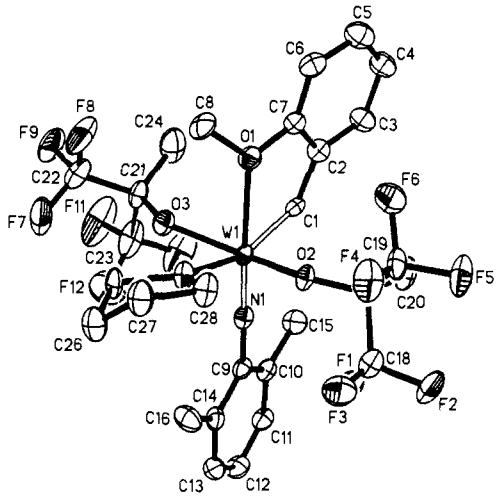


Figure 1. ORTEP diagram of **1**. Selected bond distances (Å) and angles (deg) are as follows: W-C(1), 1.943 (5); W-N(1), 1.737 (4); W-O(1), 2.346 (3); W-O(2), 1.995 (4); W-O(3), 1.995 (3); W-O(4), 2.294 (3); W-C(1)-C(2), 121.9 (4); W-N(1)-C(9), 174.6 (4); W-O(2)-C(17), 138.8 (3); W-O(3)-C(21), 138.4 (3); C(1)-W-O(2), 97.6 (2); O(2)-W-O(4), 75.2 (1); C(1)-W-O(3), 103.0 (2); O(3)-W-O(4), 75.1 (1); C(1)-W-O(1), 74.2 (2); O(1)-W-O(2), 82.0 (1); O(1)-W-O(3), 79.7 (1); O(1)-W-O(4), 79.8 (1); C(1)-W-N(1), 99.2 (2); N(1)-W-O(2), 101.2 (2); N(1)-W-O(3), 100.2 (2); N(1)-W-O(4), 107.0 (2).

reaction sequence involving the recrystallization of only the final product gave 20.7 g of **1** (32.2%, not optimized). Complex **1** resembles the arylimido tungsten alkylidene catalysts developed by Schrock and co-workers.[4a] These catalysts are known to be deactivated by the coordination of Lewis bases such as THF and sterically nondemanding phosphines and amines.[4a,8e,9a,15b] Fortunately, PPh_3, a reaction byproduct, does not coordinate to **1**. Therefore, phosphine-free **1** can readily be prepared by scavenging PPh_3 with CuCl.[15b]

The structure of **1** has been determined by X-ray diffraction.[18] An ORTEP diagram is included in Figure 1 along with selected bond distances and angles. The geometry about the metal center can best be described as a distorted octahedron with the imido and alkylidene ligands lying in the expected cis orientation.[4a] The methoxy group of the benzylidene ligand occupies an axial site of the octahedron, and the 2.346 (3) Å W-O(1) bond distance is comparable to the 2.294 (3) Å W-O(4) (THF) bond distance.[19] The W-C(1)-C(2) bond angle is approximately 23° smaller than the analogous angle reported for W(CHPh)(NAr)[OCMe-$(CF_3)_2]_2$.[4a] This smaller angle is reflected in the respective coupling constants of these two complexes: $J_{CH\alpha}$ = 151 Hz for **1** and $J_{CH\alpha}$ = 121 Hz for W(CHPh)(NAr)$[OCMe(CF_3)_2]_2$.[4a]

The coordination of the methoxy group to the tungsten metal center of **1** in solution is implied by difference NOE experiments and reactivity studies. NOEs are not observed in either direction between the methoxy group and the carbene α-proton. Donation by the methoxy group is further suggested by the lack of PPh_3 coordination and by the stability of **1**. The analogous unsubstituted benzylidene complex W(CHPh)(NAr)$[OCMe(CF_3)_2]_2$ reversibly binds PPh_3 and largely decomposes within a day in solution in its absence.[20] Two imido methyl groups are observed in the ^1H NMR spectrum of **1** at −70 °C, requiring that the aryl ring not lie in the RO-W(N)-OR plane. At room temperature, the arylimido ligand rotates freely, and deuteriotetrahydrofuran exchanges rapidly with coordinated THF.

Treatment of **1** with PMe_3 gives yellow W(CHAr')(NAr)-$[OCMe(CF_3)_2]_2(PMe_3)$. Heating a toluene solution of **1** under vacuum generates THF-free W(CHAr')(NAr)$[OCMe(CF_3)_2]_2$ (**2**) as a bright red solid. The downfield chemical shift of the α-proton of the *o*-methoxybenzylidene ligand of **2** (10.94 ppm) can be compared with the downfield shifts reported for alkylidene complexes coordinated by Lewis bases,[4a,15b] which suggests that in solution the methoxy group of **2** coordinates to the tungsten metal center.[21] As expected, **1** and **2** are active metathesis catalysts, rapidly polymerizing cyclic olefins such as norbornene and cyclooctatetraene. The acyclic olefin *cis*-2-pentene is slowly metathesized by **2**.[22] Complex **1** reacts in a Wittig-type fashion with carbonyl compounds, including esters and amides, in yields of 82-100% as measured by NMR spectroscopy.

The steric bulk of the imido ligand can be varied without greatly affecting the transfer of the *o*-methoxybenzylidene moiety from phosphorus to tungsten. For example, in addition to the (2,6-dimethylphenyl)imido complex **1**, the phenylimido (**3**) and (2,6-diisopropylphenyl)imido (**4**) complexes are obtained in good yields from the reaction sequence shown in Scheme I. To date, the transfer of other aryl carbenes in high yields has required the (2,6-dimethylphenyl)imido precursor. In all cases, the incorporation of electron-withdrawing alkoxides is necessary for successful reduction and alkylidene transfer.

Acknowledgment. We gratefully acknowledge support from the NSF and NIH, and L.K.J. thanks the NSF for a predoctoral fellowship. Funds for the purchase of the Nicolet R3m/V diffractometer system were made available from the NSF under Grant CHE-85-14495. We are grateful to Dr. David R. Wheeler for advice regarding the NOE experiments and thank Dr. Tamara A. Ulibarri for assistance.

Supplementary Material Available: Experimental details and spectroscopic and analytical data for complexes **1-4** and precursors and derivatives of these complexes, additional information regarding the polymerizations, Wittig-type reactions, and crystal structure of **1**, and tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for **1** (19 pages); listing of observed and calculated structure factors for **1** (19 pages). Ordering information is given on any current masthead page.

(18) **1** crystallizes in space group $P2_1/c$ (C^5_{2h}; No. 14) with a = 12.606 (3) Å, b = 12.981 (3) Å, c = 18.998 (5) Å, β = 91.85 (2)°, V = 3108.0 (13) Å^3, and D_{calcd} = 1.830 g cm^{-3} for Z = 4, T = 173 K. The structure was solved via an automatic Patterson method (SHELXTL PLUS). Refinement of positional and anisotropic thermal parameters led to convergence with R_F = 3.8%, R_{wF} = 4.4%, and GOF = 1.39 for 415 variables refined against all 5269 unique data with $|F_o| > 0$; [R_F = 3.1%, R_{wF} = 4.1% for those 4576 data with $|F_o| > 6.0\sigma(|F_o|)$].

(19) (a) The methoxy group coordinates to chromium in the crystal structure of $(OC)_4Cr[=C(OMe)(o\text{-}MeOC_6H_4)]$. See: Dotz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267-275. (b) For information on analogous tungsten complexes, see: Dotz, K. H.; Erben, H.-G.; Staudacher, W.; Harms, K.; Muller, G.; Riede, J. *J. Organomet. Chem.* **1988**, *355*, 177-191.

(20) Complex **2** has been isolated and characterized as its PMe_3 adduct W(CHPh)(NAr)$[OCMe(CF_3)_2]_2(PMe_3)$.

(21) In the crystal structure of the THF-free alkylidene complex W-(CHAr')[N-2,6-(i-Pr)$_2$C$_6$H$_3$][$OCMe(CF_3)_2]_2$, the methoxy group does coordinate to tungsten: Johnson, L. K.; Grubbs, R. H.; Ziller, J. W., unpublished results.

(22) The lower limit for the rate of metathesis of *cis*-2-pentene by a 3 mM toluene-d_8 solution of **2** is 1.4 equiv/min at room temperature.

Reaction Sequence Related to That of Carbon Monoxide Dehydrogenase (Acetyl Coenzyme A Synthase): Thioester Formation Mediated at Structurally Defined Nickel Centers

Pericles Stavropoulos, Michel Carrié, Mark C. Muetterties, and R. H. Holm*

Department of Chemistry, Harvard University Cambridge, Massachusetts 02138

Received March 29, 1990

The nickel-containing carbon monoxide dehydrogenases[1] (CODH) from certain bacteria such as *Clostridium thermo-*

0002-7863/90/1512-5385$02.50/0

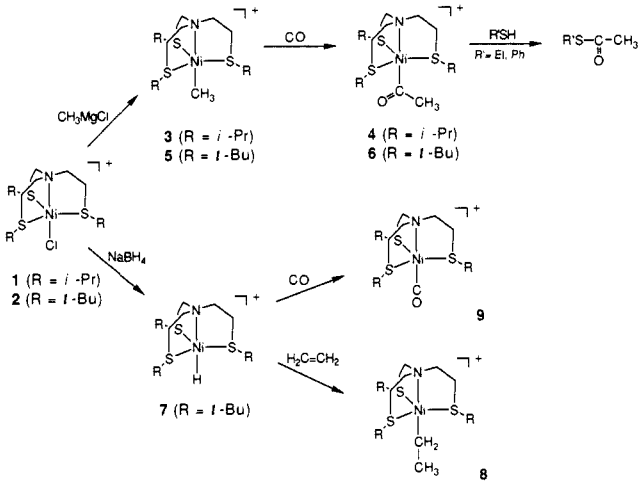


Figure 1. Reaction scheme illustrating the formation of complexes containing the [Ni^{II}–Me], [Ni^{II}–COMe], [Ni^{II}–H], [Ni^{II}–Et], and [Ni^{I}–CO] groups, starting from the [Ni^{II}–Cl] precursors **1** and **2**, and the formation of thioester by the reaction of thiols with acyl complexes **4** and **6**. Complex **1** is binuclear in the solid state, but is mononuclear in solution.[5]

aceticum[2] not only catalyze reaction 1 (via an enzyme–C_1 intermediate) but also the synthesis of acetyl coenzyme A by means of the Wood pathway.[1d,3] Although much remains to be revealed, overall reaction 2 proceeds initially by enzymatic transfer of methyl from tetrahydrofolate to a corrinoid protein and then nonenzymatic methyl transfer to CODH,

$$CO + H_2O \rightleftarrows CO_2 + 2H^+ + 2e^- \quad (1)$$

$$\text{Me-tetrahydrofolate} + \text{CoA-SH} + CO \rightarrow \text{CoA-SCOMe} + \text{tetrahydrofolate} \quad (2)$$

followed by the speculative steps of methyl migration to Ni–CO or the reverse and condensation of Ni–$COCH_3$ with CoA-SH to afford CoA–$SCOCH_3$. The most recent EXAFS study of the CO-free, EPR-silent form of CODH suggests a planar NiS_4 coordination sphere (Ni–S 2.16 (3) Å) with a nearby Fe–S cluster (Ni–Fe 3.25 Å).[4] We seek to place the multistep reactions of CODH on a rational basis. In this context, the groups [Ni–L] (L = Me, COMe, CO, H) are of immediate significance. Lacking definition of the Ni–Fe site sufficient for design of an accurate synthetic analogue, we have utilized Ni complexes of the tripod ligands $N(CH_2CH_2SR)_3$[5] (NS_3^R, R = *i*-Pr, *t*-Bu). These provide access to the desired groups [Ni–L] in a sulfur-rich environment without physiologically objectionable M–P/As and M–C coordination.[6] Pertinent reactions are summarized in Figure 1.

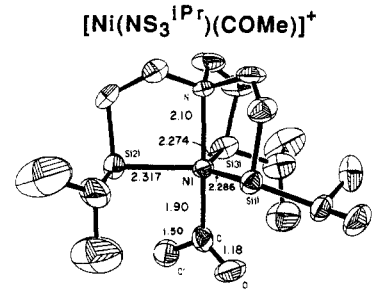


Figure 2. Structure of [Ni(NS_3^{iPr})(COMe)]$^+$ as its BPh_4^- salt, illustrating the d-TBP stereochemistry, which is quite similar to that found for **2**–**4**, **7**, and **9**. Bond angles (deg): S(1)–Ni–S(2), 109.8 (1); S(1)–Ni–S(3), 134.0 (1); S(2)–Ni–S(3), 115.3 (2); N–Ni–S, 86.8 (3)–87.4 (3); N–Ni–C, 179.6 (7); C'–C–O, 119 (1).

Green [Ni(NS_3^{iPr})Cl](BPh_4)[5] (**1**) contains a dimeric centrosymmetric cation with octahedral Ni^{II} and two Ni–Cl–Ni bridges (Ni–Cl 2.370 (5), 2.466 (5) Å), whereas mustard [Ni(NS_3^{tBu})Cl](BPh_4)[5] (**2**) includes a distorted trigonal bipyramidal cation (d-TBP, Ni–S 2.35–2.38 Å, Ni–Cl 2.295 (3) Å).[7] Both are useful starting materials; all subsequent complexes have d-TBP stereochemistry and were isolated as BPh_4^- salts.[8] Reaction of **1** with 1 equiv of MeMgCl affords deep purple [Ni(NS_3^{iPr})Me]$^+$ (**3**, 55%, δ_{Me} – 0.71, Ni–S 2.23–2.33 Å, Ni–C 1.94 (2) Å).[7] Treatment of **3** with CO (1 atm, –20 °C) leads instantaneously to red-purple [Ni(NS_3^{iPr})$COCH_3$]$^+$ (**4**, 80%, ν_{CO} 1670 cm^{-1}, δ_{COMe} 2.37),[7] which was isolated by low-temperture workup and whose structure is shown in Figure 2. A similar series of reactions starting with **2** gave blue [Ni(NS_3^{tBu})Me]$^+$ (**5**, 50%, δ_{Me} –0.82) and quantitative formation in solution of red [Ni(NS_3^{tBu})COMe]$^+$ (**6**, δ_{COMe} 2.49), which reversibly reverts to **5** and CO under reduced pressure.

Because it is now well established that acetyl-CODH formation precedes the generation of CoA–$SCOCH_3$,[9] complexes **3**/**5** and **4**/**6** can be conceived of as intermediates before the final step of condensation with CoA-SH. This step is supported by the reaction of the acyl **4** with 1 equiv of EtSH (20 h, 79%) or PhSH (12 h, 76%) to afford the indicated yields (^{1}H NMR) of thioester R'SCOMe. The more acidic thiol reacts faster, consistent with the general acid-catalyzed addition of thiols to carbonyl derivatives.[10] Reaction of labile **6** in CD_2Cl_2 with 1 equiv of EtSH (12 h, 79%) or PhSH (7 h, 76%) is even faster.

By extrapolation of the water gas shift reaction,[11] certain steps in reaction 1 may implicate [Ni–CO] and [Ni–H] species. Possibilities include [Ni–CO] + OH^- → [Ni–COOH] → [Ni–H] + CO_2, and [Ni–H] + H^+ → [Ni], [Ni] + CO → [Ni–CO]. Attempts to prepare a hydride species from **1** gave black intractable materials. However, reaction of **2** and $NaBH_4$ in THF affords red-purple [Ni(NS_3^{tBu})H]$^+$ (**7**, 40%, ν_{NiH} 1878 cm^{-1}, δ_{NiH} –37.8, Ni–S 2.22–2.23 Å).[7] Chemical proof of [Ni–H] is the conversion to **2** in chlorinated solvents and the instantaneous reaction with ethylene to give blue diamagnetic [Ni(NS_3^{tBu})Et]$^+$

(1) (a) Hausinger, R. P. *Microbiol. Rev.* **1987**, *51*, 22. (b) Walsh, C. T.; Orme-Johnson, W. H. *Biochemistry* **1987**, *26*, 4901. (c) Cammack, R. *Adv. Inorg. Chem.* **1988**, *32*, 297. (d) Ragsdale, S. W.; Wood, H. G.; Morton, T. A.; Ljungdahl, L. G.; DerVartanian, D. V. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Ed.; VCH Publishers: New York, 1988; pp 311–332.

(2) (a) Ragsdale, S. W.; Clark, J. E.; Ljungdahl, L. G.; Lundie, L. L.; Drake, H. L. *J. Biol. Chem.* **1983**, *258*, 2364. (b) Lindahl, P. A.; Münck, E.; Ragsdale, S. W. *J. Biol. Chem.* **1990**, *265*, 3873. (c) Lindahl, P. A.; Ragsdale, S. W.; Münck, E. *J. Biol. Chem.* **1990**, *265*, 3880.

(3) Wood, H. G.; Ragsdale, S. W.; Pezacka, E. *Biochem. Int.* **1986**, *12*, 421.

(4) Bastian, N. R.; Diekert, G.; Niederhoffer, E. C.; Teo, B.-K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 5581. Other EXAFS data are suggestive of ca. two Ni–S bonds (2.21 Å): Cramer, S. P.; Eidsness, M. K.; Pan, W.-H.; Morton, T. A.; Ragsdale, S. W.; DerVartanian, D. V.; Ljungdahl, L. G.; Scott, R. A. *Inorg. Chem.* **1987**, *26*, 2477.

(5) Fallani, G.; Morassi, R.; Zanobini, F. *Inorg. Chim. Acta* **1975**, *12*, 147.

(6) Certain [Ni–L] groups and connecting transformations described here have been accomplished previously only in molecules containing one or more of these bonds; cf., e.g.: (a) Sacconi, L.; Dapporto, P.; Stoppioni, P.; Innocenti, P.; Benelli, C. *Inorg. Chem.* **1977**, *16*, 1669. (b) Stoppioni, P.; Dapporto, P.; Sacconi, L. *Inorg. Chem.* **1978**, *17*, 718. (c) Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1984**, *23*, 922.

(7) X-ray diffraction data were collected at 25 °C for **1**–**4** and **7** and at –90 °C for **9**. Structures were solved by standard procedures; empirical absorption corrections were applied. Crystallographic data are given as *a*, *b*, *c*; α, β, γ; space group, *Z*, $2\theta_{min/max}$, unique data ($I > 3\sigma(I)$), $R(R_w)$ (%). **1**: 17.962 (4), 21.927 (4), 22.696 (4) Å; *Pcab*, 4, 2.0°/45.0°, 2409, 6.5 (7.0). **2**: 13.908 (2), 22.395 (4), 26.767 (4) Å; *Pbca*, 8, 3.0°/45.0°, 1574, 7.3 (7.9). **3**: 13.364 (7), 14.590 (6), 20.736 (8) Å; 92.63 (3)°, 103.46 (3)°, 90.00 (4)°; $P\bar{1}$, 4, 3.0°/40.0°, 3313, 6.1 (6.1). **4**: 11.384 (3), 13.911 (3), 14.068 (4) Å; 77.98 (2)°, 86.07 (2)°, 88.25 (2)°; $P\bar{1}$, 2, 2.0°/50.0°, 2766, 5.6 (5.6). **7**: 11.864 (6), 12.853 (6), 13.747 (5) Å; 89.21 (3)°, 89.02 (4)°, 82.67 (4)°; $P\bar{1}$, 2, 3.0°/45.0°, 1448, 7.8 (8.3). The hydride ligand of **7** was not located. **9**: 10.796 (2), 12.978 (3), 15.685 (3) Å; 80.27 (2)°, 87.63 (2)°, 73.59 (2)°; $P\bar{1}$, 2, 3.0°/42.0°, 3952, 9.1 (11.3).

(8) All operations were carried out under anaerobic conditions and all reactions were performed in THF solutions unless noted otherwise. ^{1}H NMR solvents: $(CD_3)_2CO$ (**3**, **4**), CD_2Cl_2 (**5**, **6**), THF-d_8 (**7**).

(9) Lu, W.-P.; Harder, S. R.; Ragsdale, S. W. *J. Biol. Chem.* **1990**, *265*, 3124.

(10) Lienhard, G. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1966**, *88*, 3982.

(11) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 12.

(8, 80%), which in THF is in equilibrium with 7 and ethylene. The *t*-Bu substituents evidently provide a more rigid cavity, capable of protecting sensitive ligands. In THF, 7 reacts with CO to give green paramagnetic $[Ni(NS_3^{tBu})CO]^+$ (9, 60%, ν_{CO} 2026 cm^{-1}; g = 2.005, 2.114, Ni-C 1.81 (1) Å, Ni-S 2.36-2.37 Å),[7] in which the Ni-N bond (2.22 (1) Å) trans to the carbonyl (Ni-C-O 178 (1)°) is longer than that in other members of the set.

This work provides the initial demonstrations of stable, structurally defined [Ni^{II}-Me], [Ni^{II}-COMe], [Ni^{II}-H], and [Ni^{I}-CO] species and the reaction sequence [Ni-Cl] → [Ni-CH_3] → [Ni-$COCH_3$] → CH_3COSR',[12] all in the absence of tertiary phosphine/arsine and (other) carbon ligands. While [Ni-(NS_3^R)]-type species cannot at present be claimed as analogues of different states of the Ni site in CODH, the existence and reactivity of such species lend viability to current views of certain steps in the operation of *C. thermoaceticum* CODH.[1d,3,9,13] Future accounts will provide further details on the reactivity of species based on the [$Ni(NS_3^R)$] coordination unit.

Acknowledgment. This research was supported by NSF Grant CHE 89-03283. X-ray diffraction equipment was obtained through NIH Grant 1 S10 RR 02247. We thank K. Delaney for a preliminary experiment.

Supplementary Material Available: Atom positional parameters for the BPh_4^- salts of **1-4**, **7**, and **9** (7 pages). Ordering information is given on any current masthead page.

(12) The identity of the product Ni complexes is under investigation.
(13) Harder, S. R.; Lu, W.-P.; Feinberg, B. A.; Ragsdale, S. W. *Biochemistry* **1989**, *28*, 9080.

Bovine Rhodopsin with 11-Cis-Locked Retinal Chromophore neither Activates Rhodopsin Kinase nor Undergoes Conformational Change upon Irradiation

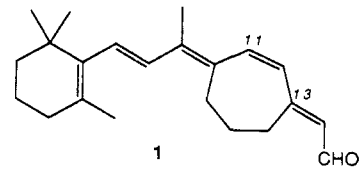
Todd Zankel,[†] Hyun Ok,[†] Randy Johnson,[†] Chia Wun Chang,[‡] Noriko Sekiya,[‡] Hideo Naoki,[‡] Kazuo Yoshihara,*[,†] and Koji Nakanishi*[,†,‡]

Department of Chemistry, Columbia University New York, New York 10027
Suntory Institute for Bioorganic Research Mishima, Shimamoto, Osaka, Japan

Received January 19, 1990

Rhodopsins belong to the multigene family of receptors which share the structural feature of seven membrane-spanning helices.[1] While most of these proteins are activated by soluble ligands, rhodopsins are activated by covalently bound 11-*cis*-retinal. It has been proposed that rhodopsin photoactivation results from 11-cis to all-trans isomerization of retinal;[2] an intermediate in the relaxation process of the conformationally excited pigment, metarhodopsin II (meta II), interacts with a series of soluble proteins, terminating in cGMP hydrolysis on one hand[3] and in phosphorylative deactivation of rhodopsin by rhodopsin kinase (RK) on the other.[4]

The 11-cis-locked cycloheptenediylidene analogue **1** forms nonbleachable pigments with opsins from various sources;[5,6] however, **1** and its 13-cis isomer, upon addition to bleached salamander rod outer segments, restores some light sensitivity through a mechanism apparently unrelated to the photoexcitation of the pigment.[7] Indirect studies with the green alga *Chlamydomonas reinhardtii* indicate that **1** restores phototaxis to a mutant that lacks retinal, also by an unknown mechanism.[8] Irradiation of bovine rhodopsin containing analgoue **1** (**1**-rhodopsin) forms two unstable intermediates as observed by picosecond measurements, a 580-nm species that is further excited to a 630-nm species,[9-11] which decays by fluorescence. In an effort to further clarify which properties of retinal are necessary and sufficient for transduction, **1**-rhodopsin was tested for (i) phosphorylation by preparations of rhodopsin kinase and (ii) conformational changes by difference FTIR spectroscopy.



1

Rhodopsin Kinase (RK) Assays. A solution of RK was prepared by established methods.[12,13] Retinal-free opsin was prepared by hexane washing with slight modifications of standard methods.[14,15] Pigments were then prepared by incorporation of chromophore into opsin, 10 mM HEPES (pH 7), and further hexane washing of pigments to remove excess chromophore. RK assays were performed as previously described with some modifications.[16] Hexane-washed opsin and **1**-rhodopsin showed no light-dependent phosphorylation (Figure 1, curves 1 and 2), while 11-cis-regenerated rhodopsin gave reasonable activity (curve 3). Phosphorylation stoichiometry of hexane-washed pigments, with a maximum of 0.15 phosphates added/pigment molecule, was generally low. Treatment of opsin with 11-*cis*-retinal, *but with no further hexane wash*, restored highest activity (curve 4); the higher activity of this pigment indicates that hexane washing decreases transduction ability and may account for the low incorporation observed. The kinase assays thus show that **1**-rhodopsin from bovine opsin has very little, if any, light-dependent biochemical activity.[17]

FTIR Difference Spectra of Rhodopsin/Metarhodopsin II In-

(1) Hall, Z. W. *Trends Neurosci.* **1987**, *10*, 99-101.
(2) Hubbard, R.; Kropf, A. *Proc. Natl. Acad. Sci. U.S.A.* **1958**, *44*, 130-139.
(3) (a) Stryer, L. *Annu. Rev. Neurosci.* **1986**, *9*, 87-119. (b) Bennett, N.; Michel-Villez, M.; Kuhn, H. *Eur. J. Biochem.* **1982**, *127*, 97-103.
(4) Kuhn, H.; Cook, J. H.; Dreyer, W. J. *Biochemistry* **1973**, *12*, 2495-2502.
(5) Akita, H.; Tanis, S. P.; Adams, M.; Balogh-Nair, V.; Nakanishi, K. *J. Am. Chem. Soc.* **1980**, *102*, 6370-6372.
(6) Crouch, R.; Nodes, B. R.; Perlman, J. I.; Pepperberg, D. R.; Akita, H.; Nakanishi, K. *Invest. Ophthalmol. Visual Sci.* **1984**, *25*, 419-428.
(7) Corson, D. W.; Cornwall, M. C.; MacNichol, E. F.; Jin, J.; Johnson, R.; Derguini, F.; Crouch, R. K.; Nakanishi, K. *Proc. Natl. Acad. Sci. U.S.A.*, in press.
(8) (a) Foster, K. W.; Saranak, J.; Derguini, F.; Rao, V. J.; Zarrilli, G. R.; Okabe, M.; Fang, J.-M.; Shimizu, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1988**, *110*, 6588-6589. (b) Foster, K. W.; Saranak, J.; Derguini, F.; Zarrilli, G. R.; Okabe, M.; Nakanishi, K. *Biochemistry* **1989**, *28*, 819-824. (c) Nakanishi, K.; Derguini, F.; Rao, V. J.; Zarrilli, G.; Okabe, M.; Lien, T.; Johnson, R.; Foster, K.; Saranak, J. *Pure Appl. Chem.* **1989**, *61*, 361-364.
(9) Buchert, J.; Stenfacic, V.; Doukas, A. G.; Alfano, R. R.; Callender, R. H.; Pande, M. J.; Balogh-Nair, V.; Nakanishi, K. *Biophys. J.* **1983**, *43*, 279-283.
(10) Birge, R. R.; Murray, L. P.; Pierce, B. M.; Akita, H.; Balogh-Nair, V.; Findsen, L. A.; Nakanishi, K. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 4117-4121.
(11) Kandori, H.; Matsuoka, S.; Shichida, Y.; Yoshizawa, T.; Ito, M.; Tsukida, K.; Balogh-Nair, V.; Nakanshi, K. *Biochemistry* **1987**, *28*, 6460-6467.
(12) Palczewski, K.; McDowell, J. H.; Hargrave, P. A. *J. Biol. Chem.* **1988**, *28*, 14067-14073.
(13) Rando, R. R.; Seckler, B., unpublished.
(14) Papermaster, D.; Dreyer, H. *Biochemistry* **1974**, *13*, 2438.
(15) Fukada, Y.; Shichida, Y.; Yoshizawa, T.; Ito, M.; Kodama, A.; Tsukida, K. *Biochemistry* **1984**, *23*, 5826-5832.
(16) To each well of a 96-well culture plate were added a glass bead, RK solution (75 μL), nucleotide solution (20 μL, 7 mM ATP, 8 mCi [^{32}P]ATP in 100 mM Na_2PO_4 (pH 7.0), 5 mM $MgCl_2$), and pigment solution (50 mL). The wells were photolyzed at different intensities for 30 s with 480-510-nm light and shaken at 100 rpm for 20 min in the dark. The reaction was quenched by transfer of 120 μL from each well to a row of wells in a dot blotter containing 500 μL of 30% CCl_3COOH, filtering through Whatman GF/B filters. The blot was placed in a bath of cold 7 mM ATP in phosphate buffer and shaken gently for 1 h, and the spots were cut out and counted.

[†] Columbia University.
[‡] Suntory Institute for Bioorganic Research.

0002-7863/90/1512-5387$02.50/0