Regio- and Stereocontrolled Nucleophilic Addition Reactions of a Phenylthio-Substituted Cyclohexadiene-Containing η^4-Molybdenum Cationic Complex

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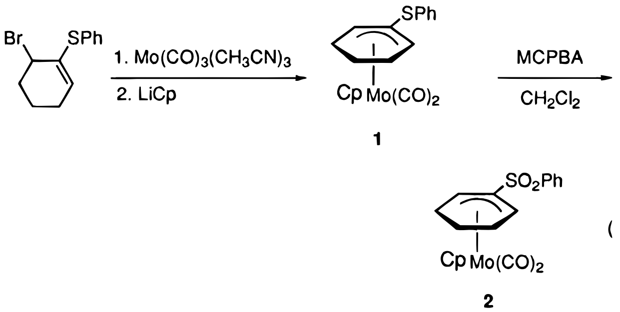
*Summary: The reaction of a new cationic complex, [Cp(CO)$_2$Mo(η^4-2-SPh-C$_6$H$_7$)]$^+$PF$_6^-$ (**3**), with carbon and sulfur nucleophiles was found to give in most cases the C-4 addition products **4** in good yield. The X-ray crystal structure of one of the addition products **4b** confirms the regio- and stereochemistry of the reaction.*

The control of regio- and stereochemistry in the carbon−carbon bond formation is one of the central issues in contemporary organic synthesis.[1] The use of (diene)molybdenum[2] and dienyliron[3] complexes has proven to be an important method for controlling the regio- and stereochemistry using the transition-metal moiety as a directing template. The addition of nucleophiles to cyclic (diene)molybdenum cationic complexes proceeds stereospecifically *trans* to the metal.[4] Unsymmetrically substituted dienyliron cationic complexes have often been used in nucleophilic addition reactions,[5] but unsymmetrical (diene)molybdenum complexes have scarcely been reported.[6] In this study we describe the synthesis of a new cationic molybdenum complex **3** bearing a phenylthio group at C-2 and the regio- and stereoselectivity in the nucleophilic addition reaction.

The η^3-2-SPh-cyclohexenyl-Mo(CO)$_2$Cp complex **1** was prepared in 43% yield by treatment of 3-bromo-2-(phenylthio)cyclohexene[7] with Mo(CO)$_3$(CH$_3$CN)$_3$ in acetonitrile, followed by the reaction with cyclopentadienyl anion (eq 1).[8] The structure of **1** was confirmed by its oxidation with *m*-CPBA to give the corresponding sulfone complex **2**[9] in 84% yield, whose structure was proven by X-ray crystallography (Figure 1).[10] The η^3-Mo(CO)$_2$Cp complex **1** was easily converted to the η^4-cationic complex **3** in 67% yield by reaction with a triphenylmethyl cation (eq 2).[11] The structure of **3** was derived from its spectroscopic data[2a] and can be inferred from its subsequent nucleophilic addition reactions.



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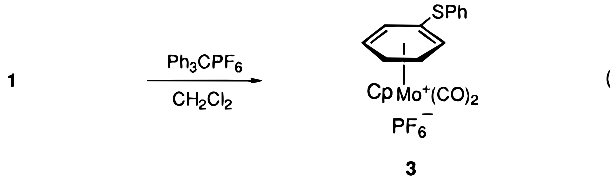

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

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[8] The preparation of η^3-2-SPh-cyclohexenyl-Mo(CO)$_2$Cp (**1**) was readily accomplished by using the procedure described by Faller et al.[2a] The modified condition is that 3-bromo-2-phenylthiocyclohexene[7] was added to a refluxing solution of Mo(CO)$_3$(CH$_3$CN)$_3$ in acetonitrile for 20 min. The unstable bright yellow crystals of [(CH$_3$CN)$_2$MoBr(η^3-SPh-C$_6$H$_8$)] could be obtained in 51% yield. The complex **1** was synthesized by adding lithium cyclopentadienide to the solution of [(CH$_3$CN)$_2$MoBr(η^3-SPh-C$_6$H$_8$)] at −78 °C. This was slowly warmed to room temperature. The solvent was removed *in vacuo*. The crude product was purified by flash column chromatography using EtOAc/hexane (1:3) as eluent to give **1** in 84% yield: R_f 0.68 (EtOAc/hexane, 1:3); mp 130−131 °C (dec); IR ($\nu_{\max}$, CH$_2$Cl$_2$) 1943, 1865 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C) δ 7.51−7.20 (5 H, m), 5.45 (5 H, s), 3.67 (2 H, br s), 2.06−1.95 (2 H, m), 1.88−1.81 (2 H, m), 1.07−0.99 (1 H, m), 0.51−0.34 (1 H, m); ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C) δ 232.1, 143.1, 128.9, 127.9, 126.1, 93.0, 70.5, 64.4, 24.0, 18.3; HRMS calcd (^{98}Mo) 408.0078, found 408.0085.

[9] A solution of **1** (1.00 g, 2.46 mmol) and *m*-CPBA (1.87 g, 50%, 5.4 mmol) in CH$_2$Cl$_2$ (50 mL) was stirred at 0 °C for 15 min. It was then washed with 10% Na$_2$S$_2$O$_3$ and then 5% NaHCO$_3$, dried (MgSO$_4$), and evaporated under vacuum. The crude product was purified by flash column chromatography using hexane/EtOAc (3:1) as eluent to give **2** (0.906 g, 84% yield), which was recrystallized from hexane/CH$_2$Cl$_2$: mp 139−141 °C (dec); IR ($\nu_{\max}$, CH$_2$Cl$_2$) 1947, 1870 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C) δ 8.01−7.97, 7.63−7.59 (5 H, m), 5.69 (5, H, s), 3.67 (2 H, br s), 1.67−1.61 (2 H, m), 1.42−1.32 (2 H, m), 0.87−0.80 (1 H, m), 0.42−0.32 (1 H, m); ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C) δ 229.1, 144.4, 132.8, 129.3, 127.1, 93.5, 85.8, 52.1, 21.4, 18.7; HRMS calcd (^{98}Mo) 439.9976, found 439.9984. Anal. Calcd for C$_{19}$H$_{18}$MoO$_4$S: C, 52.06; H, 4.14. Found: C, 52.33; H, 4.20.

S0276-7333(96)00499-2 CCC: $12.00

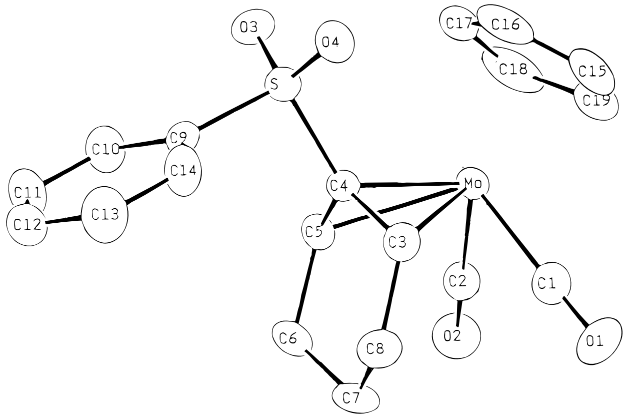

Figure 1. Crystallographic structure of complex **2**, Cp(CO)$_2$Mo(η^3-2-SO$_2$Ph-C$_6$H$_8$). Selected bond lengths (Å) and bond angles (deg): Mo−C1 = 1.947(3), Mo−C2 = 1.945(3), Mo−C3 = 2.349(3), Mo−C4 = 2.149(3), Mo−C5 = 2.332(3), S−C4 = 1.758(3), C1−Mo−C2 = 84.67(12); C1−Mo−C3 = 68.30(1), C1−Mo−C4 = 104.00(11), C1−Mo−C5 = 111.13(11), C2−Mo−C3 = 109.23(11), C2−Mo−C4 = 105.93(11), C2−Mo−C5 = 70.88(11), C3−Mo−C4 = 36.56(10), C3−Mo−C5 = 62.07(9), C4−Mo−C5 = 36.82(9), Mo−C3−C4 = 64.03(14), Mo−C4−S = 124.71(13), Mo−C4−C3 = 79.40(16), Mo−C4−C5 = 78.60(15), S−C4−C3 = 120.72(19), S−C4−C5 = 121.48(20), C3−C4−C5 = 115.77(23), Mo−C5−C4 = 64.58(14), S−C6−C5 = 121.52(19).

The reactions of **3** with various nucleophiles (eq 3) are shown in Table 1.[12] The heteroatom nucleophiles, thiolate (entry 1) and sulfonate (entry 2), reacted efficiently at room temperature to give the addition products **4a**,**b**, respectively in good yield. The ^{1}H and ^{13}C NMR spectra of **4a**,**b** agree well with similar data reported in the literature.[2a,b] The yellow single crystals of complex **4b** were grown by layering ether on a dichloromethane solution at −16 °C for 2 days. The structure of **4b** was confirmed by the X-ray analysis (Figure 2) which not only proves its regio- and stereochemistry[13] but also correlates with the structures of other addition products **4**. The reaction of **3** with active methylene compounds (entries 3−6) gave only the C-4 addition products **4c**−**f**, with the exception that methyl sodioacetoacetate (entry 7) also yielded small amount of the C-1 addition product **5g**. From these results it can be seen that the regio- and stereoselectivity of the reaction are very good and are probably attributable to the C-2 phenylthio group.

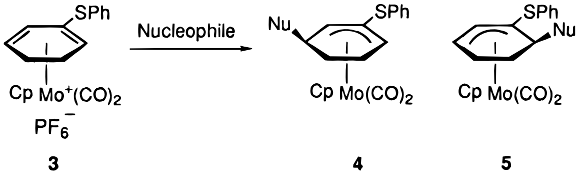

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Table 1. Nucleophilic Addition Reactions of Complex 3

entry	nucleophile[a]	reacn condition[b]	products	yields (%)[c]
1	NaSPh	A	**4a**	68
2	NaSO$_2$Ph	B	**4b**	85
3	NaCH(CN)$_2$	C	**4c**	81
4	NaCH(CO$_2$Me)$_2$	C	**4d**	68
5	NaCH(SO$_2$Ph)CO$_2$Me	C	**4e**[d]	75
6	NaC(CO$_2$Me)COCH$_2$CH$_2$CH$_2$	A	**4f**[d]	82
7	NaCH(COMe)CO$_2$Me	C	**4g**[e] + **5g** (3.3:1)	76

[a] equiv of the nucleophile was used. [b] All reactions were carried out in THF. Method A: rt, 0.5 h. Method B: rt, 4 h. Method C: 0 °C, 0.5 h. [c] Isolated yields of purified products. [d] The ratio of diastereomers was 1.3:1. [e] The ratio of diastereomers was 1.1:1.

The reaction of complex **3** with methyl sodiomalonate at 0 or −78 °C gave the same addition product **4d** in 68% and 43% yield, respectively. It is quite remarkable that in our study the phenylthio group controls the regiochemistry of the addition reaction of stabilized nucleophiles independent of the reaction temperatures used. Our results were different from what Pearson had recently reported,[6a] in which the regioselectivity of organolithiates and Grignard reagents additions to a (2-methylbutadiene)molybdenum complex was found to be influenced by the reaction temperature: at −78 °C the C-4 adduct was dominant, but at higher temperature the regioselectivity was not good.

The demetalation reaction of complex **4c** with iodine in acetonitrile at 0 °C gave a regioisomeric mixture of allylic iodides,[2b] which, due to its instability, was quickly passed through a short column of silica gel to remove the excess iodine. The crude product was then treated with sodium hydride in THF to give the cyclized product, 7,7-dicyano-2-(phenylthio)bicyclo[4.1.0]hept-2-ene (**6**) in

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(10) Crystal data for C$_{19}$H$_{18}$MoO$_4$S (**2**): fw 438.38, triclinic, space group $P\bar{1}$, $a = 7.738(3)$ Å, $b = 8.6647(17)$ Å, $c = 13.86760(0)$ Å, $\alpha = 96.368(18)°$, $\beta = 105.119(23)°$, $\gamma = 91.6442(21)°$, $V = 890.4(3)$ Å^3, $Z = 2$, $\mu = 8.504$ cm^{-1}, Mo Kα radiation ($\lambda = 0.709\ 30$ Å), $d_{calcd} = 1.635$ g/cm^3, 298 K, $F(000) = 444$, Nonius diffractometer, yellow crystal (0.40 × 0.50 × 0.60 mm), $19.00° \le 2\theta \le 23.12°$. Absorption correction was carried out by indexing crystal faces and integration: minimum and maximum transmission coefficients 0.957 and 1.000. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and treated as riding atoms. $R_f = 0.025$, $R_w = 0.026$ for 2857 reflections with $I > 2\sigma(I)$ out of 3130 unique reflections and 227 parameters ($R_f = \Sigma(F_o - F_c)/\Sigma F_o$, $R_w = [\Sigma(w(F_o - F_c)^2/\Sigma(wF_o)^2]^{1/2}$).

(11) To a stirred solution of complex **1** (2.00 g, 4.93 mmol) in dry CH$_2$Cl$_2$ (20 mL) at 0 °C under nitrogen was added Ph$_3$CPF$_6$ (1.90 g, 4.93 mmol) in one portion. The resulting mixture was stirred for 1.5 h and was then reduced to about one-half of its volume *in vacuo*. The crude product **3** was precipitated by addition of dry ether (20 mL), filtered out, and washed with dry ether (20 mL × 2) giving yellow product **3** (1.82 g, 67% yield): Mp 125−126 °C; IR (ν_{max}, CH$_2$Cl$_2$) 2200, 1950 cm^{-1}, ^{1}H NMR (C$_3$D$_6$O, 300 MHz, 25 °C) δ 7.61−7.41 (5 H, m), 6.29 (1 H, dd, $J = 7.6$, 2.7 Hz), 6.03 (5 H, s), 4.68 (1 H, dd, $J = 5.3$, 2.7 Hz), 4.41 (1 H, dt, $J = 7.6$, 3.0 Hz), 2.45−2.14 (4 H, m); ^{13}C NMR (C$_3$D$_6$O, 75 MHz, 25 °C) δ 218.3, 216.7, 135.2, 132.5, 130.9, 129.8, 100.0, 95.8, 89.9, 87.0, 74.3, 28.5, 23.9; HRMS calcd (^{98}Mo) 551.9642, found 551.9643. Anal. Calcd for C$_{19}$H$_{17}$MoF$_6$O$_2$PS: C, 41.47; H, 3.11. Found: C, 41.58; H, 3.19.

(12) General procedure for nucleophilic addition reactions of **3**: A solution of the nucleophile (0.73 mmol) in THF (2 mL) was treated with a suspension of sodium hydride (0.72 mmol, 60%) in THF (8 mL). The diene complex **3** (0.10 g, 0.18 mmol) was then added by a solid addition funnel in 30 min. The reaction could be monitored by dissolution of the THF-insoluble complex **3**. The mixture was then poured into water (20 mL) and was extracted with EtOAc (2 × 10 mL). The combined EtOAc extracts were washed with water (2 × 10 mL), dried (MgSO$_4$), and evaporated *in vacuo* to yield the crude product **4**, which was further purified by column chromatography.[13] Complex **4a**: R_f 0.5 (EtOAc/hexane, 1:3); 68% yield, mp 132−133 °C; IR (ν_{max}, CH$_2$Cl$_2$) 1936, 1861 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C) δ 7.74−7.18 (10 H, m), 5.47 (5 H, s), 3.94 (1 H, dd, $J = 5.5$, 2.6 Hz), 3.80 (1 H, t, $J = 2.7$ Hz), 3.60 (1 H, t, $J = 4.8$ Hz), 2.36−2.26 (1 H, m), 1.85−1.78 (1 H, m), 1.19 (1 H, dd, $J = 15.0$, 4.8 Hz), 0.94−0.81 (1 H, m); ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C) δ 233.2, 231.9, 140.8, 136.5, 131.0, 128.8, 128.8, 127.3, 126.3, 93.4, 72.8, 66.3, 62.7, 46.1, 24.1, 20.8. Anal. Calcd for C$_{25}$H$_{22}$MoO$_2$S$_2$: C, 58.36; H, 4.31. Found: C, 58.53; H, 4.50.

(13) The spectroscopic data for compounds **4b**−**g** and **5g** can be found in the Supporting Information.

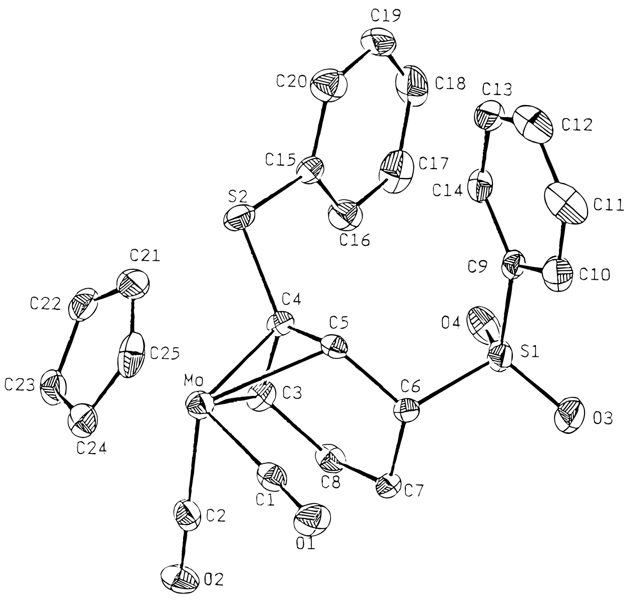
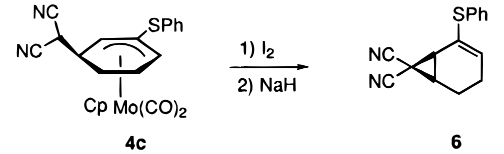


Figure 2. Crystallographic structure of complex **4b**, Cp(CO)$_2$Mo(η^3-2-SPh-4-SO$_2$Ph-C$_6$H$_7$). Selected bond lengths (Å) and bond angles (deg): Mo−C1 = 1.953(7), Mo−C2 = 1.956(7), Mo−C3 = 2.368(6), Mo−C4 = 2.213(6), Mo−C5 = 2.347(6), S2−C4 = 1.781(6), S1−C6 = 1.811(6); C1−Mo−C2 = 82.9(3), C1−Mo−C3 = 108.71(24), C1−Mo−C4 = 107.86(24), C1−Mo−C5 = 74.22(24), C2−Mo−C3 = 69.30(25), C2−Mo−C4 = 105.30(24), C2−Mo−C5 = 113.02(24), C3−Mo−C4 = 36.55(22), C3−Mo−C5 = 60.99(21), C4−Mo−C5 = 35.84(21), Mo−C3−C4 = 65.9(3), Mo−C4−S2 = 113.1(3), Mo−C4−C3 = 77.6(3), Mo−C4−C5 = 77.3(3), S2−C4−C3 = 122.5(4), S2−C4−C5 = 123.5(5), C3−C4−C5 = 114.0(5), Mo−C5−C4 = 66.9(3), S1−C6−C5 = 112.1(4), S1−C6−C7 = 106.7(4), C5−C6−C7 = 114.5(5).

54% yield (eq 4).[14] The *cis*-fused configuration of compound **6** was confirmed by comparing its proton NMR spectrum with that of 2-norcarene analogues.[15] Reaction of bicyclic compound **6** with sodium benzenethiolate provided the *trans* ring-opening product **7** in 66% yield (eq 5).[16]



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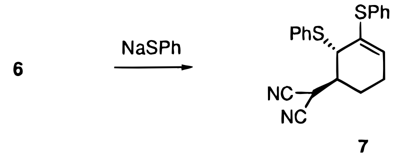

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In summary, the 2-phenylthio group on the diene molybdenum cationic complex **3** plays an important role in directing the addition almost solely at the C-4 position *trans* to the metal to give products **4** in good yield. The demetalation and cyclization of product **4c** with iodine and sodium hydride provided the bicyclic product **6**, which could be treated with another nucleophile to give a *trans*-disubstituted cyclohexene product **7**.

Acknowledgment. Financial support of this work by the National Science Council of the Republic of China (NSC 85-2113-M-030-001) is gratefully acknowledged.

Supporting Information Available: Text giving spectroscopic data for complexes **4b**−**g** and **5g** and tables giving the structure determination summary, positional and thermal parameters, bond distances, and bond angles for **2** and **4b** (14 pages). Ordering information is given on any current masthead page.

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[14] Crystal data for C$_{25}$H$_{22}$MoO$_4$S$_2$ (**4b**): fw 546.50, orthorhombic, space group *Pna*21, a = 16.896(3) Å, b = 8.0125(10) Å, c = 16.899(3) Å, α = 90°, β = 90°, γ = 90°, V = 2287.8(6) Å^3, Z = 4, μ = 7.632 cm^{-1}, Mo Kα radiation (λ = 0.7107 Å), d_{calcd} = 1.587 g/cm^3, 298 K, F(000) = 1106, Nonius diffractometer, yellow crystal (0.13 × 0.35 × 0.40 mm), 17.00° ≤ 2θ ≤ 30.80°. Absorption correction was carried out by indexing crystal faces and integration: minimum and maximum transmission coefficients 0.905 and 1.000. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and treated as riding atoms. R_f = 0.029, R_w = 0.030 for 1740 reflections with $I \geq 2\sigma(I)$ out of 2082 unique reflections and 289 parameters ($R_f = \sum(F_o - F_c)/\sum F_o$, $R_w = [\sum(w(F_o - F_c)^2)/\sum(wF_o)^2]^{1/2}$).

[15] Complex **4c** (0.28 g, 0.596 mmol) was treated with iodine (0.47 g, 1.788 mmol) in acetonitrile (5 mL) at 0 °C for 20 min, followed by passing through a short column of silica gel to remove the excess iodine using ether as the eluent. The solvent was then removed *in vacuo*. To a solution of the crude product (0.124 g) in THF (2 mL) was added a suspension of sodium hydride (2.4 mmol) in THF (5 mL) at 0 °C for 10 min. After general workup and purification by flash column chromatography, compound **6** was obtained in 54% yield: R_f 0.35 (EtOAc/hexane, 1:3), IR (ν_{max}, neat) 2280, 1475 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C) δ 7.49−7.38 (5 H, m), 6.27 (1 H, t, J = 4.4 Hz), 2.50 (1 H, d, J = 9.2 Hz), 2.46−2.40 (1 H, m), 2.34−2.27 (2 H, m), 2.15−2.08 (2 H, m); ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C) δ 132.7, 132.6, 131.7, 129.5, 128.4, 124.8, 114.8, 112.3, 31.8, 30.9, 22.1, 15.7, 13.0; HRMS calcd for 252.0722, found 252.0713. Anal. Calcd for C$_{15}$H$_{12}$N$_2$S: C, 71.39; N, 11.10; H, 4.79. Found: C, 71.39; N, 11.12; H, 4.98.

[16] Paquette, L. A.; Wilson, S. E. *J. Org. Chem.* **1972**, *37*, 3849.

[17] To a solution of compound **6** (52 mg, 0.21 mmol) in THF (2 mL) was added a suspension of sodium benzenethiolate (0.24 mmol) at 0 °C. After general workup and purification by flash column chromatography, *trans*-4-dicyanomethyl-2,3-bis(phenylthio)cyclohexene (**7**) was obtained in 66% yield: R_f 0.41 (EtOAc/hexane, 1:3), IR (ν_{max}, neat) 2300, 1565 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C) δ 7.47−7.35 (10 H, m), 5.98 (1 H, t, J = 3.8 Hz), 4.04 (1 H, d, J = 8.3 Hz), 3.68 (1 H, d, J = 4.8 Hz), 2.45−2.30 (2 H, m), 2.22−2.14 (2 H, m), 1.91−1.85 (1 H, m); ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C) δ 133.2, 132.6, 132.4, 132.3, 130.9, 129.5 (×2), 129.4, 128.4, 128.3, 111.7, 111.1, 49.8, 41.0, 24.9, 22.8, 20.6; HRMS calcd for 362.0913, found 362.0908. Anal. Calcd for C$_{21}$H$_{18}$N$_2$S$_2$: C, 69.58; N, 7.73; H, 5.00. Found: C, 69.53; N, 7.61; H, 5.09.