Figure 4. Comparison of the optical changes induced by light in a Chl-protein complex of photosystem II poised at −0.49 V (vs. NHE) as reported by Klimov et al.[14] and the difference spectra obtained on reduction of (a) Pheo and (b) Chl in DMF. Spectra have been normalized at ∼400 nm.

potential of an intermediate, X, between the ferrodoxins and P700 as equal to or greater than −0.73 V. X$^-$· has been detected[16] by ESR only at low temperatures (10 K) where it exhibits $g_z = 1.76$, $g_y = 1.86$, and $g_x = 2.06$, parameters quite distinct from those of Chl a$^-$·. However, major deviations from solution ESR spectra of the anions of bacteriopheophytins and quinones are also observed at comparable temperatures in reduced bacterial systems and arise from magnetic coupling with nearby ferrous ions.[7,36b,d,e] A similar effect, induced by an interaction of Chl$^-$· with the iron of the reduced Fe–S protein, could explain the g values of X$^-$·.[38] Ambient temperature ESR spectra of X$^-$· should conform to those reported here for Chl$^-$· if our suggestion is correct. Dynamic polarization effects have been elicited[2,6,12,13] from PS I and are readily ascribed to a radical–radical recombination mechanism[39] involving P700$^+$· and Chl$^-$·.

We have proposed here that the first reduced chemical products of green plant photosynthesis are the anions of pheophytin in PS II and chlorophyll in PS I. Such a mechanism represents a significantly more efficient conversion of incident light into chemical energy than previously assumed and yields strong reductants to drive the biochemistry of both photosystems I and II. We have also described optical and magnetic characteristics of the putative acceptors which should provide the guidelines to further test our suggestion.

References and Notes

(1) Govindjee, Ed., "Bioenergetics of Photosynthesis", Academic Press, New York, N.Y., 1975.
(2) J. Barber, Ed., "Primary Processes of Photosynthesis", Elsevier, Amsterdam, 1977.
(3) A. J. Bearden and R. Malkin, *Q. Rev. Biophys.*, **7**, 131 (1975); *Brookhaven Symp. Biol.*, **28**, 247 (1976).
(4) B. Ke, *Biochim. Biophys. Acta*, **301**, 1 (1973); *Curr. Top. Bioenerg.*, in press.
(5) P. Mathis, *Brookhaven Symp. Biol.*, **28**, 267 (1976).
(6) D. B. Knaff, *Photochem. Photobiol.*, **26**, 327 (1977).
(7) J. T. Warden and J. R. Bolton, *Acc. Chem. Res.*, **7**, 189 (1974); J. R. Bolton

and J. T. Warden, *Annu. Rev. Plant Physiol.*, **27**, 375 (1976).
(8) J. J. Katz and J. R. Norris, *Curr. Top. Bioenerg.*, **5**, 41 (1973).
(9) B. Ke, E. Dolan, K. Sugahara, F. M. Hawkridge, S. Demeter, and E. R. Shaw, *Plant Cell Physiol.*, **187** (1977).
(10) S. Demeter and B. Ke, *Biochim. Biophys. Acta*, **462**, 770 (1977).
(11) K. Sauer, S. Acker, P. Mathis, and J. A. Van Best in "Bioenergetics of Membranes", L. Packer, Ed., Elsevier, Amsterdam, 1977, p 351.
(12) K. Sauer, R. E. Blankenship, G. C. Dismukes, and A. McGuire, *Biophys. J.*, **17**, 228a (1977).
(13) G. C. Dismukes, A. McGuire, R. Blankenship, and K. Sauer, *Biophys. J.*, **21**, 239 (1978).
(14) V. V. Klimov, A. V. Klevanik, V. A. Shuvalov, and A. A. Krasnovskii, *FEBS Lett.*, **82**, 183 (1977).
(15) A. R. McIntosh and J. R. Bolton, *Nature (London)*, **263**, 443 (1976).
(16) P. Heathcote, D. L. Williams-Smith, and M. C. W. Evans, *Biochem. J.*, **170**, 373 (1978), and references therein.
(17) J. T. Warden and A. Rudnicki, *Biophys. J.*, **21**, 197a (1978).
(18) R. H. Felton, G. M. Sherman, and H. Linschitz, *Nature (London)*, **203**, 637 (1964).
(19) H. Berg and K. Kramarczyk, *Biochim. Biophys. Acta*, **131**, 141 (1967).
(20) B. A. Kiselev, Y. N. Kozlov, and Y. B. Estigneyev, *Biofizika*, **15**, 594 (1970).
(21) D. C. Borg, J. Fajer, A. Forman, R. H. Felton, and D. Dolphin, *Int. Cong. Biophys., 4th, 1973*, **2**, 528 (1973).
(22) T. Saji and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 2235 (1977).
(23) A. P. Bobrovskii and V. E. Kholmogorov, *Opt. Spektrosk.*, **30**, 32 (1971).
(24) Ye. V. Pakshina and A. A. Krasnovskii, *Biofizika*, **19**, 238 (1974), and references therein.
(25) H. Seki, S. Arai, T. Shida, and M. Imamura, *J. Am. Chem. Soc.*, **93**, 3404 (1973).
(26) A. A. Krasnovskii, *Russ. Chem. Rev.*, **29**, 344 (1960).
(27) H. Scheer and J. J. Katz, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 1626 (1974).
(28) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Am. Chem. Soc.*, **95**, 2739 (1973).
(29) B. S. Jensen and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 5211 (1975).
(30) J. S. Hyde, G. H. Rist, and L. E. G. Eriksson, *J. Phys. Chem.*, **72**, 4269 (1968).
(31) J. Fajer, A. Forman, M. S. Davis, L. D. Spaulding, D. C. Brune, and R. H. Felton, *J. Am. Chem. Soc.*, **99**, 4134 (1977).
(32) See ref 31 for parameters used.
(33) L. K. Hanson, M. S. Davis, I. Fujita, and J. Fajer, *Biophys. J.*, **21**, 195a (1978); L. K. Hanson and J. Fajer, unpublished results.
(34) I. Fujita, M. S. Davis, A. Forman, K. M. Smith, and J. Fajer, unpublished results.
(35) M. C. Thurnauer, M. K. Bowman, B. T. Cope, and J. R. Norris, *J. Am. Chem. Soc.*, **100**, 1965 (1978).
(36) (a) J. Fajer, M. S. Davis, D. C. Brune, L. D. Spaulding, D. C. Borg, and A. Forman, *Brookhaven Symp. Biol.*, **28**, 74 (1976); (b) G. Feher and M. Y. Okamura, *ibid.*, **28**, 183 (1976); (c) W. W. Parson and T. G. Monger, *ibid.*, **28**, 195 (1976); (d) P. L. Dutton, R. C. Prince, D. M. Tiede, K. M. Petty, K. J. Kaufmann, T. L. Netzel, and P. M. Rentzepis, *ibid.*, **28**, 213 (1976); (e) R. C. Prince, D. M. Tiede, J. P. Thornber, and P. L. Dutton, *Biochim. Biophys. Acta*, **462**, 467 (1977); (f) J. Fajer, M. S. Davis, D. C. Brune, A. Forman, and J. P. Thornber, *J. Am. Chem. Soc.*, **100**, 1918 (1978).
(37) R. S. Knox, *Biophys. J.*, **9**, 1351 (1969), and references therein.
(38) J. R. Bolton (private communication) has suggested that Chl$^-$· is actually bound to the Fe–S protein, thereby also lowering the reduction potential from −0.9 V in vitro closer to the value estimated by Ke et al.[9]
(39) J. K. S. Wan, S. K. Wong, and D. A. Hutchinson, *Acc. Chem. Res.*, **7**, 38 (1974); J. B. Pedersen, *J. Chem. Phys.*, **59**, 2656 (1973).

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Regiocontrolled Head-to-Tail Coupling of Allylic Boron "Ate" Complexes with Allylic Halides

Sir:

One of the basic unsolved problems of organic synthesis is the lack of selectivity in the Wurtz-type coupling reaction of allylic organometallics with allylic halides.[1] In general, two allylic moieties, one from the allylic organometallics and the other from the organic halides, combine randomly, leading to a mixture of four products (eq 1).[2] We wish to report that this difficulty, for the first time, can be alleviated by using lithium allylic boron ate complexes, which regioselectively react with allylic halides to produce the head-to-tail 1,5-dienes (eq 2).

Table I. Reaction of Allylic Organometallics with Allylic Halides[a]

entry	allylic organometallic compd	allylic halide	product[b]				yield,[c] % (isold)
			PhCH=CHCH₂ / CH₃CH=CHCH₂	PhCH=CHCH₃ / CH₂=CHCHCH₃	PhCHCH=CH₂ / CH₂CH=CHCH₃	PhCHCH=CH₂ / CH₃CHCH=CH₂	
1	$CH_3CH=CHCH_2Li$	$PhCH=CHCH_2Cl$	71	22	3	4	(75)
2	$CH_3CH=CHCH_2MgCl$	$PhCH=CHCH_2Cl$	10	72	3	15	(80)
3	$CH_3CH=CHCH_2Cu$[d]	$PhCH=CHCH_2Cl$	33	53	1	13	51
4	$CH_3CH=CHCH_2Cu$[e]	$PhCH=CHCH_2Cl$	21	59	10	10	29
5	$CH_3CH=CHCH_2B^-$ (n-C₄H₉) Li⁺	$PhCH=CHCH_2Cl$	3	97			63
		$PhCH=CHCH_2Cl$	3	97			78[f]
6	$CH_3CH=CHCH_2B^-$ (n-C₄H₉) MgCl⁺	$PhCH=CHCH_2Cl$	18	81		1	92[f]
7	$CH_3CH=CHCH_2B^-$ (n-C₄H₉) Cu⁺[g]	$PhCH=CHCH_2Cl$	35	64		1	78[f]
8	$CH_3CH=CHCH_2B^-(n\text{-}C_4H_9)_3$ Li⁺	$PhCH=CHCH_2Cl$	9	91			88[f]
9	$CH_2=CHCH_2B^-$ (n-C₄H₉) Li⁺	$PhCH=CHCH_2Cl$	$PhCH=CHCH_2CH_2CH=CH_2$				(60)[h,i]
10	$PhCH=CHCH_2B^-(n\text{-}C_4H_9)_3$ Li⁺	$CH_3CH=CH\text{-}CH_2Cl$	$PhCH(CH=CH_2)CH_2CH=CHCH_3$				(70)[j]
11	$PhCH=CHCH_2B^-(n\text{-}C_4H_9)_3$ Li⁺	$(CH_3)_2C=CH\text{-}CH_2Br$	$PhCH(CH=CH_2)CH_2CH=C(CH_3)_2$				(82)[h]
12	$CH_3CH=CHCH_2B^-$ (n-C₄H₉) Li⁺	$(CH_3)_2C=CH\text{-}CH_2Br$	$CH_3CH(CH=CH_2)CH_2CH=C(CH_3)_2$				(53)[h,i]

[a] To an ether solution of crotyl organometallics (1 mmol) was added cinnamyl chloride (1 mmol, 0.13 mL) at −78 °C (entries 1-4). The boron ate complexes were prepared by the addition of boranes (n-Bu-9-BBN and n-Bu₃B) to an ether solution of allylic magnesium, copper, or lithium compounds (entires 5-12). Allylic lithium compounds were prepared from the corresponding tin derivatives as described in the text. Isolation was carried out on a 10-mmol scale. [b] Identified by IR and ¹H NMR spectroscopy and elemental analysis. Although the precise ratio of the stereoisomers or diastereomers was not determined, the trans geometry of cinnamyl unit was retained. [c] Yield and product ratio (entries 1-8) were determined by GLC analysis, based on the halide. [d] Prepared from crotylmagnesium. [e] Prepared from crotyllithium. [f] Two equivalents of allylic boron ate complexes were used. [g] Crotylcopper was prepared from crotylmagnesium chloride. [h] No isomers were formed. [i] Accompanied by considerable amounts of the reduction product. [j] Small amounts of isomers were detected.


(1)

M = Na, Li, Mg, Zn

(2)
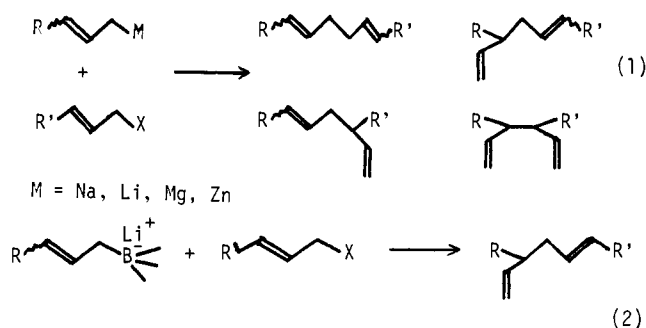
We recently reported that copper borates, such as RCH=CHB< Cu⁺,[3a] R₄B⁻ Cu⁺,[3b] and RCu·BF₃,[3b,c] and lithium borates such as di-n-alkyl-9-BBN ate complexes[4] possess a number of features making them attractive as synthetic intermediate. From both practical and theoretical angles, it appeared desirable to explore the chemical behavior of lithium, magnesium, and copper allylic boron ate complexes. The lithium borates exhibited the highest regio- and chemoselectivity toward allylic halides among the ate complexes examined. The results are summarized in Table I.

As evident, lithium crotyl borates in ether[5] enable regiocontrolled head-to-tail coupling (entries 5 and 8). Although regioselectivity via the 9-BBN ate complex is higher than that via the tri-n-butylboron ate complex, a major drawback is the formation of β-methylstyrene (~15%) through the reduction by the 9-BBN ate complex[4a] (entries 5 and 9). The corresponding copper and magnesium borates do not give a satis-

factory result (entries 6 and 7). Furthermore, these lithium borates are highly chemoselective; the coupling reaction with alkyl halides or with allylic acetates does not occur. The structure of lithium crotyl-9-BBN ate complex deserves comment. Since no evidence of the 1-methylallyl isomer is found for crotyl-9-BBN[6] and the thermodynamically more stable isomer is formed in the reaction of gem-dichloroallyllithium with Ph₃B,[7] the ate complex presumably possesses crotyl structure.[8] Actually the ate complex prepared from crotyl-9-BBN and n-BuLi exhibited an essentially similar regioselectivity.

The preparation of 3-phenyl-6-methyl-1,5-heptadiene is representative. To an ether solution of cinnamyltri-n-butyltin[9] (10 mmol, 4.07 g) was added an ether solution of phenyllithium (10 mmol) at room temperature under N₂. After stirring for a few minutes, the mixture was cooled to −78 °C. Tri-n-butylborane (10 mmol, 2.4 mL) was added and stirring was continued for a while at −78 °C. Prenyl bromide (10 mmol, 1.2 mL) was then added and the resulting mixture was allowed to warm to room temperature. Filtration through the column of alumina using petroleum ether followed by distillation gave the desired diene: 1.52 g, 82%, bp 70-71 °C (1 mmHg).

The present development prompted further interest in an application of the ate complex to heterosubstituted allyl carbanion chemistry.[10] Actually, the regiocontrolled and electronically unimpeded coupling[10a] was realized via the allyloxy carbanion–boron ate complex[11] (eq 3). While the scope and the mechanistic details remain to be further explored, it is clear that a highly regio- and chemoselective route to
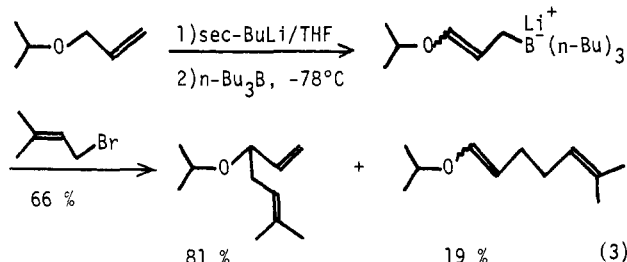
head-to-tail 1,5-dienes is now at our disposal. Further aspects of these ate complexes are under active investigation.
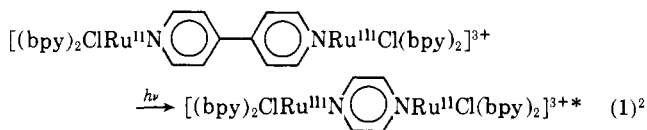
References and Notes

(1) G. Courtois and L. Miginiac, *J. Organomet. Chem.*, **69**, 1 (1974); R. A. Benkeser, *Synthesis*, 347 (1971). For a head-to-head coupling via prenylmagnesium–CuI system, see F. D-Boumechal, R. Lorne, and G. Linstrumelle, *Tetrahedron Lett.*, 1181 (1977).

(2) For coupling of allylic transition metallics with allylic halides, see R. Noyori in "Transition Metal Organometallic in Organic Synthesis", H. Alper, Ed., Academic, New York, N.Y., 1976, p 83.

(3) (a) Y. Yamamoto, H. Yatagai, K. Maruyama, A. Sonoda, and S-I. Murahashi, *J. Am. Chem. Soc.*, **99**, 5652 (1977); (b) K. Maruyama and Y. Yamamoto, *ibid.*, **99**, 8068 (1977); (c) Y. Yamamoto and K. Maruyama, *ibid.*, **100**, 3240 (1978).

(4) (a) Y. Yamamoto, H. Toi, S-I. Murahashi, and I. Moritani, *J. Am. Chem. Soc.*, **97**, 2558 (1975); (b) Y. Yamamoto, H. Toi, A. Sonoda, and S.-I. Murahashi, *ibid.*, **98**, 1965 (1976).

(5) THF was found to be an unsatisfactory solvent for the regioselective coupling.

(6) G. W. Kramer and H. C. Brown, *J. Organomet. Chem.*, **132**, 9 (1977).

(7) D. Seyferth, G. J. Murphy, and R. A. Woodruff, *J. Organomet. Chem.*, **141**, 71 (1977).

(8) Determination of the structure by NMR resulted in failure, presumably owing to poor stability of the ate complex at room temperature.

(9) Y. Tanigawa, I. Moritani, and S. Nishida, *J. Organomet. Chem.*, **28**, 73 (1971). Other tin derivatives were prepared by Seyferth's method: D. Seyferth and T. F. Jula, *ibid.*, **66**, 195 (1974).

(10) (a) D. A. Evans, G. C. Andrews, and B. Buckwalter, *J. Am. Chem. Soc.*, **96**, 5560 (1974); (b) W. C. Still and T. L. Macdonald, *J. Org. Chem.*, **41**, 3620 (1976), and references cited therein.

(11) Although the precise structure of the intermediate is not clear, the allylic boron ate complex is presumably involved by analogy with the above results. The reaction in ether in the presence of TMEDA gave the similar result. In the absence of *n*-Bu₃B, α:γ attack = 40:60.

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Outer-Sphere Intervalence Transfer

Sir:

In mixed-valence complexes where there are localized redox sites, low energy absorption bands are often observed which can be assigned to intervalence transfer (IT) transitions (e.g., eq 1).[1] The observation of an IT transition is of real value in

$$[(bpy)_2ClRu^{II}N\bigcirc\!-\!\bigcirc NRu^{III}Cl(bpy)_2]^{3+}$$

$$\xrightarrow{h\nu} [(bpy)_2ClRu^{III}N\bigcirc\!-\!\bigcirc NRu^{II}Cl(bpy)_2]^{3+*} \quad (1)^2$$

gaining insight into related thermal electron-transfer processes (eq 2). The electronic resonance energy or electron tunneling matrix element arising from electronic coupling between sites can be determined from the band intensity and the band energy
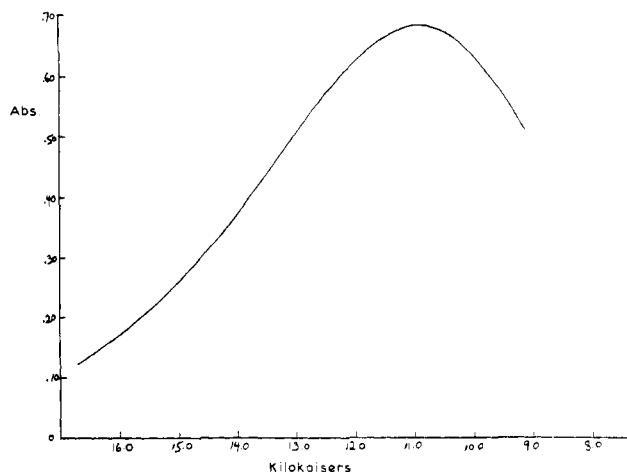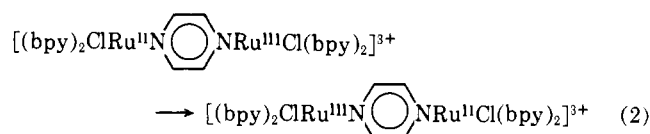
Figure 1. Low energy visible, near-infrared spectrum of a solution containing $[Ru(NH_3)_5py]^{3+}$ (3.0×10^{-3} M) and $[Fe(CN)_6]^{4-}$ (1.5×10^{-3} M) in H_2O at pH 5 (22 ± 2 °C).

and band shape give information about the vibrational barrier to electron transfer.[2a,b,3]

$$[(bpy)_2ClRu^{II}N\bigcirc NRu^{III}Cl(bpy)_2]^{3+}$$

$$\longrightarrow [(bpy)_2ClRu^{III}N\bigcirc NRu^{II}Cl(bpy)_2]^{3+} \quad (2)$$

There is no a priori requirement that IT transitions be confined to cases where there are chemically linked donor and acceptor sites. In fact, the observation of such a transition for an outer-sphere case could be of even greater value given the absence of the structural definition provided by a bridging ligand.

It has been suggested that outer-sphere IT transitions should appear in mixed-valence solids and in concentrated solutions containing complexes of the same metal in different oxidation states.[1a,3] In practice the experiments in solution are difficult both because of the low oscillator strengths expected for the bands[1a,3] and because of the low formation constants expected for like-charged ion pairs.

Miralles, Armstrong, and Haim have investigated the kinetics of reduction of $M(NH_3)_5py^{3+}$ (Co, Ru; py is pyridine) by $Fe(CN)_6^{4-}$ in aqueous solution.[4] For $[Co(NH_3)_5py]^{3+}$, electron transfer is sufficiently slow that an initial ion pair between $Co(NH_3)_5py^{3+}$ and $Fe(CN)_6^{4-}$ is detectable kinetically. Since the charge types favor ion pairing, similar ion combinations are reasonable candidates for observing outer-sphere IT transitions and we have investigated a series of them.

In sufficiently concentrated aqueous solutions (0.001 to 0.003 F) containing $Ru(NH_3)_5py^{3+}$ and $Fe(CN)_6^{4-}$, a new absorption band appears in the near-infrared at 915 nm (Figure 1).[5] The band only appears in solutions containing both the Ru(III) and Fe(II) ions and its intensity grows as the concentration of the two ions increases. An estimate of $K_{IP} \simeq 3 \times 10^3$ for the ion-pair formation constant (eq 3) can be made and compares reasonably well with the experimentally measured value for the Co(III)–Fe(II) ion pair, $[Co(NH_3)_5py,Fe(CN)_6]^-$.[4,6] Using this value of K_{IP}, $\epsilon_{max} = 40 \pm 5$ M^{-1} cm^{-1} can be estimated for the near-infrared band. As expected, the bandwidth at half-maximum, $\Delta\bar{\nu}_{1/2}$ (6.5 ± 0.3 kK) is larger than the value predicted for IT bands by Hush using a single oscillator model ($\Delta\bar{\nu}_{1/2} = (2310 \bar{\nu}_{max})^{1/2} = 4.8$ kK).[1a,b] In fact, the ratio $\Delta\bar{\nu}_{1/2}(obsd)/\Delta\bar{\nu}_{1/2}(calcd) = 1.3$ is typical of values found for dimeric mixed-valence ions.[9] It seems clear that the origin of the band is an outer-sphere, metal-metal charge transfer (MMCT) or IT transition (eq 4).