prior to diffusion of the organic oxidation product, S, away from the reduced polyoxometalate (eq 19). This is one explanation as to why the photochemical steady state with particular complexes and organic substrates is such that each polyoxometalate molecule contains more than one electron. The disproportionation of the two-electron heteropoly blues and by inference other multielectron reduced polyoxometalates as well as eq 21 and 22 are well documented.[2,21,60]

The net oxidation product, S, in the polyoxometalate-catalyzed photodehydrogenation of substrate SH$_2$, can be a chemically noninnocent species. The thermal reaction of S with the reduced polyoxometalate, e.g., eq 23, occurs rapidly in some cases, directly

$$2P^{(n+1)-} + S + 2H^+ \rightarrow 2P^{n-} + SH_2 \qquad (23)$$
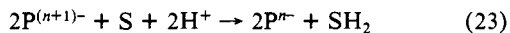
affecting the net quantum yields for production of S and light-to-chemical energy conversion. A specific example when a reaction analogous to 23 markedly reduces the overall quantum yields is water oxidation, where H$_2$O$_2$, the oxidation product analogous to S, rapidly reoxidizes the reduced polyoxometalate.

The possible intermediacy of organic groups covalently bonded to the polyoxometalates during catalytic photodehydrogenation processes cannot be ruled out at this time. Acetal, ketal, and alkoxy complexes of polyoxometalates have been made,[2,61–63] and very recently the structurally characterized tetramethoxypolyoxometalate, Na$_4$[Mo$_8$O$_{24}$(OCH$_3$)$_4$]·8MeOH,[62] and the well-characterized dimethoxy complex Mo$_2$O$_5$(OCH$_3$)$_2$[63] were both shown to evolve formaldehyde upon irradiation with UV light. Formaldehyde evolution was coupled with Mo^{VI} reduction in both cases.

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New Mono-Dinitrogen Complexes of Molybdenum That Produce Ammonia and Hydrazine[1]

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Abstract: A new, extensive series of mono-N$_2$ complexes of molybdenum is reported. The sodium amalgam reduction of MoCl$_3$(triphos), where triphos = PhP(CH$_2$CH$_2$PPh$_2$)$_2$, in tetrahydrofuran solution in the presence of 2L or L$_2$ and with a deficiency of N$_2$ led to the formation of Mo(N$_2$)(triphos)(L$_2$) (1A-F): 1A, L$_2$ = 2 PPhMe$_2$; 1B, L$_2$ = Me$_2$PCH$_2$PMe$_2$; 1C, L$_2$ = 1,2-(Me$_2$As)$_2$C$_6$H$_4$; 1D, L$_2$ = Ph$_2$PCH$_2$PPh$_2$; 1E, L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$; 1F, L$_2$ = 1,1'-(Ph$_2$PC$_5$H$_4$)$_2$Fe, DPPFe. Complexes 1C and 1E were each a mixture of isomeric mono-N$_2$ complexes. Complex 1F was isolated together with Mo(triphos)(η^2-DPPFe)(η^1-DPPFe). Complexes 1A-F all reacted with HBr in CH$_2$Cl$_2$ to afford ammonia, hydrazine, and N$_2$ (and some H$_2$) in varying yields. The highest yield of ammonia was obtained from 1F, and the highest yield of hydrazine was obtained from 1A (HCl/toluene at 70 °C).

Few of the more than 100 known mono-N$_2$ complexes of transition metals react to give more than a trace of ammonia and/or hydrazine.[2] This is in contrast to the behavior of (i) the bis-N$_2$ complexes of molybdenum and tungsten such as *cis*-W-(N$_2$)$_2$(PMe$_2$Ph)$_4$ and *trans*-Mo(N$_2$)$_2$(triphos)(PPh$_3$), where triphos = PhP(CH$_2$CH$_2$PPh$_2$)$_2$, containing at least one monodentate ligand from which high yields of ammonia and occasionally hydrazine may be obtained,[3–5] and (ii) the bridging-N$_2$ complexes of titanium,[6] zirconium,[7] and tantalum[8] from which high yields of hydrazine are obtained. We wish to report a new, extensive series of mono-N$_2$ complexes containing triphos that yield ammonia and hydrazine. These complexes contain five group 5 atoms bound to molybdenum. Only one such complex has been reported

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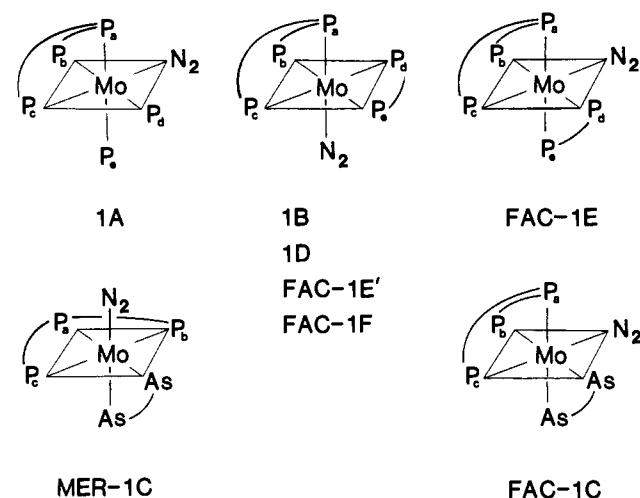(5) (a) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6153–6154. (b) Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K. *Inorg. Chem.* **1983**, *22*, 1968–1970.
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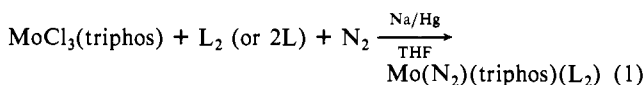(8) Rocklage, S. M.; Turner, H. W.; Fellmann, J. D.; Schrock, R. R. *Organometallics* **1982**, *1*, 703–707.

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George and Tisdale

Chart I

1A

1B
1D
FAC-1E
FAC-1E′
FAC-1F

FAC-1E

MER-1C

FAC-1C

Table I. Yields of Ammonia and Hydrazine[a]

complex[b]	NH$_3$	N$_2$H$_4$
1A	0.51	0.30
1B	0.39	0.28
1C	0.47	0.18
1D	0.06	0.39
1E	0.15	0.19
1F[c]	0.71	0.07
Mo(N$_2$)$_2$(triphos)(PPh$_3$)[d]	0.27	0.19

[a] Yields; mol/mol of starting Mo complex. [b] Treated with HBr/ CH$_2$Cl$_2$. [c] A 1F/3 mixture. Yield based upon 1F comprising 68% of the mixture. [d] Also evolved 1.29 mol of N$_2$/mol of complex: Baumann, J. A.; Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K.; Noddings, C. M., manuscript submitted for publication.

before and that was Mo(N$_2$)(PMe$_3$)$_5$.[9]

The reduction of MoCl$_3$(triphos)[10] with sodium amalgam (6 equiv.) in tetrahydrofuran solution in the presence of PMe$_2$Ph (L; 2 mol) or 1 mol of a bidentate ligand (L$_2$) under a limited[11] atmosphere of N$_2$ led to the formation in high yield of the mono-N$_2$ complexes Mo(N$_2$)(tripos)(L$_2$), 1 (eq 1). Reduction was carried out for ca. 15 h followed by filtration through Celite and reduction of the volume of the filtrate (by 60%) by *bubbling*[12] N$_2$ through the solution. To the deep red-colored solution was added methanol in aliquots (10 mL) with vigorous agitation and continued bubbling up to ca. 150 mL. During this time crystals formed. The crystals were rapidly collected by filtration, washed with methanol and pentane, dried in vacuo, and stored under N$_2$.

$$\text{MoCl}_3(\text{triphos}) + \text{L}_2 \text{ (or 2L)} + \text{N}_2 \xrightarrow[\text{THF}]{\text{Na/Hg}}$$

$$\text{Mo(N}_2)(\text{triphos})(\text{L}_2) \quad (1)$$

1A, L = PMe$_2$Ph;   1B, L$_2$ = Me$_2$PCH$_2$PMe$_2$, DMPM;

1C, L$_2$ = 1,2-(Me$_2$As)$_2$C$_6$H$_4$, DIARS;

1D, L$_2$ = Ph$_2$PCH$_2$PPh$_2$, DPPM;

1E, L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$, DPPE;

1F, L$_2$ = 1,1′-(η^5-C$_5$H$_4$PPh$_2$)$_2$Fe, DPPFe

The structures of all new complexes were assigned on the basis of their ^{31}P{^{1}H} NMR spectrum by comparison with other [Mo-triphos] complexes (see Chart I).[13,14] Complex 1A,[15] isolated in 78% yield, gave a first-order spectrum in which four of the

phosphorus atoms displayed large trans coupling constants including the PMe$_2$Ph ligands. The data clearly show that triphos is facial and N$_2$ trans to P$_c$.

Both complexes 1B[16] and 1D[17] displayed AMM′XX′ spectra. The proposed structure (*fac*-triphos, N$_2$ trans to P$_a$) is consistent with P$_a$ showing no large $^2J_{pp}$ coupling.

Complex 1E[18] was isolated as a mixture of two isomeric mono-N$_2$ complexes. Isomer *fac*-1E (59%) displayed a spectrum analogous to that for 1A. The AX$_4$ spectrum of the other isomer, *fac*-1E′, suggests a structure analogous to 1B but where coupling between the equitorial phosphorus atoms is not observed. Likewise, 1C[19] was isolated as a pair of isomeric mono-N$_2$ complexes: *mer*-1C (62%) showed two singlets consistent with a *mer*-triphos, and *fac*-1C with N$_2$ trans to P$_b$ (or P$_c$) rather than P$_a$. No attempt was made to separate either set of isomers. The IR spectrum of 1E showed two ν(NN) stretching frequencies whereas 1C only showed one.

Finally, 1F was isolated as a mixture of *fac*-1F (68%)[20] and *fac*-Mo(triphos)(η^2-DPPFe)(η^1-DPPFe), 3.[21]

In order to investigate the ammonia- and hydrazine-forming ability of each of these new mono-N$_2$ complexes, the following experiment was carried out. To a sample of 1A–F was added HBr (20–40 mol) and CH$_2$Cl$_2$ (ca. 10 mL) at −196 °C in vacuo. The mixture was allowed to warm to room temperature and the solution stirred (≥36 h). The amounts of noncondensable gas, ammonia

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(11) Reactions were successfully carried out with 4 equiv of N$_2$ in a closed system, for example, 3 g (4 mmol) of MoCl$_3$(triphos) and 100 mL of N$_2$-saturated THF in a 0.5 L vessel filled with N$_2$ (0.4 L, 16 mmol at ambient temperature).

(12) Bubbling was carried out to minimize possible irreversible loss of coordinated N$_2$ that might arise when a vacuum is used for solvent volume reduction. Only 1A shows evidence of loss of coordinated N$_2$ upon prolonged subjection to vacuum.

(13) The ^{31}P{^{1}H} NMR spectra were obtained with a Varian XL-200 spectrometer operating at 80.984 MHz. Chemical shifts (ppm) are referenced to 85% H$_3$PO$_4$. Triphos–phosphorus atom assignments are the following: central-PhP$_a$; terminal-Ph$_2$P$_b$ and -Ph$_2$P$_c$ when unsymmetrical.

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(15) Anal. Calcd for C$_{50}$H$_{55}$MoN$_2$P$_5$: C, 64.24; H, 5.93; N, 3.00; P, 16.56. Found: C, 63.56; H, 5.93; N, 2.87; P, 16.28. ^{31}P NMR[13] [C$_6$D$_6$]: 85.91 (dd, $^2J_{P_aP_c}$ = 101.5, $^2J_{P_aP_d}$ = 11.5, $^2J_{P_aP_b}$ = $^2J_{P_aP_c}$ = 0.0 Hz, P$_a$), 66.41 (ddd, $^2J_{P_bP_d}$ = 93.0, $^2J_{P_bP_c}$ ≃ 4, $^2J_{P_bP_e}$ ≃ 18 Hz, P$_b$), 58.96 (complex t, $^2J_{P_cP_d}$ ≃ $^2J_{P_cP_e}$ ≃ 18 Hz, P$_c$), 1.41 (ddt, P$_d$), -3.57 ppm (ddt, P$_e$). IR (KBr): ν(NN) 1978 cm^{-1}.

(16) Anal. Calcd for C$_{39}$H$_{47}$MoN$_2$P$_5$: C, 58.95; H, 5.96; N, 3.52; P, 19.49. Found: C, 58.13; H, 6.02; N, 3.53; P, 20.03. ^{31}P NMR[13] [C$_6$D$_6$]: AMM′XX′, 85.92 (t, $^2J_{PP}$ = 15.5 Hz, P$_a$), 63.45 (MM′, P$_b$, P$_c$), -22.40 ppm (XX′, P$_d$, P$_e$). IR (KBr): ν(NN) 1966 cm^{-1}. The initial product obtained from this reaction upon addition of methanol was Mo(triphos)(η^2-DMPM)(η^1-DMPM), 2, in which one DMPM is behaving as a monodentate ligand. Addition of further methanol to the filtrate precipitated crystals of 1B. 2: ^{31}P NMR[13] [C$_6$D$_6$; Mo(triphos)(Me$_2$P$_d$CH$_2$P$_e$Me$_2$)(Me$_2$P$_f$CH$_2$P$_g$Me$_2$)]: 97.53 (complex dt, 1, $^2J_{P_gP_f}$ = 86.7, $^2J_{P_aP_d}$ = $^2J_{P_aP_e}$ = 14.7, $^2J_{P_aP_b}$ ≃ $^2J_{P_aP_c}$ ≃ 4.4 Hz, P$_a$), 74.96 (m, 2, $^2J_{P_bP_d}$ ≃ $^2J_{P_bP_e}$ ≃ 78.5, $^2J_{P_bP_f}$ ≃ $^2J_{P_cP_f}$ ≃ 21.3 Hz, P$_b$, P$_c$), 1.49 (complex dt, 1, $^2J_{P_dP_f}$ ≃ $^2J_{P_eP_f}$ ≃ 5.6 Hz, P$_f$), -18.13 cm (m, 2, P$_d$, P$_e$), -59.54 ppm (s, 1, P$_g$).

(17) Anal. Calcd for C$_{59}$H$_{55}$MoN$_2$P$_5$: C, 67.95; H, 5.32; N, 2.69; P, 14.85. Found: C, 67.36; H, 5.37; N, 2.36; P, 13.43. ^{31}P NMR[13] [THF]: AMM′XX′, 86.97 (t, 1, $^2J_{PP}$ = 13.9 Hz, P$_a$), 63.81 (MM′, 2, P$_b$, P$_c$), 7.25 ppm (XX′, 2, P$_d$, P$_e$). IR (KBr): ν(NN) 1978 cm^{-1}.

(18) Anal. Calcd for C$_{60}$H$_{57}$MoN$_2$P$_5$: C, 68.18; H, 5.44; N, 2.65; P, 14.65. Found: C, 63.69; H, 5.44; N, 2.49; P, 14.05. *fac*-1E; ^{31}P NMR[13] [THF]: 87.94 (ddd, $^2P_{P_aP_c}$ = 106.6, $^2J_{P_aP_d}$ = 15.7, $^2J_{P_aP_b}$ = 6.8, $^2J_{P_aP_e}$ = 0 Hz, Pa), 69.36 (dddd, $^2J_{P_bP_d}$ = 101.0, $^2J_{P_bP_c}$ = 20.9, $^2J_{P_bP_e}$ = 12.6 Hz, P$_b$), 65.91 (dddd, $^2J_{P_cP_e}$ = 4.0 Hz, P$_c$), 64.01 (complex dt, P$_e$), 58.08 ppm (p, P$_c$). *fac*-1E′: ^{31}P NMR[13] [THF]: 70.74 (quin, 1, $^2J_{P_aP_x}$ = 5.9 Hz, P$_a$), 60.40 ppm (d, 4, P$_x$ = P$_{b,c,d,e}$). IR (*fac*-1E and *fac*-1E′; KBr): ν(NN) 2008, 1955 cm^{-1}.

(19) Anal. Calcd for C$_{44}$H$_{49}$As$_2$MoN$_2$P$_3$: C, 55.95; H, 5.23; N, 2.97; P, 9.84; As, 15.86. Found: C, 55.16; H, 5.25; N, 2.25; P, 9.48; As, 14.68. *fac*-1C: ^{31}P NMR[13] [C$_6$D$_6$]: 100.30 (dd, $^2J_{P_aP_c}$ = 3.6, $^2J_{P_aP_b}$ = 11.8 Hz, P$_a$), 85.91 (dd, $^2J_{P_bP_c}$ = 11.8 Hz, P$_b$), 66.80 ppm (d, P$_c$). *mer*-1C: ^{31}P NMR[13] [C$_6$D$_6$]: 91.87 (s, 1, $^2J_{P_aP_b}$ = $^2J_{P_aP_c}$ = 0 Hz, P$_a$), 63.63 ppm (s, 2, P$_b$, P$_c$). IR (*fac*- and *mer*-1C; KBr): ν(NN) 1960 (b) cm^{-1}.

(20) ^{31}P NMR[13] [C$_6$D$_6$]: AMM′X$_2$, 104.86 (complex t, 1, $^2J_{PP}$ = 13.9 Hz, P$_a$), 80.30 (MM′, dd, 2, P$_b$, P$_c$), -19.70 ppm (X$_2$, d, 2, $^2J_{PP}$ = 14.0 Hz, P$_d$, P$_e$). IR (KBr): ν(NN) 1962 cm^{-1}.

(21) ^{31}P NMR[13] [C$_6$D$_6$; Mo(triphos)(Ph$_2$P$_d$C$_5$H$_4$FeC$_5$H$_4$P$_e$Ph$_2$)-(Ph$_2$P$_f$C$_5$H$_4$FeC$_5$H$_4$P$_g$Ph$_2$)]: 99.18 (d, 1, $^2J_{P_aP_d}$ = 112.8, $^2J_{P_aP_b}$ = 0.0 Hz, P$_a$), 61.97 (d, 2, $^2J_{P_bP_d}$ ≃ $^2J_{P_cP_d}$ ≃ 13.8, $^2J_{P_bP_c}$ = 0.0 Hz, P$_b$, P$_c$), 36.95 (dt, 1, P$_d$), -20.88 (s, 1, P$_g$), -21.89 ppm (d, 2, $^2J_{P_eP_f}$ = 3.7 Hz, P$_e$, P$_f$).

and hydrazine, formed were measured quantitatively.[22] The evolved gas consisted of N_2 together with some H_2. We have not detected the presence of H_2 in similar reactions carried out with *trans*-$Mo(N_2)_2$(triphos)(PPh_3). The yields of NH_3 and N_2H_4 are given in Table I. In all cases the total nitrogen balance (including N_2 gas) exceeded 78%.

It is interesting to note that the highest yield of ammonia was obtained from the reaction with **1F**, the iron-containing phosphine ligand complex. This is the first Fe–Mo–N_2 complex to produce either ammonia of hydrazine under any conditions. The highest

yield of hydrazine was obtained when **1A** was treated with HCl (40 mol)/toluene at 70 °C for 39 h: 0.36 (NH_3), 0.48 (N_2H_4). The highest overall conversion to reduced nitrogen (in the combined form of NH_3 and N_2H_4) was also in this latter reaction. In tetrahydrofuran solution **1A** (HBr) and **1E** (HCl) gave little ammonia and no hydrazine, and **1D** (HCl) afforded all nittrogen as N_2.

Further work is in progress to expand the range of mono-N_2 complexes and isolate intermediates in the ammonia- and hydrazine-forming reactions.

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(22) For details of analytical procedures see ref 5a.

Artificial Allosteric Systems. 3. Cooperative Carbon Monoxide Binding to Diiron(II)–Gable Porphyrin–Diimidazolylmethane Complexes

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Contribution from the Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto 606, Japan. Received January 11, 1985
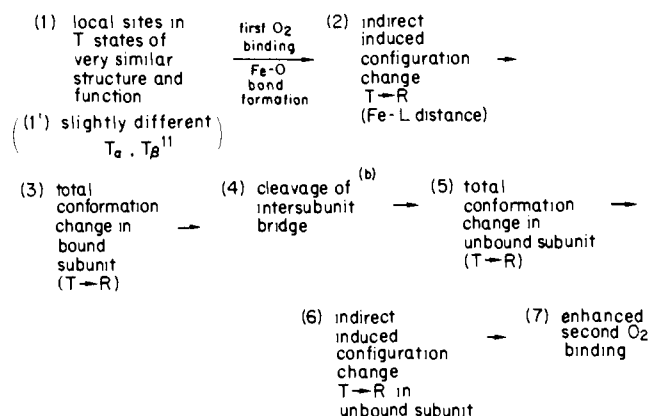
Abstract: A gable porphyrin–diiron(II)–bridging ligand complex was investigated as an artificial allosteric system of a hemoglobin type, to which CO binds cooperatively. For bridging ligand concentration ranging from 7.7×10^{-5} to 7.7×10^{-3} M, CO binds to the complex with remarkable cooperativity. The maximum Hill coefficient observed was 1.9, with N,N'-diimidazolylmethane as a bridging ligand, while with 4,4'-dipyridylmethane the maximum Hill coefficient was observed to be 1.4. This cooperativity can be interpreted by a model in which binding of a first CO molecule converts the artificial system from a hexacoordinate T–T state to a hexacoordinate R–R state with one free and one CO bound subunit. However, at low ligand concentration, cooperativity was not observed, suggesting that CO binding proceeded with retention of the T–T structure. At the ligand concentration of 0.15 M, cooperativity was not observed due to the fact that the CO free artificial system is present in the hexacoordinate R–R state. We interpreted the observed allosteric effect by a sequence of events characteristic of the native allosteric binding system—T–T states for the free system, direct structure change caused by the first CO binding, indirect induced structure change, intersubunit bond cleavage, transmission of induced structure change, and enhancement of the second CO binding.

The concept of allosterism[1] in biological phenomena is now reasonably well understood, although detailed studies have been limited to a few cases such as cooperative O_2 or CO binding to hemoglobin.[2] The simplest mechanistic interpretation of the cooperative O_2 binding is as follows: a conformational change induced at one of the subunits in the tetrasubunit-protein by the first O_2 binding causes a remarkable structure change in the unit linking two (or more) active sites of very similar local structures. Then the structure change is further transferred to the second (and/or third, fourth) active site(s) to increase the second (etc.) O_2 binding capacity.[1,2] The mechanistic profile is depicted in a somewhat specific and detailed fashion in Scheme I. Interestingly, it was recently found that the generalized mechanism also operates in certain entirely artificial systems[3-7] as shown in Table I. Thus, design of *artificial allosteric molecules or systems* is emerging as a new concept.[5] However, only very limited examples are available at present, and further study is necessary to understand allosterism in detail.

In this article, cooperativity in CO binding to Fe(II)–gable porphyrin–bridging ligand complex is described as the first

well-defined example of artificial allosteric CO binding compounds.[4a]

Scheme I. Analysis of Allosteric O_2 Binding by Hemoglobin[10]

(1) local sites in T states of very similar structure and function

(1') slightly different T_α, T_β[11]

first O_2 binding — Fe–O bond formation →

(2) indirect induced configuration change T→R (Fe–L distance)

(3) total conformation change in bound subunit (T→R) →

(4) cleavage of intersubunit bridge[b] →

(5) total conformation change in unbound subunit (T→R)

(6) indirect induced configuration change T→R in unbound subunit →

(7) enhanced second O_2 binding

a Concerning only "homotropic effects";[1] heterotropic effect, allosteric system A $\xrightarrow{\text{effector}}$ allosteric system B, is not discussed here. *b* Schematic representation may be as follows;

(T_1, T_2 : deoxy)   (R_1 : oxy , R_2 : deoxy)

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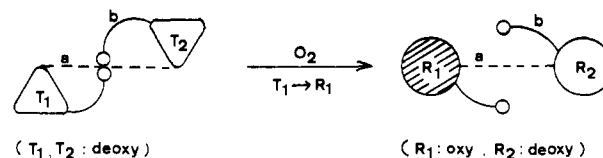
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