tetrahedron. Lett.* **1976**, 405–406.

0002-7863/87/1509-6561$01.50/0

Table I. Second-Order Nonlinear Optical Susceptibilities[a] (β, β_0), Dipole Moments[b] (μ), and Electronic Transition Energies (E) of Donor–Acceptor Molecules

compound	β[c]	β_0[c]	μ[d]	E[e]
 **1**	21	12	7.1	3.07
 **2**	31	16	8.7	2.82
 **3**	78	26	10.9	2.35
 **4**	52	25	6.9	2.71
 **5**	($\beta\mu$ = 1200)			2.06
 **6**	125	47	8.7	2.44
 **7**	390	154	10.5	2.13

[a] β was determined at 1.3 μm except for **5** and **7** which were determined at 1.58 μm. [b] μ for **1**: Clayton, J. M. et al. *J. Pharm. Sci.* **1974**, *63*, 230–234. μ for **2** and **3**: Kuder, J. E. et al. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1643–1651. [c] 10^{-30} cm^5/esu. [d] D. [e] eV.

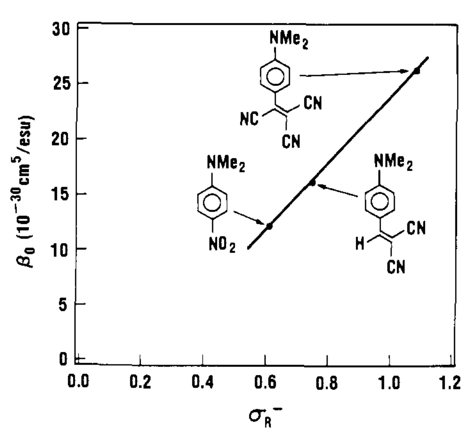


Figure 1. Plot of β_0 vs σ_R^- for compounds **1**–**3**.

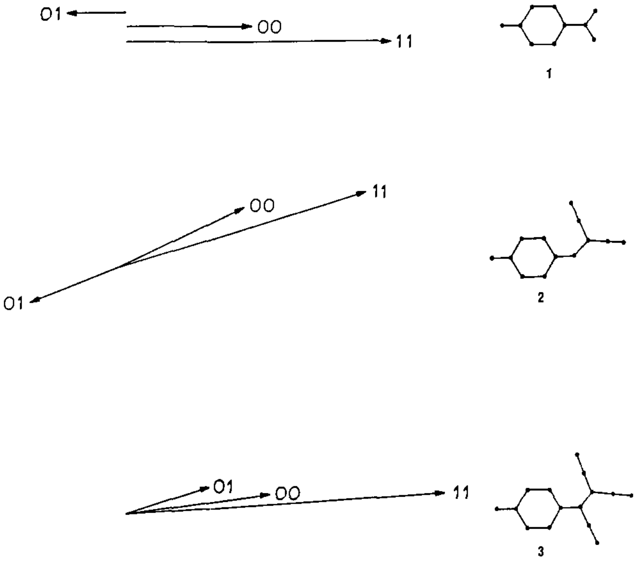


Figure 2. Electronic moments of compounds **1**–**3**: 0,0 = ground state μ; 0,1 = transition moment; 1,1 = excited state μ.

5 were prepared by novel routes involving Wittig condensations of dithiolium–PPh$_3$ with 4-nitro- and 4-tricyanovinylbenzaldehyde. Ultraviolet and visible spectra were recorded in Me$_2$SO solution. The quantities $\beta\cdot\mu$ were obtained in Me$_2$SO solution by Electric Field Induced Second Harmonic (EFISH) measurement;[7] values of β were obtained by dividing out literature or measured values of μ. A comparison of the contributions of molecular moments to β is made through the quantity β_0, in which the dependence of β on the electronic transition energies of the compounds is approximately factored out by using a two-level model which is given by[7]

$$\beta_{xxx}(-2\omega;\omega,\omega) = \frac{e^3|\mu_{01}|^2(\mu_{11} - \mu_{00})}{\hbar^2} \times F(\omega) \qquad (1)$$

where

$$F(\omega) = \frac{3\omega_0^2}{(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)} \qquad (2)$$

and where e is the electronic charge, the μ's are molecular moments. The quantity β_0 is calculated by dividing the measured value of β by $F(\omega)$ at the measured fundamental frequency, and multiplying by $F(0)$. This measure assures that comparisons among molecules with different transition energies are not greatly affected by resonant enhancements.

The increase in second order susceptibility on moving from nitro to dicyanovinyl to tricyanovinyl (**1**–**3**) is rationalized with use of Hammett constants, with an excellent correlation between σ_R^-[8] and β_0 (Figure 1). Semiempirical molecular orbital calculations[9] also predict this trend. The calculations confirm that the two-level model[10] is valid for **1**–**3** and also point out differences in the magnitudes and coincidence of certain electronic moments (Figure 2), especially the excited state dipole moment magnitudes, that contribute to the progression of β values. The value of β_0 arising from the use of the dithiolylidinemethyl group **4** is much higher than one would predict from Hammett plots, suggesting that the effectiveness of this donor might be due to properties of the excited states associated with it, rather than the ground-state properties that are typically reflected in linear free energy relationships.

The simultaneous incorporation of a superior donor and acceptor in one molecule leads to an additive effect, with $\beta\cdot\mu$ for **5** an order of magnitude larger than the prototypical **1**. (Unfortunately, we were unable to obtain an independent measurement of μ for **5** due to its poor solubility.) Lengthening the connecting group, as in **6**, also results in increased values of β and β_0, confirming previous results.[1,2,11] It has frequently been postulated[12] that the diphenylazo link would be the best possible connector of donor and acceptor substituents for optimizing electron transmission effects in compounds such as **6**. By combining the best acceptor with the best linker, we obtain molecule **7** with an exceptionally large

---

[7] Singer, K. D.; Garito, A. F. *J. Chem. Phys.* **1981**, *75*, 3572–3580.

[8] Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978.

[9] Dirk, C. W.; Twieg, R. J.; Wagnière, G. *J. Am. Chem. Soc.* **1986**, *108*, 5387–5395.

[10] Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446–457.

[11] Buckley, A.; Choe, E.; DeMartino, R.; Leslie, T.; Nelson, G.; Stamatoff, J.; Stuetz, D.; Yoon, H. *Am. Chem. Soc., Polym. Mat. Sci. Eng. Prepr.* **1986**, *54*, 502–507.

[12] Christoforu, P.; Happer, D. A. R. *Aust. J. Chem.* **1983**, *36*, 2083–2094. Dayed, S. K.; Ehrenson, S.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 9113–9122.

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 $(PMe_3)_3Rh-Otol(HOtol)$

Susan E. Kegley, Colin J. Schaverien,
John H. Freudenberger, and Robert G. Bergman*

Department of Chemistry, University of
California Berkeley, Berkeley, California 94720

Steven P. Nolan and Carl D. Hoff

Department of Chemistry, University of Miami
Coral Gables, Florida 33124

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*-$CH_3-C_6H_4$). $(PPhMe_2)_3Rh-Otol$ (**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 intermediate, $Cp^*(PPh_3)Ir(H)(OR)(HOR')$, 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