CHEMISTRY LETTERS, pp. 1089-1092, 1990.

Photoreaction of the Adduct between (η-Cyclopentadienyl)-(1,2-dicyano-1,2-ethylenedithiolato)cobalt(III) and Tributylphosphine.
Oxygenation of Coordinated Phosphine by Singlet Oxygen

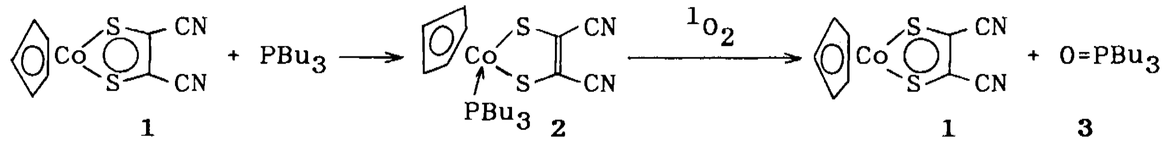
Hiroshi HATANO, Masatsugu KAJITANI, Takeo AKIYAMA,
Yoshio SAKAGUCHI,[†] Junko NAKAMURA,[†] Hisaharu HAYASHI,[†]
and Akira SUGIMORI*
Department of Chemistry, Faculty of Science and Technology,
Sophia University, Kioi-cho 7-1, Chiyoda-ku,Tokyo 102
[†]The Institute of Physical and Chemical Research,
Wako, Saitama 351-01

The title complex $[Co(cp)(S_2C_2(CN)_2)(PBu_3)]$ gives $[Co(cp)(S_2C_2(CN)_2)]$ and phosphine oxide ($O=PBu_3$) under irradiation with methylene blue or rose bengal as sensitizer in the presence of oxygen. This reaction proceeds via oxidative elimination of the coordinated phosphine by singlet oxygen. Under irradiation with 254 nm light, the adduct plays the role of a triplet sensitizer.

The five-membered metallacycle in (η-cyclopentadienyl)(1,2-ethylenedithiolato)cobalt(III) complexes, $[Co(cp)(S_2C_2XY)]$, is a kind of aromatic ring and shows unique physical and chemical properties.1) However, it also has a site of unsaturation between the metal and sulfur atoms. These dithiolato complexes react with some reagents, such as quadricyclane (Q),2) diazo compounds,3) dimethyl acetylenedicarboxylate (DMAD),4) and phosphines,5) to form the corresponding adducts.

A characteristic photochemical feature of these adducts is dissociation. For example, the adduct with Q liberates the dithiolato complex **1** and norbornadiene (isomerized form of Q) under UV-irradiation.2) We report here another type of dissociation. The dissociation of the title phosphine adduct, $[Co(cp)(S_2C_2(CN)_2)(PBu_3)]$ (**2**), proceeds via the oxidative elimination of the coordinated phosphine by singlet oxygen to give the free complex, $[Co(cp)(S_2C_2(CN)_2)]$ (**1**), and the phosphine oxide ($O=PBu_3$) (**3**).

The adduct **2** is an air-stable complex.5) In the acetonitrile solution ([1] = 2×10^{-4} mol dm^{-3}, at room temperature), no change has been observed even after the irradiation with a medium pressure mercury lamp. However, the color of the solution changes from yellow-brown to purple under the irradiation with UV- or filtered visible light (λ > 480 nm) in the presence of singlet oxygen generated by photosensitization with methylene blue (Fig.1, [methylene blue] = 1×10^{-5} mol dm^{-3}) or with rose bengal. This UV-Vis. spectral change on irradiation indicates the formation of the free complex **1** in 84% yield. The ^{31}P NMR of the products shows the formation of the phosphine oxide **3**.[6]



(1)

These results indicate that the elimination of the phosphine under irradiation occurs not via the reaction of the excited **2** with the ground state oxygen, but via the reaction of the ground state **2** with singlet oxygen. A mechanism for the elimination under the irradiation with a medium pressure mercury lamp in the presence of oxygen is shown in Eqs.2-4.

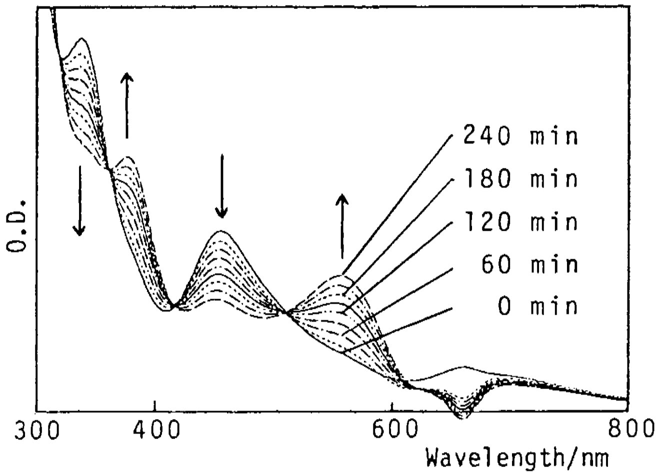


Fig.1. UV-Vis. spectral change of acetonitrile solution of the adduct **2** under the irradiation with a medium pressure mercury lamp in the presence of methylene blue.

Laser flash photolysis at 355 nm[7] also shows that the dissociation of **2** is not initiated by the spontaneous dissociation of the excited **2**.

Only a few reactions of singlet oxygen and phosphorous compounds are known.[8,9] But the oxidation of coordinated phosphine in a metal complex by singlet oxygen has not been reported.

The reaction with a low pressure mercury lamp ([1] = 2×10^{-4} mol dm^{-3}, at 30 ℃) differs from that with a medium pressure mercury lamp. During the irradiation with a low pressure mercury lamp in an acetonitrile solution in the presence of oxygen, the dithiolato complex **1** is formed. But in the absence of oxygen, **2** decomposes without giving the free complex **1**. In the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as a singlet oxygen quencher,[10] the formation of **1** is suppressed and we only observe the decomposition under the irradiation. This result suggests that the oxidative elimination of the phosphine with a low pressure mercury lamp is also the reaction between **2** and singlet oxygen.

In an acetonitrile solution with no additives, **2** is the only light-absorbing species. Therefore, the excited **2** itself should play a role as a sensitizer and should produce singlet oxygen. In order to deactivate the triplet excited state of **2**, we added 1,3-cyclohexadiene in an acetonitrile solution and irradiated with a low pressure mercury lamp in the absence of oxygen. Neither elimination nor decomposition of **2** occurred under these conditions. These results show that the excited triplet **2** sensitizes the formation of singlet oxygen in the presence of oxygen, but decomposes in the absence of oxygen.

We postulate a mechanism for the oxidative elimination of the phosphine under irradiation. The adduct in a lower excited state produced by the irradiation with a medium pressure mercury lamp is rapidly deactivated to the ground state through internal conversion. The adduct in the ground state reacts with singlet oxygen produced by sensitizers (Eqs.2-4). The adduct excited by a low pressure mercury lamp is converted to a triplet excited state through intersystem crossing. This triplet excited state adduct sensitizes the formation of singlet oxygen or decomposes in the absence of oxygen (Eqs.5,6). In every case where singlet oxygen is produced, it reacts with the coordinated phosphine and produces free complex **1** and phosphine oxide **3**.

In the benzene solution, **2** dissociates under the irradiation even with a medium pressure mercury lamp in the presence of oxygen. Further investigations are in progress now.

$$\text{Sens} \xrightarrow{h\nu} {}^1(\text{Sens})^* \longrightarrow {}^3(\text{Sens})^* \qquad (2)$$

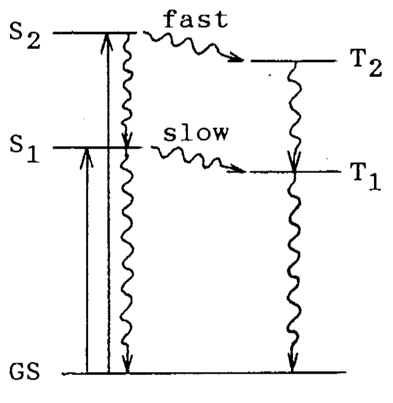
(Sens = Sensitizer)

$${}^3(\text{Sens})^* + {}^3O_2 \longrightarrow \text{Sens} + {}^1O_2^* \qquad (3)$$

$$\mathbf{2} + {}^1O_2^* \longrightarrow \mathbf{1} + \mathbf{3} \qquad (4)$$

$$\mathbf{2} \xrightarrow{h\nu} \mathbf{2}(S_2) \longrightarrow \longrightarrow \mathbf{2}(T_1) \qquad (5)$$

$$\mathbf{2}(T_1) \begin{cases} \xrightarrow{O_2} {}^1O_2^* + \mathbf{2} \longrightarrow\longrightarrow \mathbf{1} + \mathbf{3} \\ \longrightarrow \text{Decomposition} \end{cases} \qquad (6)$$



Scheme

References

1) A.Sugimori and M.Kajitani,Kagaku Zokan, 115, 113 (1988).

2) M.Kajitani,Y.Eguchi,R.Abe,T.Akiyama,and A.Sugimori,Chem.Lett.,1990,359.

3) M.Kajitani, M.Sakurada, K.Dohki, T.Suetsugu, T.Akiyama, and A.Sugimori, J.Chem.Soc.,Chem.Commun.,1990, 19.

4) M.Kajitani, T.Suetsugu, R.Wakabayashi, A.Igarashi, T.Akiyama, and A.Sugimori, J.Organomet.Chem., 293, C15 (1985).

5) S.D.Henderson, T.A.Stephenson, and E.J.Wharton, J.Organomet.Chem., 179, 43 (1979).

6) Phosphine oxide **3** was detected with ^{31}P NMR. (JEOL JNM-GX270). Signals for PBu_3, coordinated PBu_3, and $O{=}PBu_3$ appear at $\delta = -31$, 35, and 50, respectively (external reference: 1% H_3PO_4).

7) We used a 355 nm laser pulse from Nd-YAG laser.

8) K.Nahm and C.S.Foote, J.Am.Chem.Soc., 111, 1909 (1989).

9) P.R.Bolduc and G.L.Goe, J.Org.Chem., 39, 3179 (1974).

10) C.S.Foote, E.R.Peterson,and K.-W.Lee, J.Am.Chem.Soc., 94, 1032 (1972).

(Received March 29, 1990)