there might be a positive opsin charge near C_7. The reduction of the opsin shift to 2300 cm^{-1} in 5,6-dihydro BR and its *increase* to 3500 cm^{-1} in 7,8-dihydro BR provides strong independent evidence for the positive charge near C_7. More importantly, the data presented here show that this positive charge is an important spectroscopic determinant and that protein perturbations near the Schiff base end of the chromophore play a dominant role in the production of the opsin shift. A similar reanalysis of the mechanism of the opsin shift has recently been developed independently by Nakanishi and co-workers.[6,7]

In Table I we present the absorption maxima of the protonated Schiff bases and of bacterio opsin regnerated with 5,6- and 7,8-dihydroretinal. The absorption maxima of native BR and its 5,6-dihydro derivative are in good agreement with the results of ref 2, while the λ_{max} of the 7,8-dihydro derivative is found to be 445 nm.[6] Thus, the opsin shift for 7,8-dihydro BR (3500 cm^{-1}) is much larger than that of the 5,6-dihydro derivative (2300 cm^{-1}). To compare these values with the opsin shift of the native chromophore it is necessary to separate electrostatic from ground-state conformational effects. ^{13}C NMR experiments[5] have shown that bacterio opsin preferentially binds the 6-s-trans conformer rather than the 30–70° twisted 6-s-cis conformer found in solution.[11] The absorption maximum for the s-trans conformer is calculated to be red-shifted by 16–32 nm from that of the twisted s-cis conformer,[12] and locked 6-s-trans PSB analogues are red-shifted by 25 nm.[10] By use of the experimental value, the opsin shift for the native chromophore can be partitioned into $\sim$1200 cm^{-1} due to isomerization to a planar s-trans structure and $\sim$3900 cm^{-1} due to other protein–chromophore interactions.

Figure 1 presents a model for the location of the protein charges which are important for the opsin shift in bacteriorhodopsin. A negative protein residue is placed near C_5 in agreement with the "point charge" model of Nakanishi et al.[2] In addition, a positive opsin charge is placed near the C_7 position of the chromophore. To understand how the opsin shift data lead to this model it is necessary to realize that in the excited state of the retinal PSB, positive charge shifts toward the ionone ring end of the chromophore, while in the ground state the positive charge is relatively localized near the Schiff base.[12-14] A negative environmental charge near the ionone ring would thus stabilize the energy of the excited state more than that of the ground state, leading to a red shift in the absorption. A positive environmental charge near the ionone ring would have the opposite effect.[15] In the 5,6-dihydro derivative the interaction of the conjugated chain with the negative charge is essentially eliminated and the opsin red shift falls to 2300 cm^{-1}. However, in this analogue a positive charge near C_7 would still interact effectively with the conjugated chain and should contribute to a reduction of the opsin shift. When the retinal chain is further shortened in the 7,8-dihydro derivative, we see the opsin shift *increase* to 3500 cm^{-1}. This rather dramatic biphasic behavior—that is, first a reduction in the opsin shift followed by an increase in the opsin shift as the chain is truncated—is a natural consequence of the interaction of the retinal chromophore with a pair of protein charges of opposite sign (or with a strongly dipolar residue) near the ionone ring. *These dihydro data thus provide strong evidence for a dipolar pair of opsin charges near the ionone ring in bacteriorhodopsin.*

In the 7,8-dihydro derivative, a large opsin shift of 3500 cm^{-1} remains. When this value is compared to the $\sim$3900-cm^{-1} opsin shift for the native chromophore it is clear that *much of the bacterio opsin induced red shift must be due to the interaction of the protein with the Schiff base end of the chromophore.*[16] The red shift in BR is most easily explained by a weak hydrogen bond between the Schiff base proton and an electronegative group in the protein.[17] The chemical shift of ^{15}N-BR,[18] the perturbation of the $^{13}C_{15}$ resonance,[5] and recent resonance Raman data[19] strongly support this mechanism. These observations on the mechanism of the opsin shift in bacteriorhodopsin suggest that conformational distortions and the environment of the protonated Schiff base moiety may play a crucial role in λ_{max} regulation of other rhodopsins.

Acknowledgment. We thank Hans Maarten van den Brink for the loan of his study at Groenhovenstraat 10, Leiden, where the conception of this manuscript took place and Ineke van der Hoef for preparing the drawings.

Registry No. 5,6-Dihydroretinal, 19907-28-9; 7,8-dihydroretinal, 75917-44-1; retinal, 116-31-4.

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(6) Okabe et al. (Okabe, M.; Balogh-Nair, V.; Nakanishi, K. *Biophys. J.* **1984**, *45*, 272a) have listed the absorption maximum of the 7,8-dihydro BR derivative as 448 nm, in agreement with the results reported here.

(7) Rodman, H.; Honig, B.; Nakanishi, K.; Okabe, M.; Shimizu, N.; Spudich, J. L.; McCain, D. A. *Biophys. J.* **1986**, *49*, 210a.

(8) The 5,6-dihydroretinal synthesis has been described in: Myers, A. B.; Trulson, M. O.; Pardoen, J. A.; Heeremans, C.; Lugtenburg, J.; Mathies, R. A. *J. Chem. Phys.* **1986**, *84*, 633. For the preparation of 7,8-dihydroretinal, 7,8-dihydro-β-ionone was converted to (7,8-dihydro-β-ionylidene)acetaldehyde by a Petterson type olefination with the *tert*-butylimine of (trimethylsilyl)acetaldehyde (Corey, E. J.; Enders, D.; Bock, M. G. *Tetrahedron Lett.* **1976**, *1*, 7). The latter was converted by a Horner-Emmons reaction with 4-(diethylphosphonato)-3-methylcrotonitrile and subsequent DIBAL-H reduction into 7,8-dihydroretinal.

(9) The bleaching and regeneration were carried out according to: Oesterhelt, D.; Schumann, L. *FEBS Lett.* **1974**, *44*, 262. Addition of excess retinal was avoided because it led to a shift in the absorption maximum to $\sim$400 nm, presumably due to the formation of extraneous Schiff bases. HPLC extraction of these samples gave all-trans to better than 90%.

(10) A 6-s-trans locked retinal has recently been synthesized and its *n*-butylamine PSB is found to absorb at 465 nm (Lugtenburg, J.; van den Steen, R., unpublished results).

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(13) Mathies, R.% Stryer, L. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2169.

(14) Ponder, M.; Mathies, R. *J. Phys. Chem.* **1983**, *87*, 5090.

(15) Sheves, M.; Baasov, T. *Tetrahedron Lett.* **1983**, *24*, 1745.

(16) This idea has also been suggested by Muradin-Szweykowska et al.,[4d] based on BR analogues lacking the ionone ring.

(17) Blatz, P. E.; Mohler, J. H.; Navangul, H. V. *Biochemistry* **1972**, *11*, 848.

(18) Harbison, G. S.; Herzfeld, J.; Griffin, R. G. *Biochemistry* **1983**, *22*, 1.

(19) Hildebrandt, P.; Stockburger, M. *Biochemistry* **1984**, *23*, 5539.

Multicoordinatively and Multielectronically Unsaturated Transition-Metal Complex Negative Ions: Generation and Chemistry of $(OC)_2Fe^{-}\cdot$ and $(OC)_3Mn^{-}$

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The presence of coordination unsaturation in organotransition-metal complexes is required in many of the fascinating and useful reactions in organometallic chemistry, e.g., homogeneous catalysis,[1] many ligand substitution reactions,[2] CH activation,[3] and various synthetic organic transformations.[4] Studies of multicoordinatively and -electronically unsaturated (MCMEU)

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(1) (a) Parshall, G. W. *Homogeneous Catalysis: The Application and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley: New York, 1980. (b) Masters, C. *Homogeneous Transition-Metal Catalysis: A Gentle Art*; Chapman Hall: New York, 1980. (c) Nakamura, A. *Principles and Applications of Homogeneous Catalysis*; Wiley: New York, 1980. (d) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1980. (e) Grubbs, R. H. *Prog. Inorg. Chem.* **1979**, *24*, 1. (f) Kochi, J. K. *Organometallic Mechanisms and Catalysis: The Role of Reactive Intermediates in Organic Processes*; Academic Press: New York, 1978. (g) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973.

(2) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557-597.

(3) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245-269.

(4) For example, see: *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976.

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Table I. Summary of Kinetic and Primary Product Data for the Ion–Molecule Reactions of $(OC)_2Fe^{-}\cdot$ and $(OC)_3Mn^{-}$ with Small Neutral Molecules

reaction	ion + neutral reactants		product [assumed neutral]	fraction of product ion signal	k_{total},[a] cm^3 $molecule^{-1}$ s^{-1}	k_H/k_D
1	$(OC)_2Fe^{-}\cdot + H_2$	$\xrightarrow{He}$	$(OC)_2FeH_2^{-}\cdot$	1.00	$(1.7 \pm 0.01) \times 10^{-11\,c}$ $[(1.4 \pm 0.1) \pm 10^{-11}]^{b,c}$	$1.0^{d,e}$
2	$(OC)_3Mn^{-} + H_2$	$\xrightarrow{He}$	$(OC)_3MnH_2^{-}$	1.00	$(3.9 \pm 0.2) \times 10^{-11\,c}$ $[(2.6 \pm 0.1) \times 10^{-11}]^{b,c}$	$1.0^{d,e}$
3	$(OC)_2Fe^{-}\cdot + H_2O$	$\rightarrow$	$(OC)Fe(H)(OH)^{-}\cdot$ [+ CO]	1.00	$(3.9 \pm 0.3) \times 10^{-10}$ $[(1.5 \pm 0.1) \times 10^{-10}]^{b}$	2.6
4	$(OC)_3Mn^{-} + H_2O$	$\rightarrow$	$(OC)_2Mn(H)(OH)^{-}$ [+ CO]	1.00	$(1.7 \pm 0.1) \times 10^{-11}$ $[(5.6 \pm 0.5) \times 10^{-12}]^{b}$	3.0
5	$(OC)_2Fe^{-}\cdot + H_2S$	$\rightarrow$	$(OC)Fe{=}S^{-}\cdot$ [+ CO + H_2]	1.00	$(7.3 \pm 0.4) \times 10^{-10}$ $[(7.7 \pm 0.6) \times 10^{-10}]^{b}$	1.0^{f}
6a	$(OC)_3Mn^{-} + H_2S$	$\rightarrow$	$(OC)_2Mn{=}S^{-}$ [+ CO + H_2]	0.71	$(8.5 \pm 0.5) \times 10^{-10}$ $[(8.0 \pm 0.7) \times 10^{-10}]^{b}$	1.0^{f}
6b		$\rightarrow$	$(OC)_3Mn{=}S^{-}$ [+ H_2]	0.29		
7	$(OC)_2Fe^{-}\cdot + NH_3$	$\rightarrow$	$(OC)Fe(H)(NH_2)^{-}\cdot$ [+ CO]	1.00	$(1.9 \pm 0.1) \times 10^{-10}$ $[(8.5 \pm 0.5) \times 10^{-11}]^{b}$	2.1
8	$(OC)_3Mn^{-} + NH_3$	$\xrightarrow{He}$	$(OC)_3Mn(NH_3)^{-}$	1.00	$(2.0 \pm 0.1) \times 10^{-11\,c}$ $[(2.1 \pm 0.1) \times 10^{-11}]^{b,c}$	1.0^{d}
9a	$(OC)_2Fe^{-}\cdot + PH_3$	$\rightarrow$	$(OC)Fe(H)(PH_2)^{-}\cdot$ [+ CO]	0.62	$(5.1 \pm 0.3) \times 10^{-10}$	
9b		$\rightarrow$	$(OC)_2Fe({=}PH)^{-}\cdot$ [+ H_2]	0.38		
10a	$(OC)_3Mn^{-} + PH_3$	$\rightarrow$	$(OC)_3Mn({=}PH)^{-}$ [+ H_2]	0.98	$(6.8 \pm 0.2) \times 10^{-10}$	
10b		$\xrightarrow{He}$	$(OC)_3Mn(H)(PH_2)^{-}$	0.02		

[a] Although the reproducibility of the rate constants is ≥±7%, the possible systematic uncertainties in calibrations suggest that their accuracy is ±20%. [b] Determined with D_2, D_2O, D_2S, and ND_3, respectively, of >98% purity. Probable errors in k_H/k_D are ±15%. [c] Apparent bimolecular rate constant for this termolecular adduct-forming reaction. [d] The apparent bimolecular rate constants determined under identical conditions were used. [e] The rate constants used to calculate k_H/k_D were corrected for the 40% greater number of collisions of the ion with H_2 than D_2. [f] See ref 13.

transition-metal complexes will be possible only in the gas phase or in nonreactive matrices[5] where conventional solvents are absent; all that is needed is a method to produce the desired complex.[6] We now report the generation of two MCMEU complex negative ions, the 13-electron $(OC)_2Fe^{-}\cdot$ and the 14-electron $(OC)_3Mn^{-}$ species, and their reactions with the small molecules H_2, H_2O, H_2S, NH_3, and PH_3.

Our studies are carried out in a previously described flowing afterglow (FA) apparatus with helium as the buffer gas (P_{He} = 0.7 torr) at 298 K.[7] The method used to generate $(OC)_2Fe^{-}\cdot$ and $(OC)_3Mn^{-}$ is an extension of that reported for the preparation of $(OC)_3Fe^{-}\cdot$[8] and $(\eta^4\text{-}C_4H_6)Fe(CO)^{-}\cdot$.[9] When the electron gun of the FA is operated at a low emission current (EC < 50 μA), only thermal energy electrons are available for dissociative attachment when $Fe(CO)_5$ or $Mn_2(CO)_{10}$ are introduced downstream of the electron gun and $(OC)_4Fe^{-}\cdot$ or $(OC)_5Mn^{-}$ are exclusively produced. At EC = 1–3 mA, higher energy electrons are available and mixtures of $(OC)_4Fe^{-}\cdot$ + $(OC)_3Fe^{-}\cdot$[8] or $(OC)_5Mn^{-}$ + $(OC)_4Mn^{-}$ are formed. At EC = 10–12 mA, ternary mixtures containing significant signals of $(OC)_2Fe^{-}\cdot$ or $(OC)_3Mn^{-}$ result. Thus, the separate chemistry and kinetics of *each* metal carbonyl negative ion can be determined.[8,9] $(OC)_2Fe^{-}\cdot$ and $(OC)_3Mn^{-}$ are only formed in the vicinity of the electron gun due to rapid cooling of the energetic electrons required for reductive polydecarbonylation by collisions with the buffer gas.[8]

Both $(OC)_2Fe^{-}\cdot$ (m/z 112) and $(OC)_3Mn^{-}$ (m/z 139) form termolecular adducts with dihydrogen (eq 1). When the apparent

$$(OC)_xM^{-} + H_2 \xrightarrow{He} (OC)_xMH_2^{-} \quad M = Fe,\ x = 2;\ M = Mn,\ x = 3 \qquad (1)$$

bimolecular rate constants for the reactions of $(OC)_2Fe^{-}\cdot$ and $(OC)_3Mn^{-}$ with H_2 and D_2 are corrected for the larger number of collisions with H_2, no kinetic isotope effect is observed within the errors of these measurements (Table I).[10-12] Since observation of these adducts requires collisional stabilization of the initially formed, vibrationally excited adducts with the buffer gas, this step may be rate-limiting and would be the same for ion–H_2 and ion–D_2 reactions. At this time, the structures of $(OC)_xMH_2^{-}$ cannot be further defined as dihydride or dihydrogen adducts, although the dihydride structures may be thermodynamically preferred.

The reactions of $(OC)_2Fe^{-}\cdot$ with H_2O, H_2S, and PH_3 form negative ion products exclusively or mainly by replacing a CO ligand.[13] The primary and secondary reactions of $(OC)_2Fe^{-}\cdot$ with H_2O are shown in eq 2; isomeric product ion structures are

$$\underset{m/z\ 112}{(OC)_2Fe^{-}\cdot} + H_2O \rightarrow [(OC)_2Fe(H)(OH)^{-}\cdot]^* \rightarrow \underset{m/z\ 102}{(OC)Fe(H)(OH)^{-}\cdot} + CO \qquad (2a)$$

$$\underset{m/z\ 102}{(OC)Fe(H)(OH)^{-}\cdot} \xrightarrow{H_2O} \underset{m/z\ 118}{(OC)Fe(OH)_2^{-}\cdot} + H_2 \qquad (2b)$$

possible. Normal kinetic deuterium isotope effects were determined for the reactions with H_2O and NH_3 (Table I), but k_H/k_D = 1.0 for the reaction with H_2S.[14] These results along with those involving loss of H_2 and concomitant loss of (H_2 + CO) in the reaction with H_2S support our conclusion that these reactions occur by insertion of the iron complex into the neutral H–heteroatom bond.[6] We believe that decomposition (i.e., loss of CO) of the initially formed vibrationally excited adduct, $[(OC)_2Fe(H)(XH_y)^{-}\cdot]^*$, is the result of the development of exothermic (probably multiple) bond formation between Fe and the π-donor ligand; neither H_2O or NH_3 react with $(OC)_3Fe^{-}\cdot$ or $(OC)_4Mn^{-}$. The reactions of $(OC)_3Mn^{-}$ with H_2O, H_2S, and PH_3 follow similar courses to those reactions described with $(OC)_2Fe^{-}\cdot$, and the kinetic isotope effect with H_2O/D_2O (Table I) agrees with the H–heteroatom insertion mechanism by $(OC)_3Mn^{-}$.[13]

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[5] For examples of photoinsertion of metal atoms into H–X bonds of small molecules, see: Ozin, G. A.; McCaffrey, J. G.; McIntosh, D. F. *Pure Appl. Chem.* **1984**, *56*, 111–128. Kafafi, Z. H.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6134–6135 and references therein.

[6] Lane and Squires (Lane, K. R.; Squires, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6402–6403) reported formation of the novel $(OC)_3CrH^{-}$ complex from the reaction of H^{-} with $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ and certain reactions of this 14-electron MCMEU negative ion.

[7] McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4123–4128.

[8] McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 6095–6096.

[9] McDonald, R. N.; Schell, P. L.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 5578–5579.

[10] Church, et al. (Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30–32) report k_H/k_D = 1.9 for the formation of $(OC)_5Cr(H_2)$ and $(OC)_5Cr(D_2)$ by flash photolysis of $Cr(CO)_6$ in $H_2(D_2)$-saturated cyclohexane.

[11] For other examples of dihydrogen adducts, see: (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 451–452. (b) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27–30. (c) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581–5582.

[12] See Zhou et al. (Zhou, P.; Vitale, A. A.; San Filippo, J.; Saunders, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 8049–8054) for a recent kinetic isotope effect of dissociative addition of H_2/D_2 to Vaska's complex.

[13] The present results differ significantly from the simple CO ligand displacement reactions reported in the reaction of MCMEU transition-metal carbonyl positive ions: $(OC)_xFe^{+}$ (x = 1–5) with H_2O and NH_3 (Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808–4814) and $(OC)_yCo(NO)^{+}$ (y = 1–3) with H_2O, NH_3, and PH_3 (Weddle, G. H.; Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 105–109).

[14] A much smaller kinetic isotope effect for H_2S/D_2S compared to H_2O/D_2O was expected from the lower frequencies of the stretching and bending vibrations in H_2S/D_2S vs. H_2O/D_2O and the larger rate constant (lower barrier) for H_2S which is ~70% of the collision limit.

The reaction of $(OC)_3Mn^-$ with NH_3 is unique among the neutrals in Table I in that a CO ligand is *not* displaced from the adduct and we observe no kinetic isotope effect ($k_{NH_3}/k_{ND_3} = 1.0$). These facts lead us to conclude that the product is the simple adduct negative ion with NH_3 (or ND_3) occupying a metal coordination site (eq 3). This structural conclusion is supported

$$\underset{m/z\ 139}{(OC)_3Mn^-} + NH_3 \xrightarrow{He} \underset{m/z\ 156}{(OC)_3Mn(NH_3)^-} \qquad (3)$$

by the results of ion-molecule reactions of adduct *m/z* 156 where the NH_3 (or ND_3) molecule is replaced intact in its reactions with H_2O and CH_3OH. This result is interesting since it will allow for a direct comparison of the kinetics and product branching fractions as a function of the presence vs. absence of a single coordinated "solvent" molecule. The fact that $(OC)_2Fe^{-}\cdot$ inserts into the N-H bond of NH_3, but $(OC)_3Mn^-$ does not, requires that the net bonding energy produced in the former insertion reaction exceeds that which would result by insertion with the Mn species.

The above neutral molecules are the simplest members of a number of organic functional group series which are presently being investigated. These results, and those with the group IV (group 14)[15] hydrides, will be reported in due course.

Acknowledgment. We thank the National Science Foundation for support of this research and Professor D. W. Setser for the samples of D_2S and ND_3 used and helpful discussions.

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(15) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Rhenium Dinitrogen Complex (η-C_5Me_5)Re(CO)(PMe_3)(N_2). Facile Photochemical Generation of a Rhenium Intermediate and Oxidative Addition of Hydrocarbon C-H Bonds

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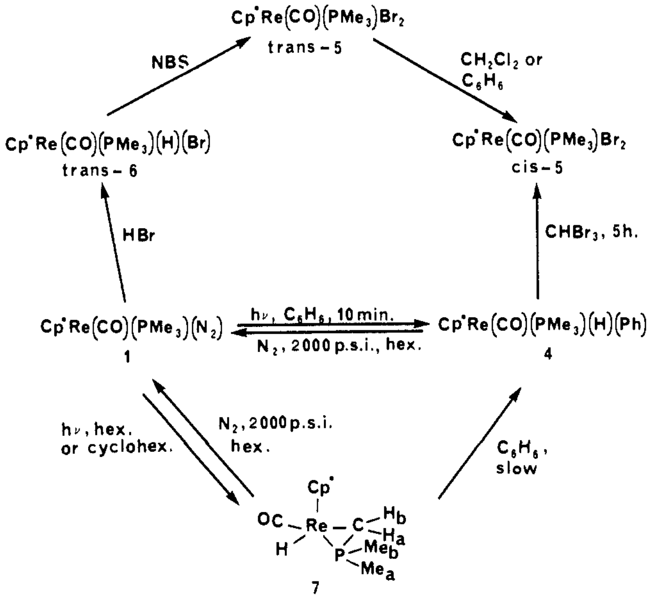
As part of our continuing investigation of dinitrogen, diazenide, hydrazide, and related ligands, we have synthesized the trimethylphosphine-substituted (pentamethylcyclopentadienyl)rhenium dinitrogen complex Cp*Re(CO)(PMe_3)(N_2) (**1**)[1] (Cp* = η-C_5Me_5). The MeCN complex [Cp*Re(CO)(MeCN)(*p*-$N_2C_6H_4OMe$)][BF_4] (**2**)[2] was treated with PMe_3 to give [Cp*Re(CO)(PMe_3)(*p*-$N_2C_6H_4OMe$)][BF_4] (**3**), which was converted to **1** by using *t*-BuLi. Complex **1** is a pale yellow solid that is stable indefinitely if air is excluded and is inert to thermal exchange of the N_2 ligand in N_2-saturated organic solvents at ambient temperature as judged from the IR and ^{15}N NMR spectra of 96% $^{15}N_\alpha$-enriched samples. Nevertheless, **1** undergoes photochemical reactions in which the N_2 ligand is readily displaced. Most interesting and topical, in view of the current interest in C-H activation by soluble transition-metal complexes,[3,4] is the concurrent formation of a rhenium intermediate capable of insertion into selected hydrocarbon C-H bonds in high yield to give isolable derivatives. Bergman and co-workers[5] have recently published the first examples of the reaction of hydrocarbon C-H bonds with rhenium intermediates photogenerated from inter alia Cp*Re($(CO)_2$)(PMe_3). Our results with the N_2 complex **1** are generally in agreement with and extend those of Bergman and likewise point to the involvement of the same, formally unsaturated, putative intermediate "Cp*Re(CO)(PMe_3)" in the photolytic reactions.[6] Some results are summarized in Scheme I.

Scheme I



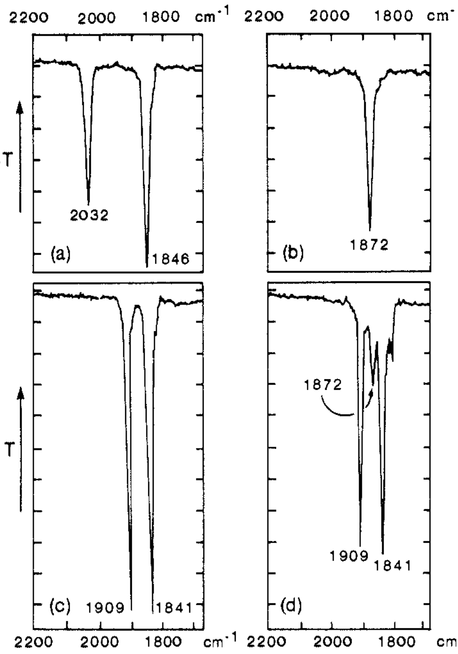


Figure 1. Comparison of the production of **4** [ν(CO) 1872 cm^{-1}] from the irradiation of Cp*Re(CO)(PMe_3)(N_2) (**1**) or Cp*Re$(CO)_2$(PMe_3) in benzene. IR spectra of (a) **1**, (b) 10-min irradiation of **1**, (c) Cp*Re$(CO)_2$(PMe_3), and (d) 10-min irradiation of Cp*Re$(CO)_2$(PMe_3).

Irradiation of **1** in benzene solution (Figure 1a) at room temperature for only 10 min (200-W Hanovia high-pressure lamp, quartz vessel, N_2 purge) resulted in quantitative conversion to a single carbonyl-containing product (Figure 1b), isolated from

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(1) For the parent dicarbonyl complex Cp*Re$(CO)_2$(N_2), see: Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 54.

(2) Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, A. H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478.

(3) Muetterties, E. L. *Chem. Soc. Rev.* **1983**, *12*, 283.

(4) For recent references, see: (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (b) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *Ibid.* **1984**, *106*, 1121. (c) Jones, W. D.; Maguire, J. A. *Organometallics* **1986**, *5*, 590.

(5) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358.

(6) Previous examples of photodissociation of N_2 from rhenium dinitrogen complexes in the presence of aromatic solvents have not resulted in isolable C-H activation products. See: (a) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379. (b) Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Organomet. Chem.* **1983**, *248*, C26.