Organometallics **1985**, *4*, 389-393

Mechanism of the Thermal Extrusion of Sulfur Dioxide from (η^5-Cyclopentadienyl)cobalt η^4-Thiophene 1,1-Dioxides to Complexed Cyclobutadienes

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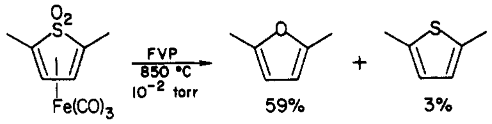
Flash vacuum pyrolysis of (η^5-cyclopentadienyl)cobalt η^4-thiophene 1,1-dioxide complexes (500–600 °C, 10^{-4} torr) effects sulfur dioxide extrusion and formation of (η^5-cyclopentadienyl)cobalt η^4-cyclobutadiene complexes. Labeling studies verify that this process occurs by an intramolecular pathway in which there is no positional isomerization. A stereochemical labeling experiment provides information which suggests that SO_2 extrusion follows a stepwise mechanism, possibly involving novel metallacyclic intermediates.

Introduction

The prospect of increasing utilization of coal and coal-derived liquids as a source of fuel and chemical feed stocks has renewed interest in the development of chemical means by which sulfur may be removed from coal.[1] Thiophene and its derivatives, which account for roughly half of all organic sulfur-containing materials in coal, have been particularly difficult to desulfurize. A potential way of eliminating sulfur from such structures would be by an oxidation–thermal desulfonation sequence. Thus, flash vacuum pyrolysis (FVP) of thiophene 1,1-dioxides derived from oxidation of the corresponding thiophenes led to the predominant formation of furans by presumed loss of "SO".[2] Small quantities of thiophenes were also produced.

Our interest focused on effecting transition-metal-mediated SO_2 extrusions from such systems in an effort to ultimately find catalytic organometallic methods by which thiophene moieties may be converted into desulfurized chemicals. Prior to our work, van Tilborg[2] pyrolyzed the iron tricarbonyl complex 1 with the expectation that SO_2 extrusion would occur to afford a metal-stabilized η^4-cyclobutadiene. Instead, the major product was the corresponding furan in addition to some of the thiophene. This study was rendered inconclusive because of extensive decomposition and metal deposition on the walls of the pyrolysis tube, most likely a result of the relatively weak Fe–CO bond (20–30 kcal mol^{-1}).[3] Our approach to this problem utilized the more robust cyclopentadienylcobalt unit wherein the Cp–Co (Cp = η^5-C_5H_5) bond strength has been estimated to be in the range of 60–70 kcal mol^{-1}.[3] Indeed, the remarkable thermal stability of the CpCo moiety has been established in previous studies aimed at discovering novel ligand rearrangements.[4] It therefore seemed promising to examine the thermal chemistry of (η^5-cyclopentadienyl)cobalt thiophene dioxides. The following discussion details the first observation of the elusive SO_2 extrusion from such complexes and describes experiments, the outcome of which has considerably narrowed the number of alternative mechanisms by which this process occurs. A preliminary report has been published.[5]



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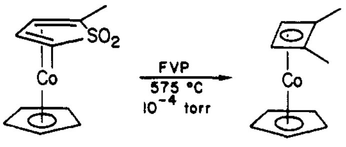
Results and Discussion

Irradiation of $CpCo(CO)_2$ and 2,5-dimethylthiophene 1,1-dioxide[6] in boiling benzene furnished the diene complex 2 (84% yield) with spectroscopic and analytical data consistent with the structure shown. In solution this compound was stable to light (medium-pressure Hg lamp) but unstable when heated beyond 200 °C to give intractable tars. In contrast, flash vacuum pyrolysis[4] of 2 afforded the cyclobutadiene complex 3 as the only isolable product (50% yield). In addition, a small amount (4% yield) of starting material was recovered, and decomposition material in the form of a cobalt mirror was found in the hot zones of the pyrolysis tube. The 1,2-disubstitution pattern in the four-membered ring of 3 was deduced from mass spectral and ^{1}H NMR data. A fragmentation peak at *m/e* 174, assignable to $CpCo(CH_3C{\equiv}CCH_3)^+$, presumably resulted from retrocyclization of the cyclobutadiene ring and loss of ethyne.[7] This ion could not have been formed directly from the 1,3-dimethyl isomer. However, because of the possibility of complicating rearrangements in the four-membered ring [4b] additional evidence for 1,2-substitution was sought by NMR spectroscopy. Gratifyingly, the ^{13}C satellites of the cyclobutadiene ^{1}H NMR signals exhibited $J(H_3H_4) < 1$ Hz. In similar compounds 1,2 disubstitution has given $J(H_3H_4) \leq 0.4$ Hz, whereas for 1,3 disubstitution $J(H_2H_4) = 9$ Hz.[4a,8]



2 3

The presence of only the 1,2-isomer indicated that SO_2 extrusion and carbon–carbon bond formation occurred without concomitant rearrangement. However, at temperatures above 620 °C 3 could be equilibrated with its

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[1] Meyers, R. A. Coal Desulfurization; Marcel Dekker: New York, 1977.

[2] (a) van Tilborg, W. J. M.; Plomp, R. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 282. (b) van Tilborg, W. J. M.; Plomp, R. *J. Chem. Soc., Chem. Commun.* **1977**, 130. (c) Fields, E. K.; Meyerson, S. *J. Am. Chem. Soc.* **1966**, *88*, 2836. (d) Squires, T. G.; Vernier, C. G.; Hodgson, B. A.; Chang, L. W.; Davis, F. A.; Panunto, T. W. *J. Org. Chem.* **1981**, *46*, 2373.

[3] Connor, J. A. *Top. Curr. Chem.* **1976**, *71*, 71.

[4] (a) Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590. (b) Ville, G.; Vollhardt, K. P. C.; Winter, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 5267; *Organometallics* **1984**, *3*, 1177. (c) Fritch, J. R.; Vollhardt, K. P. C. *Ibid.* **1978**, *100*, 3643. (d) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 409.

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[6] van Tilborg, W. J. M. *Synth. Commun.* **1976**, *6*, 583.

[7] Rausch, M. D.; Bernal, I.; Davies, B. R.; Siegal, A.; Higbie, F. A.; Westover, G. F. *J. Coord. Chem.* **1973**, *3*, 149.

[8] Brune, H. A.; Wolff, H. P.; Hüther, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys. Biol.* **1968**, *23B*, 1184.

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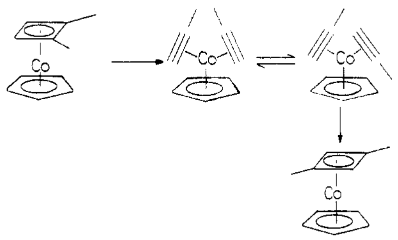
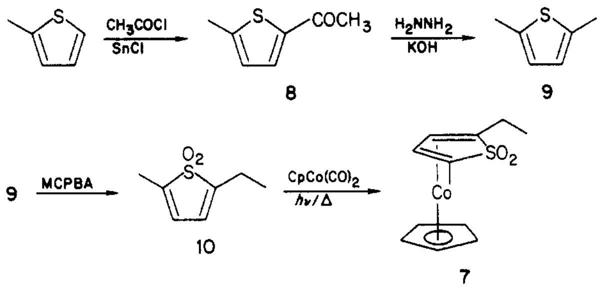
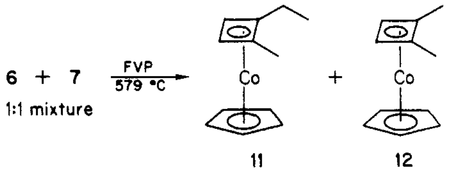
Scheme I



Scheme II

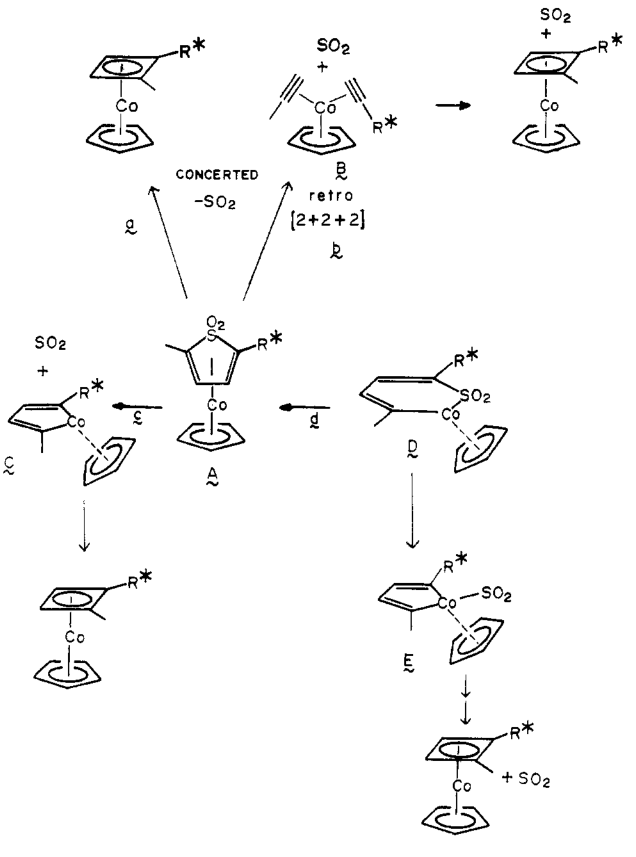


1,3-disubstituted isomer 4 [$J(H_2H_4) = 9$ Hz]. The latter was independently prepared (51% yield) by FVP of (η^5-cyclopentadienyl)cobalt 2,4-dimethylthiophene 1,1-dioxide 5, which in turn was synthesized in the same way as 2 (97% yield). Earlier work[4b,d] has shown that positional isomerizations such as that between 3 and 4 most likely proceed through retrocyclization of the four-membered ring to bis(alkyne) complexes, followed by alkyne–metal bond rotation and ring closure (Scheme I). As discussed later, it is mechanistically significant that the SO_2 extrusion reaction from 2 or 5 does not enter this manifold at the (lower) temperatures employed. That the two ligands stay attached to the metal during SO_2 extrusion was confirmed through a crossover experiment involving an equimolar mixture of the isomeric (η^5-methylcyclopentadienyl)cobalt 2,5-dimethylthiophane 1,1-dioxide (6) and (η^5-cyclopentadienyl)cobalt 2-ethyl-5-methylthiophene 1,1-dioxide (7). The former was prepared by irradiation of 2,5-dimethylthiophene 1,1-dioxide and (η^5-$CH_3C_5H_4$)$Co(CO)_2$ as described for 2. Complex 7 was obtained by the sequence of reactions shown in Scheme II. 2-Acetyl-5-methylthiophene (8), prepared by acylation of 2-methylthiophene, was reduced by the Wolff–Kishner method to give 2-ethyl-5-methylthiophene (9). The latter was converted to the 1,1-dioxide 10 with *m*-chloroperbenzoic acid. Finally, 10 and $CpCo(CO)_2$ were irradiated to afford complex 7. Flash vacuum pyrolysis of a 1:1 mixture of 6 and 7 gave equimolar amounts of the cyclobutadienes 11 and 12 (40% yield) in addition to recovered starting materials (15% yield, 6:7 ratio 1:1). As determined from ^{1}H NMR and mass spectral data, there was no indication of ligand crossover in any of the product complexes or the recovered starting materials.

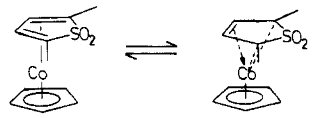


Scheme III depicts the four most reasonable mechanisms which may be proposed for loss of SO_2 from complexes 2 and 5–7. In pathway a direct loss of SO_2 would occur from A in a concerted manner. This process can be regarded as an "organometallic" cheletropic extrusion reminiscent of that observed for 2,5-dihydrothiophene dioxides,[9] which

Scheme III



Scheme IV



also involves simultaneous carbon–carbon bond formation. In contrast, b proposes a retrocyclization of A to SO_2 and a bis(alkyne) complex B which would readily convert[4b] to product either directly or via a metallacyclopentadiene of the type C.[10] The latter may be immediately accessible from A as depicted in c. Formation of C possibly could involve SO_2 expulsion from a valence tautomer of A in which the metal is bound in an η^2 manner to the ligand at C-2 and C-5 (Scheme IV). Finally, pathway d suggests a sequence beginning with metal insertion into a C–SO_2 bond to yield D, followed by loss of SO_2 to most likely give E and then C. The last mechanism is superficially related to the extensively investigated SO_2 insertion–deinsertion reactions into metal alkyls.[11]

The relative likelihood of each of these mechanisms (or their topological equivalents) was determined by carrying out a stereochemical labeling experiment. Thus, introduction of two different substituents at C-2 and C-5, one of which is chiral (as indicated in A, Scheme III), would give two diastereoisomers; the stereochemical (non)integrity of the latter during FVP was expected to provide mechanistic information about the SO_2 extrusion process. Specifically, diastereoisomerization of the product or

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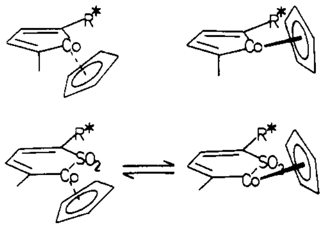
(9) Mock, W. L. *J. Am. Chem. Soc.* **1975**, *97*, 3666.

(10) (a) Yamazaki, H.; Hagihara, N. J. *J. Organomet. Chem.* **1970**, *21*, 431. (b) Gastinger, R. G.; Sullivan, D. A.; Palenik, G. J. *J. Am. Chem. Soc.* **1976**, *98*, 719. (c) McDonnell-Bushnell, L. P.; Evitt, E. R.; Bergman, R. G. *J. Organomet. Chem.* **1978**, *157*, 445. See also: (d) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

(11) Wojcicki, A. *Acc. Chem. Res.* **1971**, *4*, 344; *Adv. Organomet. Chem.* **1974**, *12*, 32.

Scheme V



Scheme VI

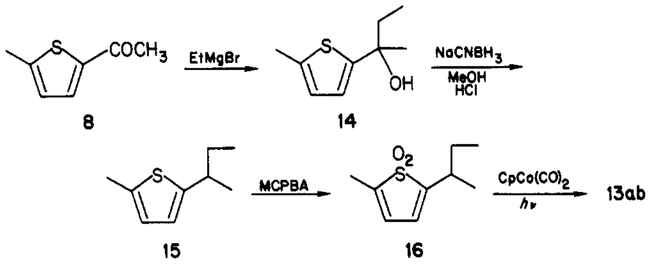


Table I. Results of the FVP of 13a and 13b

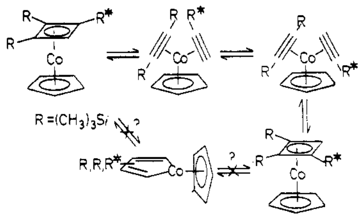
starting material	pyrolysis temp, °C	13a:13b (% yield)	17a:17b (% yield)
13a	507	87:13 (72)	50:50 (18)
	541	79:21 (37)	50:50 (36)
	575	75:25 (4)	50:50 (49)
13b	510	15:85 (70)	50:50 (18)
	540	20:80 (36)	50:50 (34)
	577	25:75 (5)	50:50 (52)

starting material was postulated to result from the intermediacy of the metallacycles C and D. As shown in Scheme V, the configurational integrity about cobalt could be lost through a rapid and reversible movement of the cyclopentadienyl ligand from one side of the metallacycle plane to the other.

With this thought in mind, the two diastereomers of (η^5-cyclopentadienyl)cobalt 2-methyl-5-*sec*-butylthiophene 1,1-dioxide (**13a,b**) were prepared (1:1 mixture) by the synthetic sequence outlined in Scheme VI. 2-Acetyl-5-methylthiophene (**8**) was treated with ethylmagnesium bromide to give the alcohol **14**. The latter was reduced to **15** through exposure to $NaCNBH_3$ and HCl in methanol.[12] Oxidation of **15** gave the 1,1-dioxide **16**, which in turn was converted to the metal complexes **13a,b** as in the preparation of **2**. The diastereomers **13a,b** were cleanly separated by HPLC.

The results of the pyrolyses of each isomer are shown in Table I. It is evident that the product cyclobutadienes **17a,b** were completely diastereoisomerized, whereas the recovered starting material did so only partially. These observations in conjunction with the absence of positional isomerization in the products or starting materials have considerably reduced the number of mechanistic options. The concerted process a in Scheme III should have produced only one cyclobutadiene isomer, while path b would have necessitated positional isomerization. The proposed configurational nonintegrity of both C and D would account for the diastereoisomerized product; however, only the intermediacy of D would provide a rationale for both stereochemical results. The unlikelihood of path c was suggested by evidence which has indicated that C might be configurationally stable under the FVP conditions employed in these experiments. Earlier work[4b] on the interconversion of diastereomeric cyclobutadiene complexes has shown that metallocyclopentadienes were not involved in this process. Scheme VII illustrates the proposed mechanism for diastereoisomerization in these systems occurring through a mechanism similar to that described earlier for positional isomerization (Scheme I). It was determined that if the metallacyclopentadienes were accessible from these systems they must have been configurationally stable. Thus, although by no means proven to be correct, path d remains as the most appealing mechanism, involving the postulate of the reversible generation of the configurationally unstable metallacycle D.

Scheme VII



Conclusion

This study of cyclopentadienylcobalt complexes of thiophene 1,1-dioxides has uncovered a novel SO_2 extrusion which may be viewed as a model step in an oxidative metal-mediated desulfurization of thiophene. Our initial premise proved to be correct in that the relatively stable CpCo unit, in contrast to $Fe(CO)_3$, remained attached to the reactive ligand and thereby gave rise to a new organometallic reaction. Labeling studies verified that this process occurs by an intramolecular pathway in which there was no positional isomerization. A stereochemical labeling experiment provided information which suggested that SO_2 extrusion follows a stepwise mechanism, possibly involving novel metallacyclic intermediates. Our hope is that this work will be of interest to mechanistic chemists in general and to those interested in particular in alternative methods for desulfurizing thiophenic structures found in industrial liquids.

Experimental Section

General Data. Melting points are uncorrected. ^1H NMR spectra were recorded on a Varian EM 390 spectrometer or UCB 250- and 200-MHz instruments equipped with Cryomagnets Inc. magnets and Nicolet Model 1180 data collection systems. ^1H NMR data are reported as follows: chemical shift in parts per million downfield of internal tetramethylsilane (multiplicity, coupling constant(s) in hertz, number of protons). Infrared spectra were obtained on either a Perkin-Elmer 297 or a Pye Unicam SP3-300 spectrometer, and all absorptions are expressed in wavenumbers (cm^{-1}). Low- and high-resolution mass spectra were recorded on AEI-MS12 and Du Pont CEC21-110B instruments, respectively, by the Mass Spectral Service at the University of California, Berkeley. Low-resolution mass spectral data are listed as m/e (intensity as a percent of base peak).

High-performance liquid chromatography was carried out with an Altex system equipped with an ultraviolet detector (254 nm) and a neutral silica gel column (Li Chrosorb Si 60, 5 μm, 10.0 mm × 25.0 cm).

Benzene was dried by distillation from CaH_2 and deoxygenated by three freeze–pump–thaw cycles. Diethyl ether and THF were distilled from sodium benzophenone ketyl prior to use. All reagents and starting materials obtained from commercial sources were used without further purification.

Flash Vacuum Pyrolysis Apparatus and Procedure. The flash vacuum pyrolysis (FVP) experiments were performed using a heated quartz tube (55 cm × 2 cm o.d.) closed at one end and connected at the other by a ground-glass joint to a cold-finger trap. The latter was attached to a vacuum line equipped with a mercury diffusion pump. An outer ground-glass 14/20 joint sealed to the top of an NMR tube was fitted to an inner 14/20

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[12] Drage, J. S.; Earl, R. E.; Vollhardt, K. P. C. *J. Heterocycl. Chem.* **1982**, *19*, 701.

ground-glass joint at the bottom of the cold-finger trap. The latter was kept full of liquid N_2 during the experiment. The FVP tube was heated by a Hoskins Type FD303A Electric Furnace, which is a tube (3.5 cm i.d. × 33 cm) surrounded by electrical heating elements, open at both ends. The temperature of the furnace was controlled by an Omega electronic thermocouple temperature controller.

The FVP experiments were carried out in the following way. The quartz tube was treated with 1,1,1,3,3,3-hexamethyldisilazane, followed by a pentane rinse. Before the tube was attached to the cold-finger trap, a 1–2-mL CH_2Cl_2 solution of the starting material was transferred to the tube. With the use of a water aspirator the CH_2Cl_2 was evaporated to leave a thin film of starting material at the closed end of the tube. The pyrolysis tube was then fitted to the cold-finger trap, and the system was evacuated to 10^{-4} torr. To sublime the starting material, a large test tube (24 cm × 3 cm o.d.) wrapped in electrical heating tape was slipped around the closed end of the pyrolysis tube and the heating tape was connected to electrical power.

After all of the starting material had sublimed, the FVP tube was allowed to cool to room temperature. Products condensed on the cold-finger were washed into the NMR tube by vacuum transfer of an NMR solvent (usually $CDCl_3$ from a solvent reservoir in the vacuum line) onto the cold-finger. Upon thawing, the solvent washed the products into the NMR tube. The products were frozen at the bottom of the NMR tube, while the latter was sealed off under vacuum. After an ^1H NMR spectrum had been recorded, the sample tube was opened and the solution subjected to chromatography.

(η^5-Cyclopentadienyl)cobalt η^4-2,5-Dimethylthiophene 1,1-Dioxide (2). 2,5-Dimethylthiophene 1,1-dioxide[6] (100 mg, 0.694 mmol) and $CpCo(CO)_2$ were dissolved in benzene (20 mL) in a 50-mL round-bottom flask. The latter was fitted with a reflux condenser which in turn was connected to an N^2/vacuum double manifold system. The solution was degassed by three freeze–pump–thaw cycles. A 300-W visible light lamp was placed 3 cm below the bottom of the flask. The solution was irradiated and heated to the boiling point for 5.5 h. The benzene was removed by vacuum transfer, and the remaining dark orange solid was washed with $CHCl_3$ to yield an orange solution. Rotary evaporation of the solvent and recrystallization of the remaining solid from toluene afforded orange crystalline **2** (mp 188–190 °C, 156 mg, 85% yield): ^1H NMR (90 MHz, $CDCl_3$) δ 5.00 (s, 2 H), 4.90 (s, 5 H), 1.70 (s, 6 H); IR ($CHCl_3$) 1260, 1150 cm^{-1}; MS, *m/e* (relative intensity) 268 (M^+, 46%), 204 (21), 189 (18), 124 (100). Anal. Calcd for $C_{11}H_{13}CoO_2S$: C, 49.25; H, 4.88. Found: C, 49.08; H, 5.00.

FVP of 2. Formation of (η^5-Cyclopentadienyl)cobalt η^4-1,2-Dimethylcyclobutadiene (3). A sample of **2** (53 mg, 0.197 mmol) was sublimed through the FVP system over a 4-h period; the furnace temperature was 575 °C, and the pressure was 1 × 10^{-4} torr. Chromatography (alumina, pentane) of the yellow material condensed in the cold finger afforded the yellow oil **3** (20 mg, 50% yield): ^1H NMR (90 MHz, $CDCl_3$) δ 4.65 (s, 5 H), 3.62 (s, 2 H), 1.60 (s, 6 H); ^{13}C satellites of the cyclobutadiene protons, $J(^{13}CH)$ = 185 Hz, $J(H_3H_4)$ < 1 Hz; MS, *m/e* (relative intensity) 204 (M^+, 63), 189 (19), 178 (6), 124 (100). Exact Mass Calcd for $C_{11}H_{13}Co$: 204.0349. Found: 204.0355.

FVP of 5. Formation of (η^5-Cyclopentadienyl)cobalt η^4-1,3-Dimethylcyclobutadiene (4). A sample of **5** (17.4 mg, 0.0649 mmol) was flash vacuum pyrolyzed at 569 °C (10^{-4} torr). The crude product was chromatographed on alumina; elution with pentane afforded the product **3** as a yellow oil (6.7 mg, 51% yield): ^1H NMR (200 MHz, $CDCl_3$) δ 4.74 (s, 5 H), 3.82 (s, 2 H), 1.51 (s, 6 H); ^{13}C NMR satellites of the cyclobutadiene protons, $J(^{13}CH)$ = 186 Hz, $J(H_2H_4)$ = 9 Hz; MS, *m/e* (relative intensity) 204 (M^+, 56), 203 (25), 189 (23), 164 (26), 124 (100). Exact Mass Calcd for $C_{11}H_{13}Co$: 204.0349. Found: 204.0341.

Elution of the chromatography column with $CHCl_3$ yielded starting material (3.8 mg, 22% yield).

(η^5-Cyclopentadienyl)cobalt η^4-2,4-Dimethylthiophene 1,1-Dioxide (5). 2,4-Dimethylthiophene 1,1-dioxide[6] (248 mg, 1.72 mmol) and $CpCo(CO)_2$ (340 mg, 1.89 mmol) were irradiated in boiling benzene (20 mL) as in the preparation of **2**. The solvent was removed by rotary evaporation, and the residue was chromatographed on alumina by eluting with $CHCl_3$. The product **5** was isolated as an orange oil (445 mg, 97% yield): ^1H NMR (200 MHz, $CDCl_3$) δ 5.04 (s, 1 H), 4.94 (s, 5 H), 4.23 (s, 1 H), 2.06 (s, 3 H), 1.60 (s, 3 H); IR ($CHCl_3$) 1260, 1150 cm^{-1}; MS *m/e* (relative intensity) 268 (M^+, 25), 204 (12), 203 (20), 189 (23), 124 (100). Exact Mass Calcd for $C_{11}H_{13}CoO_2S$: 267.9968. Found: 267.9963.

(η^5-Methylcyclopentadienyl)cobalt η^4-2,5-Dimethylthiophene 1,1-Dioxide (6). 2,5-Dimethylthiophene 1,1-dioxide (100 mg, 0.694 mmol) and (η^4-methylcyclopentadienyl)cobalt dicarbonyl (135 mg, 0.694 mmol) were irradiated in boiling benzene (20 mL) as in the preparation of **2**. Chromatography (alumina, $CHCl_3$) afforded **6** as an orange oil (115 mg, 74% yield): ^1H NMR (90 MHz, $CDCl_3$) δ 4.87 (s, 2 H), 4.60 (m, 4 H), 2.03 (s, 3 H), 1.51 (s, 6 H); IR ($CHCl_3$) 1250, 1160 cm^{-1}; MS, *m/e* (relative intensity) 282 (M^+, 17), 218 (8), 138 (31), 91 (100). Exact Mass Calcd for $C_{12}H_{15}CoO_2S$: 282.0124. Found: 282.0122.

(η^5-Cyclopentadienyl)cobalt η^4-2-Ethyl-5-methylthiophene 1,1-Dioxide (7). 2-Ethyl-5-methylthiophene 1,1-dioxide (100 mg, 0.633 mmol) and $CpCo(CO)_2$ (125 mg, 0.696 mmol) were irradiated in boiling benzene (20 mL) as in the preparation of **2**. Chromatography (alumina, $CHCl_3$) afforded **7** as an orange oil (154 mg, 86% yield): ^1H NMR (90 MHz, $CDCl_3$) δ 4.92 (s, 2 H), 4.84 (s, 5 H), 2.08 (m, 2 H), 1.60 (s, 3 H), 1.20 (t, J = 7.0 Hz, 3 H); IR ($CHCl_3$) 1250, 1160 cm^{-1}; MS, *m/e* (relative intensity) 282 (M^+, 47), 218 (10), 217 (13), 203 (21), 189 (12), 124 (100). Exact Mass Calcd for $C_{12}H_{15}CoO_2S$: 282.0124. Found: 282.0119.

2-Acetyl-5-methylthiophene (8). A 300-mL three-neck round-bottom flask was fitted with a thermometer, a 50-mL addition funnel, a magnetic stirring bar, and a $CaCl_2$ drying tube. The vessel was charged with a benzene solution (100 mL) of 2-methylthiophene (9.817 g, 0.10 mol) and acetyl chloride (7.850 g, 0.10 mol). The solution was stirred rapidly at 0 °C while stannic chloride (26.05 g, 0.10 mol) was added dropwise from the addition funnel over a 1-h period. The solution was stirred for an additional 1 h at 25 °C and then treated with dilute HCl. The benzene layer was washed once with water (25 mL) and then dried over $CaCl_2$. The benzene was removed by rotary evaporation, and the remaining liquid was purified by Kugelrohr distillation (75 °C, 0.1 torr) to yield colorless liquid **8** (8.963 g, 64% yield): ^1H NMR (90 MHz, $CDCl_3$) δ 7.45 (d, J = 3 Hz, 1 H), 6.71 (d, J = 3 Hz, 1 H), 2.48 (s, 3 H), 2.45 (s, 3 H); IR (neat) 1650 cm^{-1}; MS, *m/e* (relative intensity) 140 (M^+, 35), 125 (100). Anal. Calcd for C_7H_8OS: C, 59.97; H, 5.75; S, 22.87. Found: C, 60.24; H, 5.82; S, 22.56.

2-Ethyl-5-methylthiophene (9). 2-Acetyl-5-methylthiophene (**8**) (7.806 g, 0.0557 mol) and hydrazine hydrate (85% NH_2NH_2, 9.48 g, 0.189 mol) were added to ethylene glycol (100 mL) in a 200-mL three-neck round-bottom flask. The latter was fitted with a thermometer, a glass stopper, reflux condenser, and magnetic stirring bar. Potassium hydroxide (12 g) was added, and the solution was heated to 140–160 °C for 8 h. The ethylene glycol solution was extracted five times with pentane. The pentane extracts were combined, washed with water twice, and dried over $CaCl_2$. The pentane was removed by distillation at ambient pressure. The remaining liquid was Kugelrohr distilled (40 °C, 0.10 torr) to yield colorless liquid **9** (2.511 g, 36% yield): ^1H NMR (90 MHz, $CDCl_3$) δ 6.48 (s, 2 H), 2.71 (q, J = 7 Hz, 2 H), 2.37 (s, 3 H), 1.24 (t, J = 7 Hz, 3 H). MS *m/e* (relative intensity) 126 (M^+, 38), 111 (100). Anal. Calcd for $C_7H_{10}S$: C, 66.61; H, 7.99; S, 25.40. Found: C, 66.63; H 7.99; S, 25.26.

2-Ethyl-5-methylthiophene 1,1-Dioxide (10). A solution of 2-ethyl-5-methylthiophene (**9**) (2.235 g, 0.0177 mol) in CH_2Cl_2 (20 mL) was added to a rapidly stirred suspension of *m*-chloroperbenzoic acid (9.154 g, 0.0531 mol) maintained at 0 °C. The addition period was 1 h. The reaction mixture was stirred for an additional 2 h. The workup procedure was identical with that used by van Tilborg.[5] The crude product was chromatographed on alumina, eluting with ether–pentane mixtures. White crystals of **10** were obtained (mp 39.0–41.5 °C, 1.23 g, 44% yield): ^1H NMR (90 MHz, $CDCl_3$) δ 6.24 (s, 1 H), 6.22 (s, 1 H), 2.47 (q, J = 7 Hz, 2 H), 2.05 (s, 3 H), 1.25 (t, J = 7 Hz, 3 H); IR ($CHCl_3$) 1295, 1150 cm^{-1}; MS, *m/e* (relative intensity) 158 (M^+, 28) 110 (26), 95 (100). Anal. Calcd for $C_7H_{10}O_2S$: C, 53.14; H, 6.37; S, 20.26. Found: C, 53.43; H, 6.39; S, 19.90.

Crossover Experiment. FVP of 1:1 Mixture of 6 and 7. Formation of 11 and 12. A mixture of **6** (27 mg, 0.0957 mmol) and 7 (27 mg, 0.0957 mmol) was pyrolyzed at 575 °C (10^{-4} torr). The reaction mixture was chromatographed on alumina; elution with pentane afforded a 1:1 mixture of 11 and 12 (17 mg, 40%); elution with $CHCl_3$ gave a 1:1 mixture of 6 and 7 (8 mg, 15%).

The first fraction was found to contain only the cyclobutadiene complexes 11 and 12 (inseparable). 11: ^1H NMR (250 MHz, $CDCl_3$) δ 4.64 (m, 2 H), 4.55 (m, 2 H), 3.61 (s, 2 H), 2.02 (s, 3 H), 1.50 (s, 6 H). 12: ^1H NMR (250 MHz, $CDCl_3$) δ 4.77 (s, 5 H), 3.72 (s, 1 H), 3.65 (s, 1 H), 1.89 (q, J = 7.0 Hz, 2 H), 1.54 (s, 3 H), 1.01 (t, J = 7.0 Hz, 3H). MS of mixture of 11 and 12: m/e (relative intensity) 218 (M^+, 71), 203 (44), 189 (12), 138 (59), 124 (100). Exact Mass Calcd for $C_{12}H_{15}Co$: 218.0506. Found: 218.0507.

^1H NMR and mass spectral (m/e M^+, 282) data for the second fraction indicated the presence of only 6 and 7.

(η^5-Cyclopentadienyl)cobalt η^4-2-Methyl-5-*sec*-butylthiophene 1,1-Dioxides (13a,b). 2-Methyl-5-*sec*-butylthiophene 1,1-dioxide (**16**) (1.008 g, 5.41 mmol) and $CpCo(CO)_2$ (1.073 g, 5.96 mmol) were irradiated in boiling benzene (20 mL) as in the preparation of **2**. Chromatography afforded a 1:1 mixture of **13a,b** (1.60 g, 95% yield). The two diastereomers were cleanly separated by HPLC (silica gel, $CHCl_3$).

13a: orange oil; ^1H NMR (250 MHz, $CDCl_3$) δ 5.02 (d, J = 3.8 Hz, 1 H), 4.99 (d, J = 3.8 Hz, 1 H), 4.92 (s, 5 H), 2.37 (m, 1 H), 1.88 (m, 1 H), 1.60 (s, 3 H), 1.52 (m, 1 H), 1.06 (d, J = 7.0 Hz), 0.90 (t, J = 7.4 Hz, 3 H); IR ($CHCl_3$) 1254, 1161 cm^{-1}; MS, m/e (relative intensity) 310 (M^+, 53) 246 (6), 244 (28), 124 (100). Exact Mass Calcd for $C_{14}H_{19}CoO_2S$: 310.0437. Found: 310.0439.

13b: orange oil; ^1H NMR (250 MHz, $CDCl_2$) δ 5.00 (s, 2 H), 4.94 (s, 5 H), 2.02 (m, 1 H), 1.75 (m, 1 H), 1.59 (s, 3 H), 1.37 (m, 1 H), 1.35 (d, J = 7.0 Hz, 3 H), 0.95 (t, J = 7.4 Hz, 3 H); IR ($CHCl_3$) 1252, 1165 cm^{-1}; MS m/e 310 (M^+, 57), 246 (5), 244 (27), 124 (100). Exact Mass Calcd for $C_{14}H_{19}CoO_2S$: 310.0437. Found: 310.0437.

2-(1-Hydroxy-1-methylpropyl)-5-methylthiophene (14). 5-Acetyl-2-methylthiophene (**8**) (18.543 g, 132 mmol), dissolved in dry diethyl ether (50 mL), was added over a 2-h period to a diethyl ether solution (150 mL) of ethylmagnesium bromide (0.15 mol). After being stirred overnight, the solution was treated with 25% NH_4Cl. The diethyl ether layer was washed twice with water and then dried over $CaCl_2$. The solvent was removed by rotary evaporation, and the resulting crude liquid was Kugelrohr distilled (100 °C, 0.1 torr) to afford colorless liquid 14 (16.750 g, 74% yield): ^1H NMR (90 MHz, CCl_4) δ 6.49 (d, J = 3 Hz), 6.37 (m, 1 H), 2.33 (s, 3 H), 2.12 (s, 1 H), 1.78 (q, J = 7 Hz, 2 H), 1.42 (s, 3 H), 0.80 (t, J = 7 Hz, 3 H); IR (neat) 3410, 3160, 2970, 2920, 2880, 1454, 1370, 1230, 1160, 1125, 1047, 989, 911, 799 cm^{-1}; MS, m/e (relative intensity) 170 (M^+, 0.8), 153 (12), 152 (100), 138 (10), 137 (99.6), 125 (18), 123 (52). Anal. Calcd for C_9H_4OS: C, 63.48; H, 8.29; S, 18.83. Found: C, 63.35; H, 8.08; S, 19.02.

2-Methyl-5-*sec*-butylthiophene (15). The alcohol 14 (16.650 g, 97.8 mmol) and $NaCNBH_3$ (6.776 g, 108 mmol) were dissolved in absolute methanol (120 mL). A pinch of Methyl Orange indicator was added to the reaction mixture to give an intense yellow solution. A 6 N HCl solution was added dropwise until the solution became reddish pink. When the acid was consumed, the yellow color returned, and more HCl was added to again give the reddish pink color. This sequence was repeated until addition of HCl produced no effect. The solution was diluted with diethyl ether, washed three times with saturated NaCl solution, and dried over $CaCl_2$. Rotary evaporation of the solvent afforded a slightly yellow liquid; Kugelrohr distillation gave colorless liquid **15** (14.27 g, 95% yield): ^1H NMR (250 MHz, $CDCl_3$) δ 6.60 (s, 2 H), 2.82 (apparent sextet, J = 7.0 Hz, 1 H), 2.49 (s, 3 H), 1.61 (m, 2 H), 1.28 (d, J = 7.0 Hz, 3 H), 0.94 (t, J = 7.0 Hz, 3 H); MS, m/e (relative intensity) 154 (M^+, 22), 139 (7), 125 (100). Anal. Calcd for $C_9H_{14}S$: C, 70.07; H, 9.15; S, 20.78. Found: C, 69.94; H, 9.06; S, 20.96.

2-Methyl-5-*sec*-butylthiophene 1,1-Dioxide (16). A solution of **15** (3.857 g, 25 mmol) in CH_2Cl_2 (15 mL) was added over a 1-h period to a rapidly stirred suspension of *m*-chloroperbenzoic acid (12.93 g, 75 mmol) in CH_2Cl_2 maintained at 0 °C. The solution was stirred for an additional 3 h at 0 °C. Workup of the reaction mixture was carried out as described in the literature.[6] Chromatography of the crude product (alumina, diethyl ether–pentane mixtures) afforded the colorless oil **16** (1.163 g, 25% yield): ^1H NMR (250 MHz, $CDCl_3$) δ 6.22 (apparent s, 2 H), 2.70 (apparent sextet, J = 7.0 Hz, 1 H), 2.06 (s, 3 H), 1.74 (m, 1 H), 1.57 (m, 1 H), 1.22 (d, J = 7.0 Hz, 3 H), 0.90 (t, J = 7.0 Hz, 1 H); IR ($CHCl_3$) 1290, 1225, 1135 cm^{-1}; MS, m/e (relative intensity) 186 (M^+, 9), 169 (7), 157 (3), 125 (49), 107 (100), 91 (84), 79 (63). Exact Mass Calcd for $C_9H_{14}O_2S$: 186.0714. Found: 186.0717.

FVP of Complexes 13a,b. Formation of (η^4-Cyclopentadienyl)cobalt η^4-1-Methyl-2-*sec*-butylcyclobutadienes (17a,b). The diastereomers **13a,b** were independently subjected to flash vacuum pyrolysis at temperatures between 507 and 575 °C. In each experiment about 30 mg of the starting material was used. The reaction mixtures were chromatographed on alumina using pentane to elute the cyclobutadiene complexes **17a** and **17b** and then using $CHCl_3$ to elute the complexes **13a,b**. The results are shown in Table I. The complexes **17a,b** were inseparable: yellow oil; ^1H NMR (250 MHz, $CDCl_3$) δ 4.78 (s, 5 H), 4.77 (s, 5 H), 3.74 (s, 1 H), 3.72 (s, 1 H), 3.61 (s, 1 H), 3.60 (s, 1 H), 1.58 (s, 3 H), 1.56 (s, 3 H), 1.43–1.15 (m, 4 H), 1.02 (d, J = 5.0 Hz, 3 H), 1.00 (d, J = 5.0 Hz, 3 H) 0.87 (t, J = 7.6 Hz, 3 H), 0.83 (t, J = 7.6 Hz, 3 H); MS, m/e (relative intensity) 246 (M^+, 74), 231 (24), 217 (60), 124 (100). Exact Mass Calcd for $C_{14}H_{19}Co$: 246.0818. Found: 246.0817.

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