*Journal of Organometallic Chemistry*, 430 (1992) C64–C67
Elsevier Sequoia S.A., Lausanne
JOM 22716PC

Preliminary communication

# Adduct between quadricyclane and ($\eta^5$-cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III): formation and structure

Masatsugu Kajitani, Hiroshi Hatano, Tetsuji Fujita, Tetsuyuki Okumachi, Hirotaka Nagao, Takeo Akiyama and Akira Sugimori

*Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho 7-1, Chiyoda-ku, Tokyo 102 (Japan)*

(Received January 10, 1992)

## Abstract

The reaction of ($\eta^5$-cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III) (**1**) in quadricyclane (Q) at 90°C gives 1:1 adducts of **1** and Q. The main adduct (40% yield) has a unique structure, in which the 5- and 7-positions of norbornene are bonded to Co and S of **1**. A mechanism of the formation of the adduct (by the use of deuterium-labeled Q), including a skeletal rearrangement of Q, is proposed.

The square-planar bis(1,2-ethylenedithiolato)metal complexes (metal: Ni, Pd, and Pt) are known to form 1:1 adducts with dienes, such as norbornadiene (NBD) [1], and with strained molecules, such as quadricyclane [1,2]. In these adducts, the S atoms of different dithiolene rings are bridged by the norbornene-5,6-diyl group. However, the study of these adduct formation of the dithiolato metal complexes with NBD or Q has been limited only to bis(dithiolato)metal complexes, and no investigation has been done on the mono(dithiolato)metal complexes.

Here we report the first example of a new type of insertion of strained hydrocarbon into the metal–sulfur bond, evidenced by the X-ray structural characteristics of the adduct, and the mechanism of its formation. We found that ($\eta^5$-cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III) (**1**) shows unique reactivities towards Q: The complex **1** forms 1:1 adducts with Q and catalyzes the isomerization of Q to NBD. The manner of the addition reaction of Q to **1** is quite different from that to bis(dithiolato)metal complexes. Under the same conditions, **1** does not react with norbornadiene (NBD).

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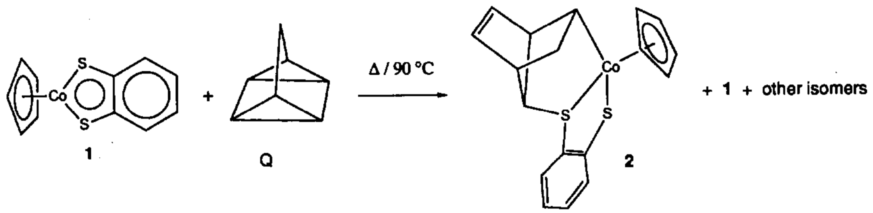
Correspondence to: Dr. M. Kajitani or Dr. A. Sugimori, Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho 701, Chiyoda-ku, Tokyo 102, Japan.



*Preparation of 2.* The free complex **1** was synthesized by Heck's method [3]. The free complex **1** (50 mg, $1.9 \times 10^{-4}$ mol) was placed in a Schlenk-tube under an argon and quadricyclane (Q) (5 cm$^3$, $5 \times 10^{-2}$ mol) was added. The mixture was then heated at 90°C for 3 h. After the reaction, excess Q was removed under reduced pressure and the residue was chromatographed on silica-gel (Wako-gel C-300; eluent, $C_6H_{14}/CH_2Cl_2 = 1/1$, v/v). Unreacted **1** was recovered from the first fraction (26%). The adduct **2** was obtained from the second fraction and the other two adducts were obtained from the third fraction. After evaporation of the solvents, **2** was obtained as brown powdery solid (27.0 mg) in 40% yield. Pure **2** was obtained from recrystallization from ethanol–benzene (4/1, v/v) at −30°C. Dark purple needles [m.p. 160–167°C (decomp)]. Anal. Found: C, 60.48; H, 4.99. $C_{18}H_{17}CoS_2$ calcd.: C, 60.66; H, 4.81%.

*Structure of 2.* The structure of **2** was determined by single-crystal X-ray analysis [4]. The ORTEP drawing of **2** is given in Fig. 1, together with some selected bond angles and the bond distances of **2**.

Adduct **2** has a unique structure, as described in the following two points: (1) the hydrocarbon moiety bridges between metal (Co) and sulfur (S) of the metalladithiolene ring without breaking the Co–S bond (Co–S(1) = 2.201(2) Å, Co–S(2) =

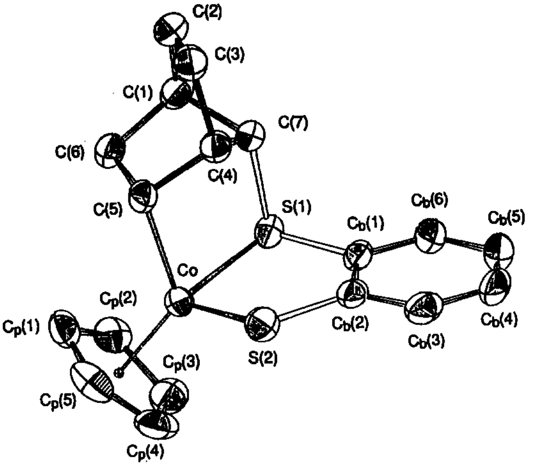


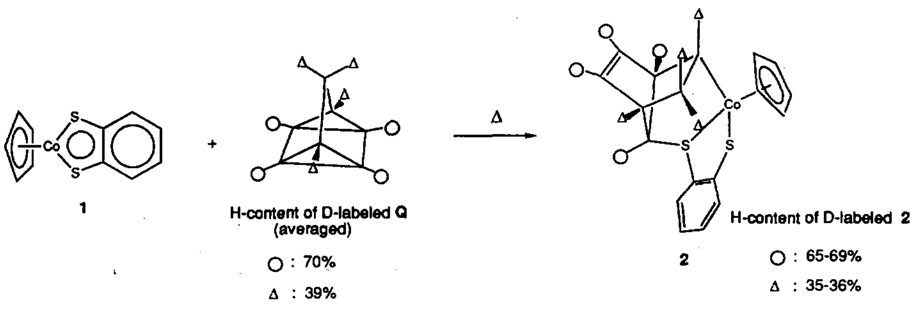
Fig. 1. ORTEP drawing of adduct **2** (Thermal ellipsoids at 50% probability; H atoms are omitted for clarity). Selected bond distances (Å) and bond angles (°): Co–S(1), 2.201(2); Co–S(2), 2.238(2); Co–C(5), 2.031(4); S(1)–$C_b$(1), 1.788(5); S(2)–$C_b$(2), 1.749(5); S(1)–C(7), 1.839(4); $C_b$(1)–$C_b$(2), 1.390(6); C(5)–C(6), 1.550(7); C(2)–C(3), 1.294(8); S(1)–Co–S(2), 91.7(1); S(1)–Co–C(5), 83.3(1); S(2)–Co–C(5), 95.2(1); Co–S(1)–$C_b$(1), 102.8(1); Co–S(2)–$C_b$(2), 101.8(2); Co–S(1)–C(7), 100.1(2); S(1)–$C_b$(1)–$C_b$(2), 118.6(3); S(2)–$C_b$(2)–$C_b$(1), 122.4(4); C(1)–C(7)–C(4), 94.2(4).

2.238(2) Å) (This is the marked difference between the cases of **2** and of reported bis(dithiolato)metal complexes (M = Ni, Pd, and Pt) [1,2] in which the hydrocarbon bridges between two sulfur atoms of two different dithiolene rings), and (2) in adduct **2**, Co and S are bridged by C(5)(edge carbon) and C(7)(bridge carbon) of $C_7H_8$ in norbornene form.

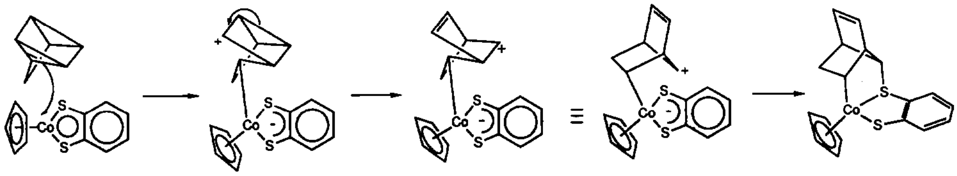
Adduct **2** has a piano-stool structure. The central metal is coordinatively saturated, in contrast with the penta-coordinative structure of the free complex **1**. The dithiolatometal ring is folded at two sulfur atoms and the angle of the planes consisting of metal–S–S and of S–S–C–C is 16° for **2**.

*Spectral data of 2.* The following spectral data of adduct **2** can be reasonably assigned according to the structure determined by single-crystal X-ray analysis. $^1H$ NMR(270 MHz, $CDCl_3$, TMS): $\delta = 1.46$ (dd, 1H, $H_{6\text{-}endo}$, $J_{6\text{-}endo\text{-}5} = 6.8$, $J_{gem} = 14.3$ Hz), 2.09 (dd, 1H, $H_{6\text{-}exo}$, $J_{6\text{-}exo\text{-}1} = 4.6$, $J_{gem} = 14.3$ Hz), 2.70 (d, 1H, $H_7$, $J_{7\text{-}1} = 1.9$ Hz), 2.77 (ddd, 1H, $H_1$, $J_{1\text{-}7} = 1.5$, $J_{1\text{-}2} = 3.0$, $J_{1\text{-}6\text{-}exo} = 4.6$ Hz), 3.40 (br. s, 1H, $H_4$), 3.70 (dd, 1H, $H_{5\text{-}endo}$, $J_{5\text{-}4} = 1.1$, $J_{5\text{-}6\text{-}endo} = 6.8$ Hz), 4.98 (s, 5H, $C_5H_5$), 5.65 (dd, 1H, $H_3$, $J_{3\text{-}4} = 3.0$ $J_{3\text{-}2} = 5.7$ Hz), 5.94 (dd, 1H, $H_2$, $J_{2\text{-}1} = 3.0$, $J_{2\text{-}3} = 5.7$ Hz), 6.77 (td, 1H, H at $C_b(4)$, $J = 7.5$ Hz, $J = 1$ Hz), 6.96 (td, 1H, H at $C_b(5)$, $J = 7.5$ Hz, $J = 1$ Hz), 7.28 (dd, 1H, H at $C_b(3)$, $J = 7.5$ Hz, $J = 1$ Hz), and 7.55 (dd, 1H, H at $C_b(6)$, $J = 7.5$ Hz, $J = 1$ Hz). $^{13}C\{^1H\}$NMR (67.94 Hz, $CDCl_3$): $\delta = 27.0$ (s, C(5) of $C_7H_8$), 39.9 (C(6) of $C_7H_8$), 46.6 (C(1) of $C_7H_8$), 58.5 (C(4) of $C_7H_8$), 77.2 (C(7) of $C_7H_8$), 87.2 ($C_5H_5$), 121.3 ($C_b(4)$), 128.5 ($C_b(5)$), 129.3 (C(3)(olefinic) of $C_7H_8$), 129.4 ($C_b(6)$), 130.7 ($C_b(3)$), 133.3 ($C_b(1)$), 134.6 (C(2)(olefinic) of $C_7H_8$), and 159.5 ($C_b(2)$). MS (70 eV): $m/z$ 356 ($M^+$, 4%), and 264 ($M^+ - C_7H_8$, 100%). UV–Vis ($CH_2Cl_2$): $\lambda_{max}$(nm) (log $\epsilon$) 235 (4.17), 278 (4.25), 323 (4.02), 435 (3.07), and 519 (2.96).

*Mechanism of adduct formation.* Skeletal carbon rearrangement or shift of hydrogen (or hydride) should take place to form **2** from Q. For the elucidation of the reaction mechanism we prepared deuterium-labeled quadricyclane as follows: the compound was prepared by a Diels–Alder reaction of cyclopentadiene-$d_6$ (deuterium-content, 60%) with *trans*-1,2-dichloroethylene [5], followed by dechlorination [6] and cyclization [7] according to literature methods. The deuterated Q has 70% of $^1H$ content (averaged content) at the edge positions (marked as ○ in Scheme 1), and 39% $^1H$ content (averaged content) at the bridge and the bridgehead positions (marked as Δ in Scheme 1). The analysis of $^1H$ NMR spectra of the adducts from deuterated Q and **1** gives the following results: (1) two *geminal*



Scheme 1.



Scheme 2.

hydrogens at the edge (bonded to C(6)) in adduct **2** have the same $^1$H content as that at the bridge in the deuterated Q and (2) two bridgehead hydrogens have different $^1$H contents. These results strongly suggest that only one skeletal rearrangement is involved and that no hydrogen atom shift takes place in the formation of the adducts. The addition of Q to **1** can be described as the following stepwise process (Scheme 2): (1) the nucleophilic attack of Q to the metal results in the formation of Co–C bond, carbenium ion in the $C_7H_8$ moiety, and negatively charged metalladithiolene ring; and (2) the skeletal carbon rearrangement occurs to form a more stabilized carbenium ion, which forms a bond with a negatively charged sulfur atom of the dithiolene ring. The mechanism in which Q approaches **1** from the 4-membered ring-side can be excluded, as the 4-membered ring-side approach requires the shift of a hydrogen atom to produce **2**.

**Acknowledgements.** This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas on Organic Unusual Valency (No. 02247102) and a Grants-in-Aid for Scientific Research (Nos. 02640406 and 03640464) from the Ministry of Education, Science and Culture of Japan, and by the Asahi Glass Foundation.

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4 Crystal data for adduct **2** ($C_{18}H_{17}S_2Co$), Formula weight 356.37: triclinic, space group $P\bar{1}$, $a = 10.722(4)$, $b = 12.518(5)$, $c = 5.980(3)$ Å, $\alpha = 93.70(4)$, $\beta = 94.62(4)$, $\gamma = 111.18(3)°$, $U = 742.2(6)$ Å$^3$, $Z = 2$, $D_c = 1.595$ g cm$^{-3}$, $D_m = 1.572$ g cm$^{-3}$, $\mu = 14.125$ cm$^{-1}$ for Mo-$K_\alpha$, Observed reflections 2467, $R = 0.0464$; $R_w = 0.0482$, $F(000)$ 736, $2\Theta_{max} = 60.0°$, Crystal dimensions = 0.12×0.12×0.20 mm, total reflections = 4862, Indep. Reflect. = 3084, Obsd.Criteria = $F_0 \geq 3\sigma(F_0)$, No. of Param. = 259. Apparatus used RIGAKU AFC-5, Mo-$K_\alpha$ ($\lambda = 0.71068$ Å), $\omega$ scan technique.

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