Oligomerization Chemistry of a Metallabenzene Cycloadduct. Synthesis and Structure of an Organometallic Crown Compound[1]

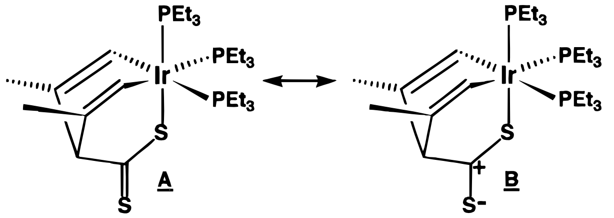
John R. Bleeke,* Robert Behm, and Alicia M. Beatty

Department of Chemistry, Washington University, St. Louis, Missouri 63130

Received December 17, 1996[⊗]

Summary: The CS_2 adduct of "iridabenzene" undergoes dimerization and cyclotrimerization reactions by linking subunits through thiocarbonyl sulfur centers. The cyclotrimerization product (compound **4***) has been structurally characterized and contains a novel organometallic trithia-12-crown-3 ring system.*

During the past several years we have been studying the reaction chemistry of a metallabenzene complex, $\overline{CH{=}C(Me)CH{=}C(Me)CH{=}Ir}(PEt_3)_3$ (**1**).[1,2] "Iridabenzene" **1** is ideally suited to participate in cycloaddition reactions because (a) it has a square pyramidal coordination geometry with an open face that allows close approach of substrate molecules and (b) it possesses a reactive metalladiene moiety held rigid in a cisoid geometry. Earlier, we reported that treatment of **1** with carbon disulfide leads to a clean [4 + 2] cycloaddition reaction in which the substrate adds across iridium and C3 of the iridabenzene ring, producing adduct **2** (Scheme 1).[1] The X-ray crystal structure of **2** is shown in Figure 1;[3] important bond distances and angles are reported in the figure caption. One striking feature of the structure of **2** is the relatively long C8−S2 bond length, 1.678(12) Å. This bond, although formally a double bond, is as long as single bond C8−S1, suggesting that resonance structure **B** is an important contributor to bonding in **2**. This view is supported by the observation that C8 resonates far downfield in the ^{13}C NMR spectrum (δ 252.0),[4] indicating a substantial positive charge on C8. We now report that the basicity of S2 also plays an important role in the chemistry of **2**, allowing subunits of **2** to be linked together in novel dimerization and trimerization reactions.



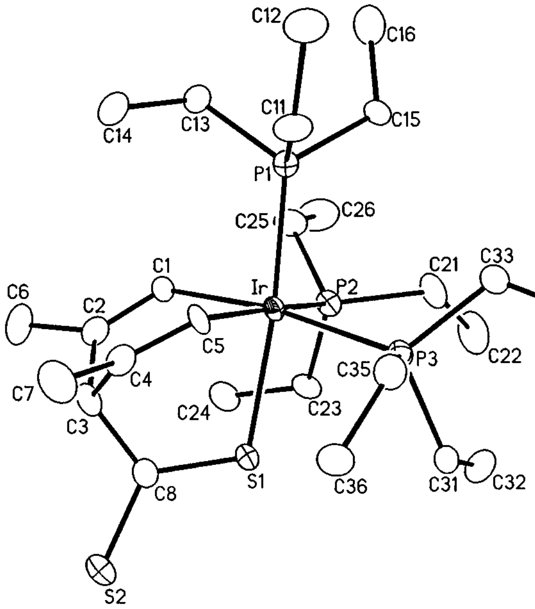


Figure 1. ORTEP drawing of $CH{=}C(Me)CHC(Me){=}CHIr\text{-}[SC(S)](PEt_3)_3$ (**2**). Selected bond distances (Å): Ir-P1, 2.317(3); Ir-P2, 2.396(4); Ir-P3, 2.405(4); Ir-S1, 2.418(3); Ir-C1, 2.077(11); Ir-C5, 2.078(15); S1−C8, 1.672(16); S2−C8, 1.678(12); C1−C2, 1.307(21); C2−C3, 1.558(19); C2−C6, 1.520(20); C3−C4, 1.544(16); C3−C8, 1.504(17); C4−C5, 1.323(21); C4−C7, 1.518(25). Selected bond angles (deg): S1−Ir−C1, 86.5(3); S1−Ir−C5, 85.2(3); C1−Ir−C5, 84.3(5); Ir−S1−C8, 106.4(4); Ir−C1−C2, 124.0(9); C1−C2−C3, 120.1(11); C2−C3−C4, 109.0(9); C2−C3−C8, 109.9(12); C4−C3−C8, 108.5(10); C3−C4−C5, 120.9(14); Ir−C5−C4, 123.0(9); S1−C8−S2, 121.7(7); S1−C8−C3, 120.1(9); S2−C8−C3, 118.2(11).

When compound **2** is dissolved in tetrahydrofuran-d_8 at room temperature and monitored by $^{31}P\{^1H\}$ NMR spectroscopy, six new signals slowly grow in. One of these signals (a singlet) is due to free PEt_3, while the other five resonances are due to dimer **3** (Scheme 1).[5] The PEt_3 ligands on the tris(phosphine) subunit of **3** give rise to three doublet-of-doublet signals, while the PEt_3 ligands on the bis(phosphine) subunit give rise to two doublets. The presence of five inequivalent phosphines in **3** clearly indicates that one of the *equatorial* phosphines (i.e., one of the phosphines *trans* to the iridacyclohexadiene ring) has been replaced by sulfur rather than the unique axial phosphine. If axial PEt_3 replacement had occurred, the dimeric product would have retained mirror-plane symmetry and only three PEt_3 signals would have been expected. Replacement of an

---

[⊗] Abstract published in *Advance ACS Abstracts*, March 1, 1997.

[1] Metallacyclohexadiene and Metallabenzene Chemistry. 12. Part 11: Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606. Part 10: Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Clayton, T. W., Jr.; Robinson, K. D. *J. Am. Chem. Soc.* **1994**, *116*, 4093.

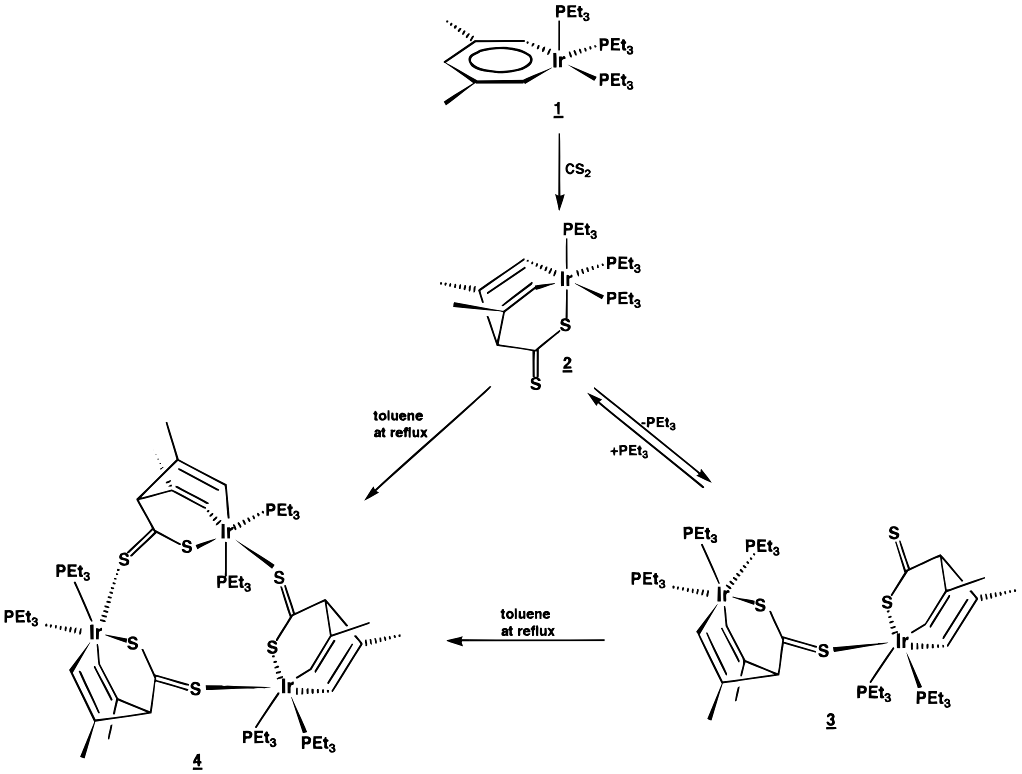
[2] Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271.

[3] Crystal data for **2**: yellow prism, 0.18 × 0.24 × 0.14 mm; triclinic, space group $P\bar{1}$, $a = 10.624(6)$ Å, $b = 10.998(7)$ Å, $c = 15.492(7)$ Å, $\alpha = 84.35(4)°$, $\beta = 88.40(4)°$, $\gamma = 62.47(4)°$, $V = 1597.0(15)$ Å^3, $Z = 2$, $d_{calcd} = 1.489$ g/cm^3, $\mu = 44.74$ cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 23 °C, $\theta-2\theta$ scanning technique, 5670 unique reflections with $3.0° < 2\theta < 50.0°$ collected, 3563 reflections with $I > 3\sigma(I)$ used in refinement; semi-empirical absorption correction; $R = 0.0450$, $R_w = 0.0548$, GOF = 0.89.

[4] Full NMR characterization for **2** is given in Part 11 of this series of papers (see ref 1).

S0276-7333(96)01070-9 CCC: $14.00

Scheme 1



equatorial phosphine can be readily rationalized on the basis of bond lengths; the Ir-P_{eq} bonds in compound **2** (2.396(4) and 2.405(4) Å) are significantly longer and therefore weaker than the Ir-P_{ax} bond (2.317(3) Å). The arrangement of the phosphines in **3** is confirmed by the $^{13}C\{^1H\}$ NMR spectrum, where three of the four ring C_α signals show strong C−P coupling due to the presence of a *trans* PEt_3 ligand, while the fourth C_α signal does not because it lies *trans* to the linking sulfur atom.[5]

At room temperature, an equilibrium between compounds **2** and **3** in tetrahydrofuran-d_8 is reached in about 6 h and the equilibrium ratio of **2**:**3** is approximately 2:1. As the temperature of the sample is raised, the equilibrium shifts toward dimer **3** and at 55 °C, the equilibrium ratio of **2**:**3** stands at ~1:1. Cooling the sample back to room temperature causes the original equilibrium to be reestablished. Addition of excess PEt_3 to the mixture converts all of the dimer back to monomer.

Dimer **3** can be isolated in pure form by stirring **2** in tetrahydrofuran for 6 h, removing the volatiles (including free PEt_3), readding tetrahydrofuran, stirring for another 6 h, removing the volatiles, etc. After five cycles, the sample contains >90% compound **3**, which crystallizes as yellow prisms upon cooling to −30 °C.[6]

When compound **2** or **3** is heated in toluene at reflux, while purging with N_2 to remove PEt_3, trimer **4** (Scheme 1) is cleanly and irreversibly generated.[7] The $^{31}P\{^1H\}$ NMR spectrum of **4** consists of six doublets due to six phosphines that are each coupled to one neighboring phosphine.[8] The presence of six inequivalent phosphines clearly indicates that the three subunits have been linked together as shown in Scheme 1. Note that three of the phosphine ligands lie approximately in the plane of the three iridium atoms, while the other three lie roughly perpendicular to that plane. Of the three perpendicular phosphines, one projects above the iridium plane while the other two project below it. If all three perpendicular phosphines were to project in the same direction, the molecule would possess 3-fold symmetry and only two phosphine signals would be expected in the ^{31}P NMR spectrum. Space-filling models suggest that this high-symmetry arrangement would result in

---

(5) Spectroscopic data for **3**: ^1H NMR (tetrahydrofuran-d_8, 22 °C): δ 7.70 (m, H_α, 1), 7.05 (m, H_α, 2), 6.82 (m, H_α, 1), 5.00 (s, H_γ, 1), 4.81 (s, H_γ, 1), 2.5−2.1 (m, ring CH_3 and PEt_3 CH_2s, 42), 1.6−1.2 (m, PEt_3 CH_3s, 45). $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8, 22 °C): δ 251.1 (s, C=S), 233.0 (s, C=S), 133.5 (s, C_β), 131.4 (s, C_β), 131.2 (s, C_β), 130.0 (s, C_β), 129.4 (dd, J_{C-P} = 83.5 Hz, 9.0 Hz, C_α), 129.2 (dt, J_{C-P} = 77.7, 8.3 Hz, C_α), 128.4 (dt, J_{C-P} = 75.9 Hz, 8.0 Hz, C_α), 120.1 (s, C_α), 90.2 (s, C_γ), 88.4 (s, C_γ), 27.8 (d, J_{C-P} = 8.8 Hz, ring CH_3), 27.4 (s, ring CH_3), 26.9 (d, J_{C-P} = 7.2 Hz, ring CH_3), 26.8 (d, J_{C-P} = 8.0 Hz, ring CH_3), 19.4 (d, J_{C-P} = 30.9 Hz, PEt_3 CH_2s), 18.7 (d, J_{C-P} = 24.4 Hz, PEt_3 CH_2s), 18.4 (d, J_{C-P} = 22.8 Hz, PEt_3 CH_2s), 16.6 (d, J_{C-P} = 30.9 Hz, PEt_3 CH_2s), 15.9 (d, J_{C-P} = 21.9 Hz, PEt_3 CH_2s), 9.6 (s, PEt_3 CH_3s), 9.3 (s, PEt_3 CH_3s), 9.2 (s, PEt_3 CH_3s), 8.3 (s, PEt_3 CH_3s), 8.2 (s, PEt_3 CH_3s). $^{31}P\{^1H\}$ NMR (tetrahydrofuran-d_8, 22 °C): δ −25.6 (d, J_{P-P} = 13.9 Hz, PEt_3 on bis(phosphine) subunit, 1), −27.7 (dd, J_{P-P} = 15.8 Hz, PEt_3 on tris(phosphine) subunit, 1), −33.3 (d, J_{P-P} = 13.9 Hz, PEt_3 on bis(phosphine) subunit, 1), −36.6 (dd, J_{P-P} = 15.8 Hz, PEt_3 on tris(phosphine) subunit, 1), −37.5 (dd, J_{P-P} = 15.8 Hz, PEt_3 on tris(phosphine) subunit, 1).

(6) Synthesis of compound **3**. Compound **2** (0.26 g, 3.7×10^{-4} mol) was dissolved in ~30 mL of tetrahydrofuran and stirred at 25 °C for 6 h (to establish equilibrium between **2** and **3**). The volatiles (including PEt_3) were then removed under vacuum. The resulting yellow residue was redissolved in tetrahydrofuran, stirred for an additional 6 h, and again stripped to dryness. This procedure was repeated five times, leading to a yellow powder that contained **3** in >90% purity. The powder was dissolved in acetone and cooled to −30 °C overnight, producing crystals of **3**. Yield: 76%. Anal. Calcd for $C_{46}H_{93}Ir_2P_5S_4$: C, 42.05; H, 7.15. Found: C, 42.35; H, 7.50.

(7) Synthesis of compound **4**. Compound **2** (0.34 g, 4.7×10^{-4} mol) was dissolved in ~30 mL of toluene and heated at reflux for 1.5 h, while purging with a slow stream of N_2 to remove PEt_3. The toluene was then removed under vacuum, and the yellow residue was dissolved in pentane and filtered through Celite. The pentane was removed under vacuum, and the resulting yellow powder was dissolved in acetone. Slow evaporation of the acetone solution yielded crystalline **4**. Yield: 97%. Anal. Calcd for $C_{60}H_{117}Ir_3P_6S_6$: C, 40.18; H, 6.59. Found: C, 40.16; H, 6.73.

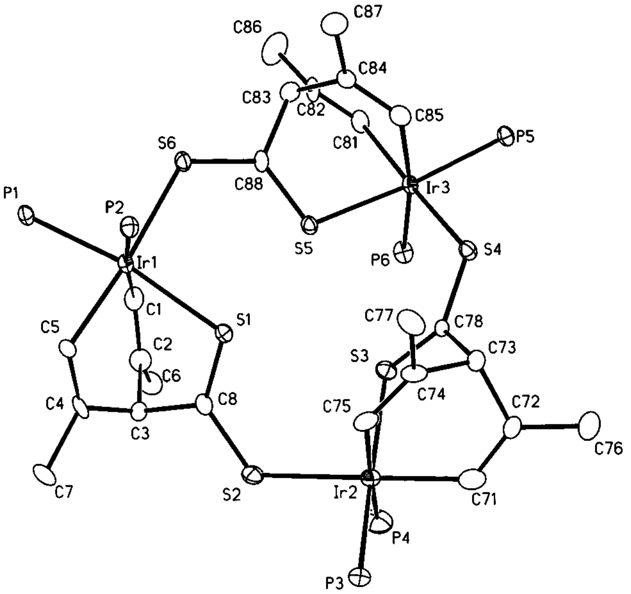
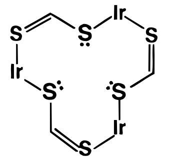


Figure 2. ORTEP drawing of {CH═C(Me)CHC(Me)═CHIr[SC(S)](PEt$_3$)$_2$}$_3$ (**4**), with ethyl groups on PEt$_3$ ligands removed for clarity. Selected bond distances (Å): Ir1−S1, 2.411(3); Ir1−S6, 2.442(3); Ir2−S3, 2.402(3); Ir2−S2, 2.417(4); Ir3−S5, 2.386(3); Ir3−S4, 2.432(3); S1−C8, 1.655(12); S2−C8, 1.713(11); S3−C78, 1.662(12); S4−C78, 1.683(10); S5−C88, 1.662(10); S6−C88, 1.667(11). Selected bond angles (deg): S1−Ir1−S6, 98.71(10); S3−Ir2−S2, 91.84(11); S5−Ir3−S4, 89.11(10); C8−S1−Ir1, 104.2(5); C8−S2−Ir2, 122.5(5); C78−S3−Ir2, 106.0(3); C78−S4−Ir3, 122.2(4); C88−S5−Ir3, 106.6(4); C88−S6−Ir1, 122.6(4); S1−C8−S2, 126.5(9); S3−C78−S4, 126.4(6); S5−C88−S6, 126.5(7).

intolerable steric interactions involving the three perpendicular PEt$_3$ ligands.

The structure of compound **4** has been confirmed by X-ray crystallography (Figure 2).[9] As expected, one perpendicular phosphine (P2) lies above the iridium plane while the other two (P4 and P6) lie below it. The three thiocarbonyl C−S bonds in **4** are actually slightly longer than the three internal C−S bonds (1.69 vs 1.66 Å), again indicating the importance of the resonance structure that places a formal negative charge on sulfur (*vida supra*). Consistent with this picture is the observation that the three Ir−S bonds involving thiocarbonyl sulfurs are only slightly longer than the three internal Ir−S bonds (2.43 vs 2.40 Å). Perhaps the most interesting feature of the structure of **4** is the presence of an organometallic trithia-12-crown-3 ring.[10] Although the



S$_3$ cavity in **4** appears to be too small to accommodate guests,[11] one can easily visualize synthetic strategies for expanding the ring while maintaining the S$_3$ binding pocket. Higher oligomers may also be obtainable through appropriate steric tuning of the precursors. Investigations in these directions are underway.

Acknowledgment. We thank the National Science Foundation (Grants CHE-9003159 and CHE-9303516) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A loan of IrCl$_3$•3H$_2$O from Johnson-Matthey Aesar/Alfa is gratefully acknowledged. Washington University's X-ray Crystallography Facility was funded by the NSF's Chemical Instrumentation Program (Grant CHE-8811456). R.B. thanks the U.S. Department of Education for a G. A. A. N. N. Fellowship.

Supporting Information Available: ORTEP diagrams, structure determination summary tables and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for **2** and **4** (23 pages). Ordering information is given on any current masthead page.

OM961070A

---

(8) Spectroscopic data for **4**: ^{1}H NMR (benzene-d_6, 22 °C): δ 8.00 (m, H$_\alpha$, 1), 7.57 (m, H$_\alpha$, 1), 7.05 (m, H$_\alpha$, 1), 6.92 (m, H$_\alpha$, 2), 6.73 (m, H$_\alpha$, 1), 5.34 (s, H$_\gamma$, 1), 5.31 (s, H$_\gamma$, 1), 5.23 (s, H$_\gamma$, 1), 2.51 (s, ring CH$_3$s, 6), 2.46−2.38 (s, ring CH$_3$s, 12), 2.34−1.72 (m, PEt$_3$ CH$_2$s, 36), 1.12−0.88 (m, PEt$_3$ CH$_3$s, 54). ^{13}C{^{1}H} NMR (benzene-d_6, 22 °C): δ 238.1 (s, C═S), 237.1 (s, C═S), 231.3 (s, C═S), 138.2 (dd, $J_{C-P} = 86.6$, 10.8 Hz, C$_\alpha$), 133.1 (dd, $J_{C-P} = 83.1$ Hz, 10.8 Hz, C$_\alpha$), 131.7 (dd, $J_{C-P} = 83.8$ Hz, 10.1 Hz, C$_\alpha$), 131.6 (s, C$_\beta$), 131.3 (s, C$_\beta$), 131.2 (s, C$_\beta$), 130.5 (s, C$_\beta$), 128.8 (s, C$_\beta$), 128.3 (s, C$_\beta$), 122.6 (dd, $J_{C-P} = 10.1$ Hz, 5.5 Hz, C$_\alpha$), 121.6 (dd, $J_{C-P} = 7.5$ Hz, C$_\alpha$), 121.2 (dd, $J_{C-P} = 8.1$ Hz, C$_\alpha$), 89.0 (s, C$_\gamma$), 88.6 (s, C$_\gamma$), 27.3 (s, ring CH$_3$), 27.2 (s, ring CH$_3$), 27.2 (d, ring CH$_3$), 27.1 (s, ring CH$_3$), 26.6 (d, $J_{C-P} = 8.4$ Hz, ring CH$_3$), 26.5 (d, $J_{C-P} = 8.4$ Hz, ring CH$_3$), 17.8 (d, $J_{C-P} = 20.3$ Hz, PEt$_3$ CH$_2$s), 17.7 (d, $J_{C-P} = 30.0$ Hz, PEt$_3$ CH$_2$s), 16.6 (d, $J_{C-P} = 30.9$ Hz, PEt$_3$ CH$_2$s), 16.5 (d, $J_{C-P} = 21.9$ Hz, PEt$_3$ CH$_2$s), 16.0 (d, $J_{C-P} = 31.7$ Hz, PEt$_3$ CH$_2$s), 15.4 (d, $J_{C-P} = 22.7$ Hz, PEt$_3$ CH$_2$s), 8.8 (s, PEt$_3$ CH$_3$s), 8.4 (s, PEt$_3$ CH$_3$s), 8.3 (s, PEt$_3$ CH$_3$s), 8.2 (s, PEt$_3$ CH$_3$s), 8.0 (s, PEt$_3$ CH$_3$s), 7.9 (s, PEt$_3$ CH$_3$s). ^{31}P{^{1}H} NMR (acetone-d_6, 22 °C): δ −21.7 (d, $J_{P-P} = 13.4$ Hz, 1), −27.1 (d, $J_{P-P} = 14.2$ Hz, 1), −27.4 (d, $J_{P-P} = 15.5$ Hz, 1), −28.2 (d, $J_{P-P} = 15.5$ Hz, 1), −30.9 (d, $J_{P-P} = 14.2$ Hz, 1), −34.1 (d, $J_{P-P} = 13.4$ Hz, 1).

(9) Crystal data for **4**: yellow irregular, 0.66 × 0.52 × 0.46 mm; triclinic, space group $P\bar{1}$, $a = 12.082(3)$ Å, $b = 12.636(6)$ Å, $c = 25.244(9)$ Å, $\alpha = 91.61(3)°$, $\beta = 97.30(3)°$, $\gamma = 101.58(3)°$, $V = 3739(2)$ Å^3, $Z = 2$, $d_{calcd} = 1.593$ g/cm^3, $\mu = 56.54$ cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 22 °C, ω scanning technique, 9960 unique reflections with $3.0° < 2\theta < 55.0°$ collected, 6929 reflections with $I > 2\sigma(I)$ used in refinement; semi-empirical absorption correction; $R = 0.0476$, $R_w = 0.0966$, GOF = 1.07.

(10) For a review of crown compounds, see: Hiraoka, M. *Crown Compounds-Their Characteristics and Applications*; Elsevier: Amsterdam, 1982, and references cited therein.

(11) In the solid state, the distance from each sulfur atom to the center of the ring is only about 2.0 Å.