Synthesis of (η^5-Cyclopentadienyl)(η^4-cyclopenta-2,4-dien-1-thione)cobalt by the Reaction of Cobaltacyclopentadiene Derivative with CS$_2$ in the Presence of Co(I) Complex

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(η^5-Cyclopentadienyl)(η^4-2,3,4,5-tetraphenylcyclopenta -2,4-dien-1-thione)cobalt was obtained by the reaction of (η^5-cyclopentadienyl)triphenylphosphinecobalta-2,3,4,5-tetraphenylcyclopentadiene with CS$_2$ in the presence of cobalt(I) complex in quantitative yield, which was also converted quantitatively to (η^5 -cyclopentadienyl) (η^5 -1- methylmercapto -2,3,4,5- tetraphenylcyclopentadienyl)cobalticinium iodide by the treatment with methyl iodide.

Reactions of organometallic complexes with CS$_2$ involves occasionally the disproportion of CS$_2$ giving rise to CS-coordinated complexes.[1] While a few examples of further insertion of the coordinated CS are reported to take place in the case of Os to give thioketometallacycle complexes,[2] the generation of CS-insertion product for other metal complexes has been limited so far.[3] Herein, we report the synthesis of (η^5-cyclopentadienyl)(η^4 -2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-thione)cobalt and its cobalticinium salt by the reaction of (η^5-cyclopentadienyl)triphenylphosphinecobalta-2,3,4,5-tetraphenylcyclopentadiene (1) with CS$_2$ in the presence of a Co(I) complex and further reaction with an alkyl halide, respectively.

Although Yamazaki et al. have reported that the reaction of (η^5- cyclopentadienyl)triphenylphosphinecobaltacyclopentadiene derivatives with CS$_2$ leads to the formation of a dithiolactone derivative,[4] we could obtain a dramatically different result when we carried out the reaction in the presence of Co(I). The reaction of **1** with CS$_2$ (50 equiv) was carried out in toluene at 80 °C for one day in the presence of 1 equiv of (η^5-cyclopentadienyl)(η^4-cycloocta-1,4-diene)cobalt (**4**) to give (η^5-cyclopentadienyl)(η^4-2,3,4,5- tetraphenylcyclopenta -2,4- dien-1- thione)cobalt (**2**) in 94% isolated yield as a dark purple powder (Scheme 1).[5]

The FAB MS spectrum of **2** showed a molecular ion corresponding to (η^5-cyclopentadienyl)(η^4-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-thione)cobalt$^+$ at m/z 524 (M$^+$). The ^{1}H-NMR spectrum of **2** (in CDCl$_3$) reveals peaks at 4.95 (C$_5$H$_5$, s, 5H) and 6.97-7.78 ppm (C$_6$H$_5$, m, 20H). In the ^{13}C-NMR spectrum of **2** (in CDCl$_3$), the peak of the cyclopentadienyl group was detected at 88.06 ppm and that of the thiocarbonyl carbon was observed at 144.23 ppm.[6] The relatively higher field shift of the thiocarbonyl group is probably due to the contribution of the resonance structure (**B**) in **2**, not only the limited structure (**A**) (Scheme 2). This is demonstrated by the fact that the compound (**2**) reveals unique solvatochromism phenomenon; that is, in toluene or benzene, **2** is purple-colored and turns to red in (or by the addition of) methanol. This behavior might be also originated from the equilibrium between structures (**A**) and (**B**) whose distribution depends on the character of the solvents.

From the same reaction system, (η^5-cyclopentadienyl)(triphenylphosphine)cobaltacyclobuta-2,4-dithioxy-3-thione (**5**) was

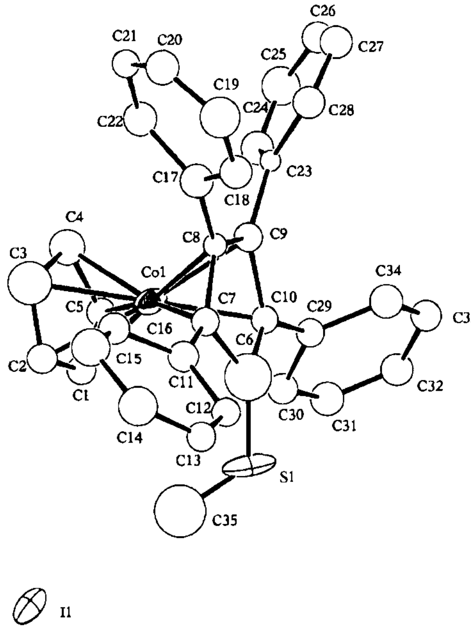
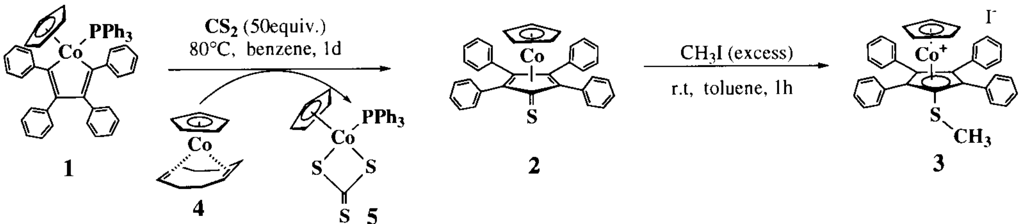
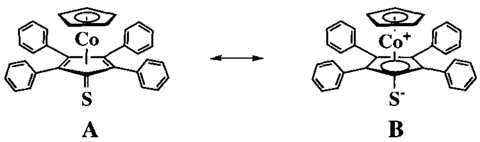


Figure 1. The ORTEP view of **3**. Selected bond distances and angles are follows.: Col-C1 2.03(5), Col-C8 1.99 (4), Col-C10 2.10(5), S1-C35 1.63(8), S1-C6 1.60(7), C1 - C2 1.44 (6), C2 - C3 1.35 (7), C6-C7 1.61 (8), C7-C8 1.46 (6), C8 - C9 1.38 (6), C6-C10 1.63 (8) Å; C6-S1-C35 112 (4), S1- C6-C7 137(5), S1-C6-C10 115(5), C7-C6-C10 101(4), C6-C7-C8 104(4), C7-C8-C9 119(4)°.



Scheme 1.



Scheme 2.

also obtained in 57% isolated yield as black crystals on standing the reaction mixture.

The obtained **2** was further converted quantitatively to red crystals of (η^5- cyclopentadienyl) (η^4 -2,3,4,5- tetraphenylcyclopenta-2,4-dien-1-thionyl)cobalticinium iodide (**3**) by the treatment with excess of iodomethane at rt for 1h in toluene, similarly to the case of the derivative of (η^5-cyclopentadienyl)(η^4-iminocyclopenta-2,4-diene)cobalt as reported by Yamazaki et al. (Scheme 1).[3g,7] The structure of the cobalt complex (**3**) was supported by spectroscopic methods and the X-ray crystallographic analysis (Figure 1).[8]

References and Notes

1 a) J. D. Gilbert, M. C. Braid, and G. Wilkinson, *J. Chem. Soc. (A)*, **1968**, 2198. b) G. R. Clark, K. R. Grudy, R. O. Harris, S. M. James, and W. P. Roper, *J. Organomet. Chem.*, **90**, C37 (1975). c) T. J. Collins and W. P. Roper, *J. Organomet. Chem.*, **139**, C9 (1977). d) T. J. Collins and W. P. Roper, *J. Organomet. Chem.*, **139**, C56 (1977). e) H. Werner and K. Leonhard, *Angew. Chem., Int. Ed.*, **18**, 627 (1979). f) J. Fortune and A. R. Manning, *J. Organomet. Chem.*, **190**, C95 (1980).

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4 The reaction of cobaltacyclopentadienes with CS_2 to give dithiolactone derivatives has been reported. See, Y. Wakatsuki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, **1973**, 280. By the same group, related reactions of the cobaltacyclopentadienes with nitriles, isocyanates, sulfur, etc. have been also reported. See, a) P. Hong and H. Yamazaki, *Synthesis*, **1977**, 50. b) Y. Wakatsuki and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, **1978**, 1278. c) H. Yamazaki and Y. Wakatsuki, *J. Organomet. Chem.*, **139**, 157 (1977). d) Y. Wakatsuki and H. Yamazaki, *J. Organomet. Chem.*, **139**, 169 (1977). e) F. W. Grevels, Y. Wakatsuki, and H. Yamazaki, *J. Organomet. Chem.*, **141**, 331 (1977). f) Y. Wakatsuki and H. Yamazaki, *J. Organomet. Chem.*, **149**, 385 (1978). g) H. Yamazaki and Y. Wakatsuki, *Bull. Chem. Soc. Jpn.*, **52**, 1239 (1979). h) K. Yasufuku, A. Hamada, K. Aoki, and H. Yamazaki, *J. Am. Chem. Soc.*, **102**, 4363 (1980). i) Y. Wakatsuki, H. Yamazaki, and H. Iwasaki, *J. Am. Chem. Soc.*, **95**, 5781 (1973). j) P. Hong and H. Yamazaki, *Tetrahedron Lett.*, **15**, 1333 (1977).

5 The experimental procedure is shown as follows: a toluene (5 mL) solution of **1** (0.371 g, 0.5 mmol), CS_2 (1.9 g, 25 mmol), and **4** (0.116 g, 0.5 mmol) was heated at 80 °C for 1 day in a degassed sealed tube. After the work up of the reaction mixture, the cobalt complex (**2**) was obtained in 94% yield as a dark purple solid (0.245 g, 0.47 mmol) by column chromatography (SiO_2, benzene:THF = 30:1): mp, 264-266 °C; ^{1}H-NMR (400MHz, in $CDCl_3$, δ, ppm) 4.95 (C_5H_5, s, 5H), 6.97-7.78 (C_6H_5, m, 20H); ^{13}C-NMR (100MHz, δ, ppm) 88.06, 94.15, 127.35, 127.88, 128.04, 128.28, 131.41, 131.59, 132.03, 132.38, 144.23; IR (KBr, cm^{-1}) 3052, 2963, 1499, 1445, 1400, 1258, 1073, 826, 702. Anal. Found: C, 77.69; H, 4.91%. Calcd for $C_{34}H_{25}CoS$: C, 77.85; H, 4.80%.

6 The signal of the thiocarbonyl carbon of (η^5-cyclopentadienyl)(η^4-cyclopenta-2,4-dien-1-thione)ruthenium has been also observed at rather high field (161.82 ppm) that has been explained by the interaction with Ru atom on the neighboring molecule. See, M. Sato and M. Sensui, *Chem. Lett.*, **1996**, 991.

7 The experimental procedure is shown as follows: a benzene (10 mL) solution of **2** (0.105 g, 0.2 mmol) and iodomethane (0.5 mL, 8 mmol) was stirred at rt for 1 h. By the evaporation, **3** was obtained as a red solid quantitatively, which was further purified by recrystallization from benzene: mp, >300 °C; ^{1}H-NMR (400MHz, in $CDCl_3$, δ, ppm) 2.08 (CH_3, s, 3H), 5.80 (C_5H_5, s, 5H), 6.99-7.56 (C_6H_5, m, 20H); ^{13}C-NMR (100MHz, in $CDCl_3$, δ, ppm) 19.03, 89.07, 100.54, 101.54, 102.97, 127.47, 127.60, 128.59, 128.86, 129.60, 129.94, 131.30, 131.50; IR (KBr, cm^{-1}) 3050, 2917, 1445, 1414, 1182, 1074, 853, 737, 700, 621. Anal. Found: C, 63.00; H, 4.32%. Calcd for $C_{35}H_{28}CoSI$: C, 63.07; H, 4.23%.

8 Crystal data for **3**, $C_{35}H_{25}CoSI$, FW=663.48, red crystal, monoclinic, Cc(#9), a=9.748(5)Å, b=17.977(4)Å, c=16.740 (5)Å, β=95.18(3)°, V=2924(1)Å^3, Z=4, D_c=1.507g/cm^3, F_{000}=1324, μ(MoKα)=17.36cm^{-1}, T=296K. 2840 measured reflections, 2671 unique reflections with I>5.00σ(I) used in refinement, empirical absorption correction (ω-scan), R = 0.084 and R_ω = 0.087.