



Solid state and crystalline state-specific ($\omega \rightarrow \alpha$) photoisomerization-linked dioxygenation reaction of (ω -substituted alkyl)cobalt complexes

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ABSTRACT

A unique tandem reaction ($\omega \rightarrow \alpha$) photoisomerization-linked dioxygen insertion to Co–C bond was found to occur to afford (α -substituted alkylperoxy)bis(diphenylglyoximate)(L)cobalt(III) complexes, when (ω -substituted alkyl)bis(diphenylglyoximate)(L)cobalt(III) complexes were irradiated with visible light under an aerobic condition in the solid and crystalline state. The reaction proceeds efficiently, when the substituent has a character to stabilize the radical at the carbon attached and also to destabilize the Co–C bond of the intermediate α -substituted alkyl cobalt complexes.

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Solid state organic reactions have attracted much attention, not only from purely chemical interest, but also from the view point of 'green chemistry'. Since a reactive group of a molecule is surrounded and constrained by other molecules in the solid-state, the reaction proceeds with high selectivity, or a unique reaction can occur which does not proceed in a solution state.

We have previously reported that (β -substituted ethyl and γ -substituted propyl) (L)bis(dimethylglyoximate)cobalt(III) complexes isomerize to the corresponding α -substituted ethyl and α -substituted propyl complexes, respectively, on visible light-irradiation in the solid-state¹ and asymmetric photoisomerization takes place when the crystal lattice is chiral.² These reactions do not proceed in solution and therefore we designated them as 'solid state-specific reactions'.¹

Since visible light triggers homolysis of Co–C bond to give alkyl radical and Co(II) species, the solution-state photoreaction of alkylcobaloximes results in the formation of alkylperoxycobaloxime complexes³ under an aerobic condition. However, dioxygen-insertion reactions have not been observed so far in the above mentioned solid-state reactions^{1,2} and also solid-state photoracemization⁴ of optically active alkylcobaloxime complexes in spite of an aerobic condition. Intramolecular cyclization did not occur as well in the solid state photoreaction of several (olefin-con-

taining alkyl)bis(dimethylglyoximate)(base)cobalt(III) complexes⁵ despite the fact that the reactive group contains a radical acceptor (olefinic double bond) in itself. The reason for these unsuccessful attempts was considered that the molecules are so closely packed in each crystal lattice and the volume of each reaction cavity is too restricted for the reactive group to move correctly to give a desired reaction product.

Recently, we realized that the introduction of bulky substituents such as phenyl or furyl on the peripheral position of the in-plane ligands remarkably increased the reaction rates of photoisomerization of β -substituted ethyl complexes due to the enlarged reaction cavity.⁶ This prompted us to examine the photoreaction of such complexes having bulky substituents on the in-plane ligands. At first, we examined the photoreaction of 2-allyloxyethylbis(diphenylglyoximate)(benzylamine)cobalt(III),⁷ compound code **1(1AHe)**, in the solid state⁷ in expectation of intramolecular cyclization, but the cyclization did not occur (compound code, **1(1AHe)**, is given according to a generalized coding system described later). Instead, however, we found a novel and unexpected reaction: solid state and crystalline state-specific photoisomerization-linked dioxygen insertion reaction which we would like to report here. This is also the first distinct example⁸ of dioxygen insertion of alkylcobaloxime type complexes in the solid state photoreaction.

A powdered sample of compound **1(1AHe)** was suspended in an insoluble liquid (liquid paraffin, nujol) and was irradiated with a solar simulator (light source of a 500 W Xe lamp regulated with a constant flux density of 100 mW/cm²) for several hours. After

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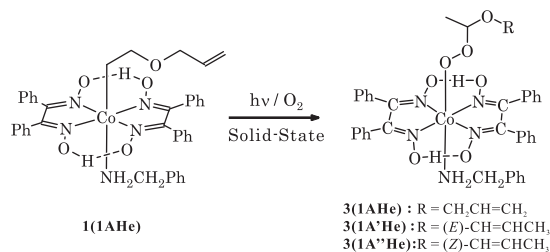


Figure 1. Solid state ($\beta \rightarrow \alpha$) photoisomerization-linked dioxygenation of (2-allyloxyethyl)(benzylamine)bis(diphenylglyoximate)cobalt(III)

removing nujol by filtration and washing with hexane, the product was purified by silica gel column chromatography (using chloroform as an eluent) to give a single spot on TLC whose R_f value (0.26, solvent system: hexane/ethyl acetate(6/4)) is considerably lower compared to that of the substrate (0.38), implying that the product has a rather high polarity. The behavior and NMR characteristic suggested that isomerization of substrate **1(1AHe)** and dioxygen insertion to the Co–C bond might occur even in the solid state. The structure of the isolated sample was confirmed by 400 MHz ¹H NMR spectrum⁷ and microanalysis⁷ to be **3(1AHe)** shown in Figure 1 (Compound code **3(1A'He)** is also given according to a generalized coding system described later): the signals which appeared at δ 5.08 ppm (1H, q, J = 5.4 Hz, Co–OOC(methylvinylxy)HCH₃) and at δ 1.23 ppm (3H, d, J = 5.4 Hz, Co–OOC(methylvinylxy)HCH₃) are assigned to be methine (attached to two oxygen atoms) and methyl protons (coupled with the methine proton), respectively, and signals of olefin protons appeared at δ 6.18 ppm (1H, dq, J = 12.3, 1.5 Hz, CH₃CH=CHO–) and δ 4.88 ppm (1H, dq, J = 6.8, 12.2 Hz, CH₃CH=CHO–) and also methyl protons attached to an olefinic methine appeared at δ 1.43 ppm (3H, dd, J = 6.8, 1.5 Hz, CH₃CH=CHO–). Other ¹H NMR data relating to axial base and in-plane ligands are given in Ref. 7.

Thus, compound **1(1AHe)** was considered to isomerize to the α -complex in a photochemical equilibrium with α -C radical and Co(II) species which finally gave **3(1A'He)** by the reaction with

dioxygen and also isomerization of the olefinic double bond on light irradiation under an aerobic condition in the solid state. In fact, crude products contained **3(1AHe)** (22%), **3(1A'He)** (3%) in addition to **3(1AHe)** (14%) (except for substrate **1(1AHe)** (43%)), in an early stage (30 min irradiation) of the reaction. After irradiation for 12 h the ratio of **3(1AHe)** decreased to 1%, and those of **3(1AHe)** and **3(1A'He)** reached 90% and 3%, respectively.

Several β -substituted ethyl and γ -substituted propyl bis(diphenylglyoximate)cobalt(III) complexes (**1(1XYL)** and **1(2XYL)**) were prepared and examined whether the above mentioned reaction took place or not, in view of the scope and limitation of this reaction. Here, the compound code is given as follows: the number outside parenthesis (**1–3**), the number in parenthesis, large letter (**A–F**), and small letter (**a–e**) are defined as the type of complexes (**1**: substrates, **2**: the isomerized α -complexes, **3**: O₂-inserted α -complexes), the number of methylene (**n**), symbolic letter for ω -substituent X and Y (**A**: allyloxy, **B**: OPh, **C**: Ph, **D**: COOMe, **E**: CN, **F**: Me, **H**: H), and symbolic letter for the axial ligand L (**a**: pyridine, **b**: 4-cyanopyridine, **c**: 4-methylpyridine, **d**: butylamine, **e**: benzylamine) in a generalized formula, respectively (see Fig. 2 and Table 1).

A powdered sample of each substrate was suspended in an insoluble liquid (nujol) and irradiated for a certain period, similarly as in the case of **1(1AHe)**. Crude products were obtained after removing nujol by filtration and washing with hexane. The ratios of substrate, the α -complex formed by isomerization, and the dioxygen-inserted α -complex of each reaction were determined by ¹H NMR spectra of the crude products (see Supplementary data). The results are summarized in Table 1.

The reaction with the substrate having alkoxy, phenoxy, or phenyl as the ω -substituent (X and/or Y) on the alkyl group proceeded generally to afford the α -alkylperoxy cobalt complex (type **3** complex) in a moderate to excellent yield. The reaction with the substrate having COOMe or CN as the ω -substituent did not afford the alkylperoxy cobalt complex (type **3** complex) efficiently, but the intermediate α -alkyl cobalt complex (type **2** complex) was formed as the main product (entries 9–14 and 21–22). Although the α -substituted alkyl cobalt complex (type **2** complex) was not

Table 1

Solid state-specific ($\omega \rightarrow \alpha$) photoisomerization-linked dioxygenation of (ω -substituted alkyl)bis(diphenylglyoximate)(L)cobalt(III), XYCH(CH₂)_nCo(dpgH)₂L

Entry	Substrate 1(nXYL)					Time (h)	Substrate recovered (%)	Product Yield (%)	
	Code	n	X ^a	Y ^a	L ^b			2(nXYL)	3(nXYL)
1	1(1AHe)	1	O-Allyl(A)	H	e	12	0	0	94 ^c
2	1(1BHa)	1	OPh(B)	H	a	10	3	0	62
3	1(1BHb)	1	OPh(B)	H	b	25	0	0	72
4	1(1CHa)	1	Ph(C)	H	a	25	22	0	43
5	1(1CHb)	1	Ph(C)	H	b	10	18	0	53
6	1(1CHc)	1	Ph(C)	H	c	25	27	0	39
7	1(1CHd)	1	Ph(C)	H	d	10	15	0	55
8	1(1CCa)	1	Ph(C)	Ph(C)	a	10	0	0	90
9	1(1DHa)	1	COOMe(D)	H	a	10	34	44	4
10	1(1DHB)	1	COOMe(D)	H	b	25	0	34	21
11	1(1DHC)	1	COOMe(D)	H	c	25	9	38	12
12	1(1EHa)	1	CN(E)	H	a	5	79	20	1
13	1(1EHa)	1	CN(E)	H	a	10	48	39	2
14	1(1EHa)	1	CN(E)	H	a	15	33	44	2
15	1(1FHa)	1	Me(F)	H	a	2	0	0	0
16	1(2BHa)	2	OPh(B)	H	a	1	0	0	99
17	1(2CHa)	2	Ph(C)	H	a	10	13	0	34
18	1(2CCa)	2	Ph(C)	Ph(C)	a	5	60	0	31
19	1(2CCa)	2	Ph(C)	Ph(C)	a	10	36	0	46
20	1(2CCa)	2	Ph(C)	Ph(C)	a	25	15	0	77
21	1(2DHa)	2	COOMe(D)	H	a	5	0	71	0
22	1(2EHa)	2	CN(E)	H	a	5	9	66	0

^a Substituent (X and Y): A = allyloxy, B = phenoxy, C = phenyl, D = COOCH₃, E = CN, F = CH₃, H = H.

^b Axial ligand (L): a = pyridine, b = 4-cyanopyridine, c = 4-methylpyridine, d = butylamine, e = benzylamine.

^c Total yield of **3(1AHe)** (1%), **3(1A'He)** (90%) and **3(1A''He)** (3%): A' = (E)-(2)-methylvinylxy, A'' = (Z)-(2)-methylvinylxy (See also Fig. 1).

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