Reactions of Coordinated Molecules. 37. Carbon–Carbon Bond Formation between Adjacent Acyl Ligands in (Triacylrhenato)boron Halide Complexes

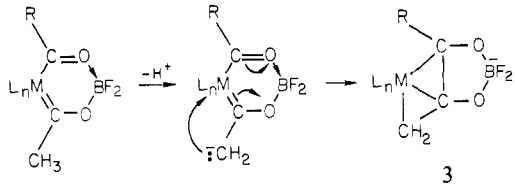
C. M. Lukehart* and W. L. Magnuson[1]

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235. *Received June 6, 1983*

Abstract: When (triacylrhenato)boron halide complexes of the type [*fac*-$(OC)_3Re(CH_3CO)_2(RCO)]BX$, where R is methyl or isopropyl and X is F or Cl, are treated with KH, a proton is removed from an acetyl ligand to give anionic η^3-allyl complexes of the general formula {*fac*-$(OC)_3Re[\eta^3\text{-}CH_2COCO(R)](CH_3CO)BX\}^-$. Formation of the η^3-allyl complexes occurs by an interligand, C–C bond formation between two of the original acyl-carbon donor atoms of the triacylrhenato ligand.

Introduction

There is considerable current interest in developing methods of effecting metal-mediated reductive coupling of carbon donor atoms of adjacent ligands. Examples of reductive coupling of carbon donor atoms of terminal isocyanide and carbonyl ligands have been reported.[2-4] We have discovered a similar coupling of adjacent acyl ligands in ferra-, mangana-, and rhena-β-diketonato-BF_2 complexes, **1**.[5,6] This coupling proceeds after formation of the α-enolate anion, **2**, as shown in eq 1, to afford

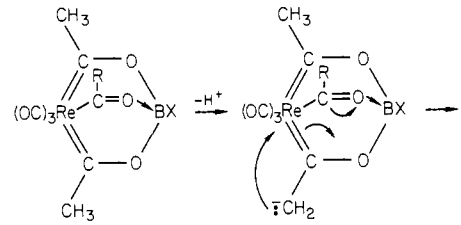


(1)

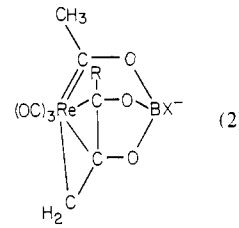
1 **2** **3**

anionic η^3-allyl complexes, **3**. The two acyl-carbon donor atoms undergo reductive coupling via a formal oxidation of the metal atom. However, the metal atom is reduced to its original oxidation state with the concomitant formation of a bond to the methylene carbon atom, thereby generating the η^3-allyl ligand.

We now report that (triacylrhenato)boron halide complexes undergo a similar coupling of adjacent acyl ligands as shown in eq 2. Removal of a proton from one of the methyl substituents of a (triacylrhenato)boron halide complex, **4**, generates the α-enolate anion **5**. Subsequent interligand C–C bond formation affords the anionic complex **6**, which contains the newly formed η^3-allyl ligand and a formal boroxycarbenoid ligand. The coupling of two of the acyl ligands in (triacylrhenato)boron halide complexes extends this unusual (though apparently general) interligand C–C bond-formation reaction to another class of organometallic compounds.



4 **5**



(2)

6

Experimental Section

All reactions and other manipulations were performed under prepurified nitrogen at 25 °C unless stated otherwise. Tetrahydrofuran (THF), toluene, and hexane were dried over Na/K alloy with added benzophenone. Methylene chloride and acetone-d_6 were dried over P_2O_5.

Infrared (IR) spectra were recorded on a Perkin-Elmer 727 spectrometer in 0.10-mm sodium chloride cavity cells with the solvent as a reference and a polystyrene film as a calibration standard. ^1H NMR spectra were obtained on JEOL MH-100 and FX-90Q NMR spectrometers with Me_4Si as an internal reference. Microanalysis was performed by Mic Anal Organic Microanalysis, Tucson, AR, or by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of [*fac*-$(OC)_3Re(CH_3CO)_3]BX$, Where X = F (7) and Cl (8). The previously reported procedure[7] was modified to essentially double the yield of the desired products. After the published procedure was followed for reacting acetylpentacarbonylrhenium with 2 molar equiv of methyllithium followed by treatment with BF_3 or BCl_3, the crude reaction residue was extracted with 2 × 25 mL of toluene. The extract was filtered, and the filtrate was reduced to ca. 7 mL. This solution was placed onto a Florisil (60–100 mesh) column, and the product was eluted with a 1:1 mixture of CH_2Cl_2:hexane. The pure products were isolated in 40–44% yield as yellow solids.

General Preparation of the [*fac*-$(OC)_3Re(CH_3CO)_2(i\text{-}PrCO)]BX$ Complexes 9 and 10. To a solution of 1.00 g (2.52 mmol) of isobutyrylpentacarbonylrhenium[8] in 60 mL of CH_2Cl_2 at 0 °C was added 2.3 molar equiv of low-halide methyllithium as a 1.4 M ether solution. The resulting suspension was stirred at 0 °C for 1 h, and then the solvent was removed at 0 °C under reduced pressure. The reaction residue was suspended in 60 mL of CH_2Cl_2 at −78 °C, and gaseous boron trihalide was bubbled into this suspension at a slow rate for 90 s. The reaction mixture was stirred at −78 °C for 15 min and at 0 °C for an additional 15 min. The solvent was then removed under reduced pressure. The reaction residue was extracted with 2 × 30 mL of toluene. This extract was filtered, and the filtrate was concentrated to *ca.* 7 mL under reduced pressure. This solution was placed on a 2.5 cm × 13 Florisil column (60–100 mesh). The product, **9** or **10**, was eluted with a 1:3 CH_2Cl_2

(1) On leave from the Department of Chemistry, Kentucky Wesleyan College, Owensboro, KY.

(2) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 617–618.

(3) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712–4715.

(4) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146–147 and references therein.

(5) Lukehart, C. M.; Srinivasan, K. *J. Am. Chem. Soc.* **1981**, *103*, 4166–4170.

(6) Lenhert, P. G.; Lukehart, C. M.; Srinivasan, K. *J. Am. Chem. Soc.* **1984**, *106*, 124–130.

(7) Hobbs, D. T.; Lukehart, C. M. *Inorg. Chem.* **1980**, *19*, 1811–1813.

(8) Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *Inorg. Chem.* **1976**, *15*, 2393–2397.

0002-7863/84/1506-1333$01.50/0

hexane mixture as a lemon yellow band. Removal of the solvent under reduced pressure afforded **9** or **10** as a yellow solid. The detailed characterization of each complex is provided below.

[*fac*-(OC)$_3$Re(CH$_3$CO)$_2$(*i*-PrCO)]BF (9). Dark yellow solid (53%): mp 106–107 °C; IR (hexane) ν (CO) 2030 (m), 1960 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.15 (hept, 1, CH, J = 6.8 Hz), 2.64 (s, 6, CH$_3$), 0.95 (d, 6, *Me*$_2$CH, J = 6.8 Hz). Anal. (C$_{11}$H$_{13}$BFO$_6$Re): C, H, F.

[*fac*-(OC)$_3$Re(CH$_3$CO)$_2$(*i*-PrCO)]BCl (10). Yellow solid (35%): mp 104–105 °C; IR (CH$_2$Cl$_2$) ν (CO) 2040 (m), 1970 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.14 (hept, 1, CH, J = 6.8 Hz), 2.65 (s, 6, CH$_3$), 0.96 (d, 6, *Me*$_2$CH, J = 6.8 Hz). Anal. (C$_{11}$H$_{13}$BClO$_6$Re): C, H, Cl.

General Preparation of the Me$_4$N{*fac*-(OC)$_3$Re[η^3-CH$_2$COCO(R)](CH$_3$CO)BX} Complexes, 11–14. To 30 mL of THF was added 0.028–0.037 g of KH which had been washed previously with 2 × 10 mL of hexane and 10 mL of THF. To this stirred suspension was added 0.33–0.50 g of the appropriate [*fac*-(OC)$_3$Re(CH$_3$CO)$_2$(RCO)]BX complex, **7–10**, in small portions at 25 °C. Immediate evolution of hydrogen followed each addition of the rhenium complex. The resulting yellow suspension was stirred at 25 °C for 30 min and at 0 °C for 30 min. After this time interval, no unreacted KH was observed. The solvent was removed under reduced pressure. To the residue was added 4–5 mL of a saturated solution of Me$_4$NCl in degassed water. The suspension was stirred vigorously for 5 min at 0 °C and was then extracted with 3 × 4 mL of CH$_2$Cl$_2$. The combined extracts were dried over 4-Å molecular sieves. The dried extract was filtered through a Schlenk frit. The filtrate was reduced to ca. 10 mL and was treated with 2–4 mL of hexane to induce crystallization at −15 °C. The products **11–14** were isolated as yellow crystals in yields of 25–32%. The detailed characterization of each complex is provided below.

Me$_4$N{*fac*-(OC)$_3$Re[η^3-CH$_2$COCO(CH$_3$)](CH$_3$CO)BF} (11). Light yellow crystals (28%): mp 157–160 °C dec; IR (THF) ν (CO) 1987 (s), 1897 (s), 1873 (vs) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 3.18 (s, 12, Me$_4$N$^+$), 2.86 (d, 1, CH$_2$ *syn*-H, J = 4.4 Hz), 2.45 (s, 3 Me acetyl), 2.26 (d, 1, CH$_2$ *anti*-H, J = 4.4 Hz), 1.97 (s, 3, Me-allyl). Anal. (C$_{13}$H$_{20}$BFNO$_6$Re): C, H, N.

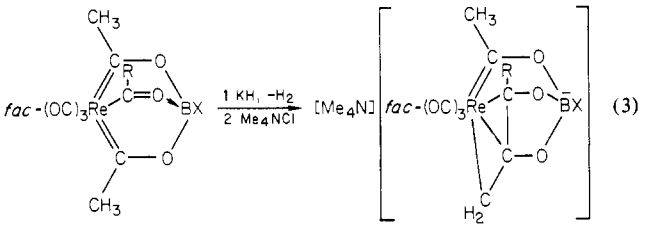
Me$_4$N{*fac*-(OC)$_3$Re[η^3-CH$_2$COCO(CH$_3$)](CH$_3$CO)BCl} (12). Light yellow solid (26%): mp 156–158 °C dec; IR (THF) ν (CO) 2000 (vs), 1910 (s), 1890 (vs) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 3.44 (s, 12, Me$_4$N$^+$), 2.88 (d, 1, CH$_2$ *syn*-H, J = 3.9 Hz), 2.47 (s, 3, Me acetyl), 2.22 (d, 1, CH$_2$ *anti*-H, J = 3.9 Hz), 2.02 (s, 3, Me-allyl). Anal. (C$_{13}$H$_{20}$BClNO$_6$Re): C, H, N.

Me$_4$N{*fac*-(OC)$_3$Re[η^3-CH$_2$COCO(*i*-Pr)](CH$_3$CO)BF} (13). Yellow solid (25%): mp 160–182 °C dec; IR (THF) ν (CO) 2000 (vs), 1910 (vs), 1885 (vs) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 3.44 (s, 12, Me$_4$N$^+$), 2.89 (d, 1, CH$_2$ *syn*-H, J = 3.9 Hz) 2.46 (s, 3, Me-acetyl), 2.18 (d, 1, CH$_2$ *anti*-H, J = 3.9 Hz), 1.53 (m, 1, Me$_2$C*H*, $J \approx 6$ Hz), 1.21 (d, 3, *Me*$_2$CH, J = 8.3 Hz), 1.14 (d, 3, *Me*$_2$CH, J = 8.3 Hz). Anal. (C$_{15}$H$_{24}$BFNO$_6$Re): C, H, N.

Me$_4$N{*fac*-(OC)$_3$Re[η^3-CH$_2$COCO(*i*-Pr)](CH$_3$CO)BCl} (14). Yellow solid (32%): mp 155–170 °C dec; IR (THF) ν (CO) 1995 (vs), 1910 (vs), 1890 (vs) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 3.45 (s, 12, Me$_4$N$^+$), 2.94 (d, 1, CH$_2$ *syn*-H, J = 3.9 Hz), 2.47 (s, 3, Me^6 acetyl), 2.22 (d, 1, CH$_2$ *anti*-H, J = 3.9 Hz), 1.53 (m, 1, Me$_2$C*H*, $J \approx 7$ Hz), 1.21 (d, 3, *Me*$_2$CH, J = 8.8 Hz), 1.14 (d, 3, *Me*$_2$CH, J = 8.8 Hz). Anal. (C$_{15}$H$_{24}$BClNO$_6$Re): C, H, N.

Results

The general base induced, interligand C–C bond-formation reaction is shown in eq 3. Reaction of the (triacylrhenato)boron halide complexes **7–10** with KH results in immediate evolution of hydrogen gas and the formation of the anionic η^3-allyl complexes **11–14** after cation exchange. When both methyl and isopropyl substitutents are present, deprotonation occurs specifically at a methyl substituent (which is the kinetically preferred site of deprotonation[9]). Formation of the η^3-allyl ligand via interligand C–C coupling apparently proceeds as shown in eq 2. The (η^3-allyl)(boroxycarbenoid) complexes **11–14** are formed in good yield as yellow solids that have excellent stability to heat and exposure to air.



(3)

7, R = Me; X = F
8, R = Me; X = Cl
9, R = *i*-Pr; X = F
10, R = *i*-Pr; X = Cl

11, R = Me; X = F
12, R = Me; X = Cl
13, R = *i*-Pr; X = F
14, R = *i*-Pr; X = Cl

The IR and ^{1}H NMR spectral data are consistent with the formation of the η^3-allyl complexes **11–14**. The IR spectra of the neutral reactant complexes **7–10** show the expected two-band pattern in the ν(CO) region for a *fac*-(OC)$_3$ML$_3$ type of complex. The higher frequency peak of A symmetry occurs at ca. 2040 cm^{-1}, and the lower frequency band of E symmetry occurs at ca. 1965 cm^{-1}. In the product complexes **11–14**, the molecular symmetry is lowered to C_1. The corresponding A band appears at ca. 1996 cm^{-1}, and the corresponding E band is now split into two bands at average frequencies of 1907 and 1885 cm^{-1}. The average shift to lower frequency of 61 cm^{-1} for the carbonyl stretching bands is consistent with an increase in electron density at the rhenium atom upon forming the anionic η^3-allyl complexes.

^{1}H NMR spectral data confirm the formation of the η^3-allyl complexes **11–14**. For the reactant complexes **7** and **8**, the three methyl substituents appear as a singlet resonance at δ ca. 2.67. Upon conversion to the products **11** and **12**, the remaining acetyl methyl protons appear as a singlet at δ ca. 2.46 while the methyl group which is attached to the η^3-allyl ligands appears as a singlet resonance at δ ca. 2.00. The original methyl group which has undergone deprotonation is transformed into an η^3-allyl CH$_2$ terminus. The syn and anti protons appear at δ ca. 2.87 and 2.24, respectively.

For the reactant complexes **9** and **10**, the two acetyl methyl protons appear as a single singlet resonance at δ 2.65. The isopropyl methyl groups appear as a single doublet resonance at δ 0.96, and the methine proton appears as a heptet at δ 3.14. Upon conversion to the η^3-allyl complexes **13** and **14**, the remaining acetyl methyl group appears as a singlet resonance at δ 2.46, and the syn and anti allyl protons of the allyl CH$_2$ terminus appear as doublets at δ ca. 2.92 and 2.20. The isopropyl methine resonance occurs at δ 1.53, which indicates that the isopropyl group is bonded to an allyl carbon atom rather than to an acyl carbon atom as in complexes **9** and **10**. Also, the isopropyl methyl groups are now anisochronous and appear as two doublets centered at δ 1.21 and 1.09. This observed anisohcronism is expected because of the low symmetry of these complexes.

In the ^{1}H NMR spectra of **13** and **14**, an additional set of isopropyl methyl resonances are observed as doublets centered at δ 0.87 and 0.70. These chemical shifts correspond to the chemical shifts of isopropyl methyl groups which are attached to acyl carbon atoms, as in **9** and **10**. We assigned these peaks to a minor isomer in which the interligand C–C coupling occurs between two acetyl acyl-carbon donor atoms, thereby affording an isobutyryl group in the boroxycarbenoid portion of the product. Relative integration indicates a minor isomer abundance of 4% for complex **13** and 16% for complex **14**.

In complexes **12–14**, the methyl resonance for the Me$_4$N$^+$ cation appears as a singlet at δ 3.44 in acetone-d_6 solution. For complex **11**, this resonance occurs at δ 3.18 in CD$_2$Cl$_2$ solution.

Discussion

The conversion of the (triacylrhenato)boron halide complexes **7–10** to the η^3-allyl complexes **11–14**, as shown in eq 3, demonstrates an extension of the interligand C–C coupling reaction to a second class of organometallic compounds. This interligand coupling is formally similar to that discovered previously with the metalla-β-diketonato–BF$_2$ complexes because a single Lewis structure representation of the bonding in these (triacyl-

(9) House, H. O.; Trost, B. M. *J. Org. Chem.* **1965**, *30*, 1341–1347.

rhenato)boron halide complexes is composed of a rhena-β-diketonate ligand system and a boroxycarbenoid ligand. However, X-ray structural studies indicate that considerably more carbenoid character is present in the Re-C acyl bonds of the (triacylrhenato)boron halide complexes than is present in the corresponding Re-C acyl bonds of rhena-β-diketonate complexes.[10,11] From this structural evidence, the (triacylrhenato)boron halide complexes appear to have a significantly different electronic structure from that of metalla-β-diketonate complexes.

The structural characterization of the η^3-allyl complexes **11**-**14** is essentially unambiguous because of the close correspondence between the ^{1}H NMR spectral data of these complexes and those data of the similar and well-characterized complexes $Me_4N\{cis\text{-}(OC)_4Re[\eta^3\text{-}CH_2COCO(Me)BF_2]\}$ (**15**) and $Me_4N\{cis\text{-}(OC)_4Re[\eta^3\text{-}CH_2COCO(i\text{-}Pr)BF_2]\}$ (**16**).[6,15] In complexes **11** and **12**, the methyl substituent on the allyl ligand is required to occupy an anti position. The resonance for this methyl group in **11** and **12** appears at δ ca. 2.00. In complex **15**, the anti methyl resonance occurs at δ 2.13. Similarly, the syn and anti allyl CH_2 proton resonances of **11** and **12** that appear at δ 2.87 and 2.24, respectively, are observed at δ 2.88 and 1.68 in **15**.

For complexes **13** and **14** where the isopropyl group is located predominantly in an allyl anti position the methine proton resonances at δ 1.53 are very close to the chemical shift of δ 1.46 for the methine proton resonance of **16**. Similarly, the isopropyl methyl doublets of **13** and **14** that appear at δ 1.21 and 1.09 are observed in **16** at δ 1.40 and 1.17. The syn- and anti allyl CH_2 proton resonances of **13** and **14** appear at δ ca. 2.92 and 2.20, respectively, and at δ 2.97 and 1.69, respectively, in complex **16**.

From these comparisons, the formation of η^3-allyl ligands in complexes **11**-**14** that possess either an *anti*-methyl or *anti*-isopropyl substituent is apparent. The reason for the slight downfield shift of the allyl anti CH_2 proton resonances in **11**-**14** relative to the corresponding resonances in the model complexes **15** and **16** is not understood, but this may reflect an electronic influence of the unique carbenoid ligand in these new complexes. However, the correspondence between the chemical shifts of the allyl syn CH_2 proton resonances for these two classes of complexes is excellent.

Acknowledgment. C.M.L. thanks the National Science Foundation (Grant No. CHE-8106140), the donors of the Petroleum Research Fund administered by the American Chemical Society, and the University Research Council of Vanderbilt University for support of this research. C.M.L. also acknowledges support from the Alfred P. Sloan Foundation as a Research Fellow. W.L.M. wishes to thank Mr. K. Srinivasan for technical assistance during this project.

Registry No. **7**, 73199-27-6; **8**, 73199-28-7; **9**, 88562-90-7; **10**, 88562-91-8; **11**, 88548-43-0; **12**, 88548-45-2; **13**, 88548-47-4; **14**, 88548-49-6.

(10) Lukehart, C. M.; Warfield, L. T. *Inorg. Chim. Acta* **1980**, *41*, 105-110.

(11) Baskar, A. J.; Lukehart, C. M. *J. Organomet. Chem.* **1983**, *254*, 149-157. In $[fac\text{-}(OC)_3Re(CH_3CO)_3]BBr$, the average Re-C acyl distance is 2.04(3) Å, while in $[cis\text{-}(OC)_4Re(CH_3CO)_2]_2Cu$,[12] $[cis\text{-}(OC)_4Re(CH_3CO)_2]H$,[13] and $[PhC(NH_2)_2][cis\text{-}(OC)_4Re(CH_3CO)_2]$[14] the average Re-C acyl distances are 2.152 (5), 2.16 (2), and 2.182 (6) Å, respectively.

(12) Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* **1980**, *19*, 311-315.

(13) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1976**, *98*, 2365-2367.

(14) Lenhert, P. G.; Lukehart, C. M.; Sotiropoulos, P. D.; Srinivasan, K. *Inorg. Chem.*, in press.

(15) For general reference to relevant η^3-allyl ^{1}H NMR data see: (a) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, 189-197. (b) Green, M. L. H.; Nagy, P. L. I. *Adv. Organomet. Chem.* **1964**, *2*, 325-363. (c) McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601-1607.

Photoinduced Electron Transfer in Polychromophoric Systems. 2.[1] Protonation Directed Switching between Tri- and Bichromophoric Interaction

Ger F. Mes, Hendrik J. van Ramesdonk, and Jan W. Verhoeven*

Contribution from the Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands. *Received May 17, 1983*

Abstract: The synthesis of a series of molecules D^2-D^1-A is described in which two electron donor chromophores (D^1, a trialkylamino group, and D^2, a (substituted) anilino group) and an electron acceptor chromophore (A, a (cyano)naphthyl group) are linked by a saturated paraffinic skeleton of well-defined conformation, which maintains closest atom-atom distances of 2.4 and 4.7 Å between A and D^1, and D^2, respectively. The fluorescence spectra of the trichromophoric molecules display an intramolecular charge-transfer emission at significantly lower energy than bichromophoric molecules D^1-A lacking the anilino donor. Together with the response of the charge-transfer fluorescence to substituents in the anilino group, this implies that in the emissive excited state a substantial positive charge develops at D^2. Photoinduced electron transfer in bichromophoric molecules D^1-A is effectively canceled upon selective protonation of D^1 in acidified polar media. Under these conditions the trichromophoric systems, however, are found to switch to a mode of electron transport involving direct long-range electron transfer from D^2 to A.

Electron transport along a chain of redox centers plays a crucial role in the biological energy transformation of the respiratory chain[2,3] and of the photosynthetic system.[4-7] Relatively little is known about the way in which the structure and spatial arrangement of these redox centers direct the rate and the pathway of electron transfer. The study of bichromophoric molecules incorporating an electron donor (D) and acceptor (A) moiety within a single molecule of well-defined conformation has been

(1) For part 1, see: Mes, G. F.; van Ramesdonk H. J.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 55-56.

(2) Malmström, B. G. *Annu. Rev. Biochem.* **1982**, *51*, 21-59.

(3) "Tunneling in Biological Systems"; Chance, B., De Vault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds.; Academic Press: New York, 1979; pp 453-557.

(4) Blankenship, R. E.; Parson, W. W. *Annu. Rev. Biochem.* **1978**, *47*, 635-653.

(5) Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 6676-6686.

(6) Chidsey, C. E. D.; Roelofs, M. G.; Boxer, S. G. *Chem. Phys. Lett.* **1980**, *74*, 113-118.

(7) Boxer, S. G.; Chidsey, C. E. D.; Roelofs, M. G. *J. Am. Chem. Soc.* **1982**, *104*, 1452-1454.

0002-7863/84/1506-1335$01.50/0