An Oxygen Adduct of Cobaltocene

By H. Kojima,* S. Takahashi, and N. Hagihara

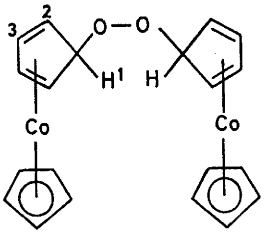
(*The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka* 565, *Japan*)

Summary Treatment of cobaltocene with oxygen in ether at low temperature produces a novel oxygen adduct of cobaltocene, $[(C_5H_5)_2Co]_2O_2$, with an oxygen bridge between two cyclopentadienyl groups.

The reaction, under oxygen, of cobaltocene with organic compounds having an active hydrogen atom gives a π-cyclopentadienyl-(1-*exo*-organylcyclopentadiene)cobalt complex in high yield.[1] We suggested that an oxygen adduct of cobaltocene might be an intermediate in the reaction and now report the isolation and characterisation of such an adduct. When dried oxygen gas was passed through a solution of cobaltocene in Et_2O at −78°, an orange solid was instantly formed, the reaction taking place even at an oxygen pressure of < 100 mmHg. The orange compound (I) is unstable and decomposed rapidly in air and after a few hours under nitrogen at room temperature to give cobalticinium hydroxide.

Gas titrations with CH_2Cl_2 or Et_2O solutions of cobaltocene at −78°, gave end-points on consumption of one mole of oxygen per two moles of cobaltocene. Hydrolysis of (I) with aqueous H_3PO_4 at −78° gave hydrogen peroxide and $[(\pi\text{-}C_5H_5)_2Co]^+[H_2PO_4]^-$ quantitatively in the molar ratio 1 : 2. From the reaction of (I) with benzoyl chloride at −78°, dibenzoyl peroxide and $[(\pi\text{-}C_5H_5)_2Co]^+Cl^-$ were formed quantitatively in the molar ratio 1 : 2.

These results show that (I) is $[(C_5H_5)_2Co]_2O_2$, with an oxygen bridge between two cyclopentadienyl rings. Compound (I) had an i.r. spectrum similar to those of π-cyclopentadienyl-(1-*exo*-organylcyclopentadiene)cobalt complexes apart from a strong absorption bandat 887 cm^{-1} assignable to ν_{O-O}. The n.m.r. spectrum indicated the presence of a π-cyclopentadiene group [δ 2·3 (1-H), 2·57 (2-H), 4·69(π-C_5H_5), and 5·04(3-H)].



(I)

We also studied the $^{18}O_2$ substitution of (I). In the case of mononuclear oxygen complexes such as $(RNC)_2NiO_2$, isotopic substitution of O_2 shifts the ν_{O-O} band by an amount (*ca.* 50 cm^{-1}) equivalent to that calculated for a simple harmonic oscillator.[2] However, the isotopic shift for ^{18}O attached to large organic groups is expected to be smaller.[3] The complex obtained from the reaction between cobaltocene and $^{18}O_2$ (purity 92%) had an absorption band at 884 cm^{-1}. This small ^{18}O-shift (3 cm^{-1}) is consistent with the suggested structure.

Bridged structures are known for the tetrafluoroethylene[4] and acrylonitrile complexes[5] of cobaltocene, but (I) appears to be the first example of a transition-metal complex co-ordinated by an organic peroxide. The oxygen adduct (I) is an active reagent for the oxidative cleavage of a carbon–carbon bond in α-diketones and *o*-quinones to give cobalticinium carboxylates.

We thank Professor T. Miyazawa, and Dr. A. Nakamura for helpful discussions.

(*Received*, *5th February* 1973; *Com.* 148.)

---

[1] H. Kojima, S. Takahashi, H. Yamazaki, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1970, **43**, 2272.

[2] R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, 1970, **9**, 2367, and references therein.

[3] S. Pinchas and I. Laulicht, 'Infrared Spectra of Labelled Compounds,' Academic Press, London, 1971, p. 256; K. Domiroth, A. Berndt, and R. Volland, *Chem. Ber.*, 1966, **99**, 3040.

[4] H. H. Hoehn, L. Prett, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 1961, 2738.

[5] H. Kojima, H. Yamazaki, and N. Hagihara, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, 1971, **28**, 113.