Preparation and Characterization of Half-Sandwich Cobalt(III) Complexes of Cp Ligands with a Rigid Thioanisole Side-Chain

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New sulfur functionalized cyclopentadiene ligands, 1-[2-(thioanisole)]-2,5-dimethylcyclopentadiene (**3**), 1-[2-(thioanisole)]-2,3,5-trimethylcyclopentadiene (**4**), and 1-[2-(thioanisole)]-2,3,4,5-tetramethylcyclopentadiene (**5**), were prepared. In these ligands, the S-donor atom is connected to a cyclopentadiene ring by a rigid phenylene spacer. CpCo(III)-diiodo half-sandwich complexes (**6-8**) were obtained from reaction the ligands (**3-5**) with $Co_2(CO)_8$, followed by treatment of I_2. Substitution reaction of CpCo(III)-diiodo complexes with MeLi yielded the corresponding CpCo(III)-dimethyl complexes (**9-11**). Further transformation to the corresponding cationic cobalt complexes (**12-14**) were achieved by reaction of the CpCo(III)-dimethyl complexes with $HB(Ar_F)_4 \cdot 2Et_2O$ and trapping with CD_3CN. The new sulfur functionalized cyclopentadiene ligands having a rigid phenylene spacer and the corresponding cobalt complexes were characterized by ^1H, ^{13}C and ^{19}F NMR spectroscopy. The diiodo Complex **6** was also characterized by a single crystal X-ray diffraction method.

Key Words : Cyclopentadienyl, Cobalt(III) complex, X-ray structure

Introduction

Cyclopentadienyl ligand systems with additional donor atom are attracting a lot of interest in the chemistry of transition metal complexes.[1-4] In cyclopentadienyl complexes of transition metals, cyclopentadienyl ligand is known to stabilize metal fragments in both low and high oxidation states and is usually regarded as substitutionally inert. The effect of an additional donor group, however, strongly depends on the nature of the metal and the donor group. The hemilabile situation is expected in compounds where a soft donor, such as thio group, interacts with a hard late transition metal in high oxidation states.[6] Half-sandwich complexes of late transition metals with intramolecular coordination of phosphorous,[2c,4,7] nitrogen,[2c,4] and oxygen[8] atoms were well known in the literature (Figure 1).

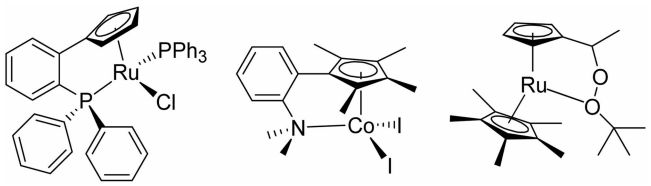


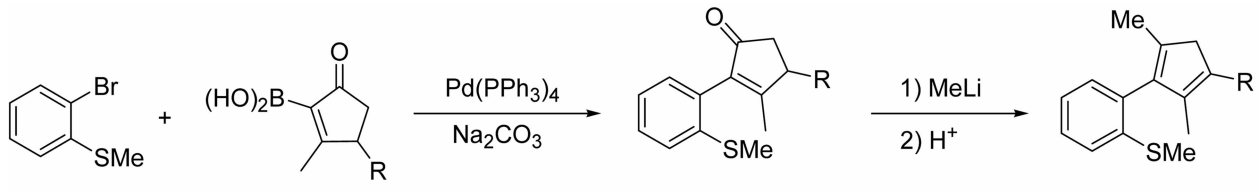
Figure 1

However, a few thioalkyl-substituted Cp complexes[4,9] have been reported so far in the literature and there has been no report about sulfur functionalized Cp* ligands with a rigid aromatic spacer. Herein, we report preparation and characterization of sulfur functionalized cyclopentadienyl ligands with a rigid phenylene tether and their corresponding Co(III) complexes as part of our continuing effort for development of efficient polymerization catalysts.[10]

Results and Discussion

Thioanisole compounds substituted with dimethylcyclopentadienyl, trimethylcyclopentadienyl, and tetramethylcyclopentadienyl moiety at 2-position were prepared through Suzuki cross-coupling reaction or nucleophilic addition route.

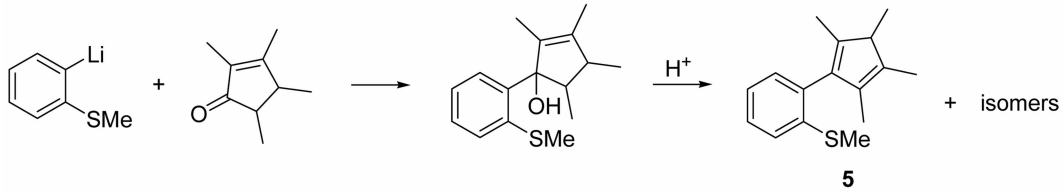
Dimethyl- or trimethyl-cyclopentadiene derivatives having a thioanisole moiety were synthesized using the Suzuki cross-coupling reaction of 2-bromothioanisole with 2-dihydroxyboryl-3-methyl-2-cyclopenten-1-one or 2-dihydroxyboryl-3,4-dimethyl-2-cyclopenten-1-one as a key step (Scheme 1).



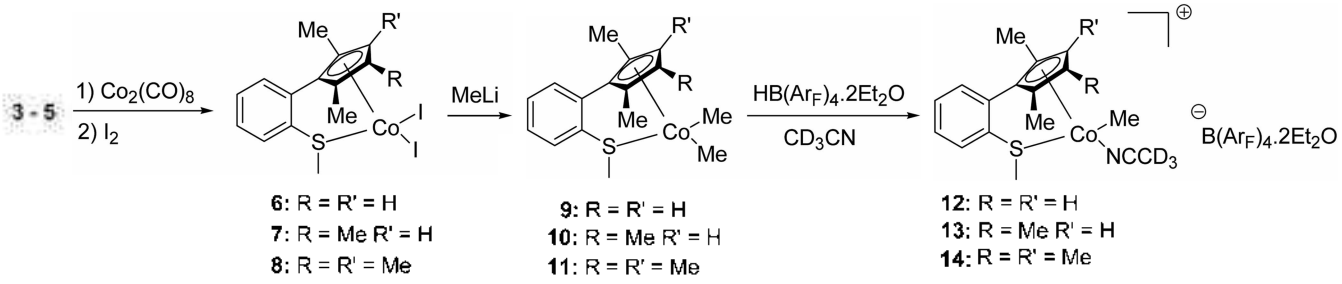
1: R = H
2: R = Me

3: R = H
4: R = Me

Scheme 1



Scheme 2



Scheme 3

The boronic acids, 2-dihydroxyboryl-3-methyl-2-cyclopenten-1-one and 2-dihydroxyboryl-3,4-dimethyl-2-cyclopenten-1-one,[11] were excellent substrates for the Suzuki coupling reactions with the 2-bromothioanisole under the conventional Suzuki coupling reaction conditions to give the corresponding cyclopentenone compounds (**1** and **2**) in 78-82% yields. The cyclopentenone compounds with thioanisole moiety (**1** and **2**) were converted to the corresponding cyclopentadiene compounds (**3** and **4**) by the nucleophilic 1,2-addition of MeLi on carbonyl group and the subsequent dehydration in acidic work up. The cyclopentadiene compounds, 1-[2-(thioanisole)]-2,5-dimethylcyclopentadiene (**3**) and 1-[2-(thioanisole)]-2,3,5-trimethylcyclopentadiene (**4**), exist as a single isomer at room temperature and characterized unambiguously by ^{1}H and ^{13}C NMR spectra.

Tetramethyl-cyclopentadiene derivatives having a thioanisole moiety were also synthesized using nucleophilic addition of 2-lithiothioanisole, which was obtained by treating BuLi to 2-bromothioanisole, to tetramethylcyclopentenone as a key step (Scheme 2).

Reaction of 2-lithiothioanisole and 2,3,4,5-tetramethyl-2-cyclopentenone in ether at low temperature and the following acid-catalyzed dehydration gave the Cp compound, 1-[2-(thioanisole)]-2,3,4,5-tetramethylcyclopentadiene (**5**) in good yield. The ^{1}H NMR spectroscopic analysis indicates that the freshly prepared compound was a mixture of three isomers, the ratio of which changed with time. When the cyclopentadiene sample was left at ambient temperature, one of the isomers was found to become the major one after several days. It has been reported that a single isomer was obtained after vacuum distillation.[12] Similar behavior has also been observed for a *N,N*-dimethylaminophenyltetramethylcyclopentadiene[8a] and 2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenol ligand system.[13]

The half-sandwich CpCo (III) complexes with the thioanisole-substituted cyclopentadiene ligands (**3-5**) were prepared as shown in Scheme 3.

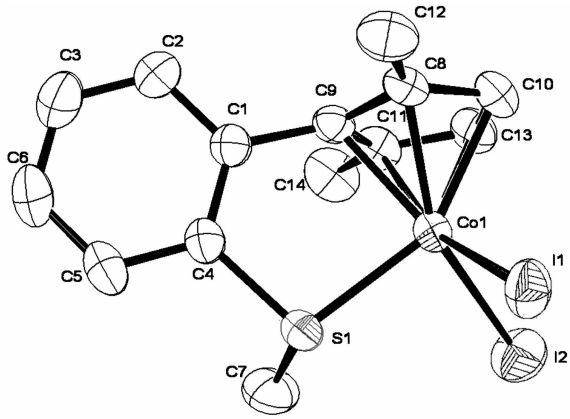


Figure 2. ORTEP diagram of complex **6** (30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Co(1)-C(8) 2.090(3), Co(1)-C(9) 2.032(3), Co(1)-C(10) 2.074(63), Co(1)-C(11) 2.067(4), Co(1)-C(13) 2.071 (4), Co(1)-I(1) 2.594(5), Co(1)-I(2) 2.586(5), Co(1)-S(1) 2.256(9), C(4)-S(1)-Co(1) 100.62(12), C(4)-S(1)-C(7) 100.00(2), C(7)-S(1)-Co(1) 113.64(2), C(9)-Co(1)-I(1) 125.26(10), C(9)-Co(1)-I(2) 141.76(10), S(1)-Co(1)-I(1) 91.55(3), S(1)-Co(1)-I(2) 94.12(3)

Treatment of cyclopentadiene compounds (**3-5**) with dicobalt octacarbonyl[13] at room temperature produced the intermediate dicarbonyl complexes, which were oxidized by iodine without isolation, to give the corresponding CpCo(III) diiodo complexes (**6-8**) as green crystalline solids. The oxidation reaction with iodine was carried out at an elevated temperature in order to ensure intramolecular coordination of the sulfur moiety on the cyclopentadiene ligands. The molecular structure of **6** was confirmed by X-ray crystallography (Figure 2). The S-atom of the Cp ligand is coordinated to the cobalt center in intramolecular fashion. From the crystal data it was observed that Co(1)-S(1) bond length is 2.256 Å, which is longer than Co-S bond length in the Cp-Co complex having sulfur-donor with aliphatic chain tether (2.175 Å)[9] and Co-N bond length in the Cp-Co complex

having nitrogen-donor with rigid aromatic tether (2.205 Å).[8a] The C(9)-Co(1) distance (2.032 Å) is shorter than that of C(10)-Co(1) (2.074 Å) and C(13)-Co(1) (2.071 Å) distances, indicating that Co center is not centered below the Cp ring but shifted towards the S-Me substituent. Similar kinds of shifts were observed for other donor functionalized half-sandwich Cp-Co complexes.[4,8b]

The diiodo compounds were reacted with 2.2 equiv. of MeLi at −30 °C to produce the corresponding dimethyl compounds (**9-11**) in 58-90% yields as a reddish brown solid. Single Co(**Me**$_2$) signals were observed as singlets at 1.01 and 0.64 ppm for symmetrical Me_2Cp (**9**) and Me_4Cp (**11**) complexes on ^{1}H NMR spectra, respectively. In case of Me_3Cp (**10**) complex, however, two singlet signals were observed at 0.78 and 0.88 ppm on ^{1}H NMR spectrum. These dimethyl cobalt complexes were stable for several days under inert atmosphere at room temperature. Protonation of dimethyl complexes with $HB(Ar_F)_4{\cdot}2Et_2O$ at low temperature in CD_3CN afforded the corresponding cationic complexes (**12-14**) in quantitative yields. These kind of cationic complex species would be used in polymerization process as "activator-free" catalysts.[9] Unfortunately, the newly prepared CpCo(III) complexes with thioanisole moiety were unable to act as a catalyst to any kind of polymerizations.

In summary, we were able to synthesize new cyclopentadiene based chelating ligand systems, in which the S-donor group is connected to the cyclopentadienyl moiety by a rigid phenylene tether. Using these ligand systems various half-sandwich Co(III) complexes were synthesized and the molecular structure of **6** was also elucidated.

Experimental Section

Reactions with organometallic reagents were carried out under a nitrogen atmosphere using standard glove box and schlenk line techniques. The solvents were dried according to the reported procedures.[15] The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Varian Mercury Plus 400. Elemental analyses were carried out at the Inter-university Centre Natural Science Facilities, Seoul National University. $NaB(Ar_F)_4$[16] and $HB(Ar_F)_4{\cdot}2Et_2O$[14a] were prepared according to the literature procedures.

Compound 1. The boronic acid 2-dihydroxyboryl-3-methyl-2-cyclopenten-1-one (0.86 g, 6.13 mmol), Na_2CO_3 (0.93 g, 8.75 mmol), $Pd(PPh_3)_4$ (0.20 g, 0.18 mmol) and 2-bromothioanisole (1.17 g, 5.74 mmol) were added into a Schlenk flask inside a glove box. The flask was brought out and DME (16 mL) and degassed water (6 mL) were added. The flask was sealed with screw-cap and heated at 95 °C overnight. The solution was cooled to room temperature and the organic phase was extracted with ethyl acetate (35 mL) using a separatory funnel. The organic phase was collected and the water phase was extracted further with additional ethyl acetate (15 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtered. Removal of the solvent by rotary evaporator gave a residue which was purified by precipitation with hexane, followed by filtration and washing with hexane. The Product obtained as light yellow colored solid. Yield was 78%. ^{1}H NMR (C_6D_6): δ 1.62 (s, 3H, Cp-CH_3), 1.91 (dd, J = 18.4, 2.8 Hz, 1H, Cp-H), 1.97 (s, 3H, CH_3), 2.05 (dd, J = 18.4, 2.8 Hz, 1H, Cp-H), 2.14 (dd, J = 18.4, 2.8 Hz, 1H, Cp-H), 2.25 (dd, J = 18.4, 2.8 Hz, 1H, Cp-H), 7.03 (dd, J = 5.2, 1.6 Hz, 2H, C_6H_4), 7.07-7.12 (m, 2H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 15.88, 17.92, 31.42, 34.97, 124.91, 126.38, 128.60, 130.46, 132.69, 138.88, 141.90, 171.89, 204.91 ppm. Anal. Calc. ($C_{13}H_{14}OS$): C, 71.52; H, 6.46%. Found: C, 71.24; H, 6.40%.

Compound 2. The compound was synthesized according to same conditions and procedure as that of **1** using the boronic acid, 2-dihydroxyboryl-3,4-dimethyl-2-cyclopenten-1-one (0.80 g, 5.22 mmol). Yield was 82% (0.98 g). ^{1}H NMR (C_6D_6): (Major) δ 0.92 (d, 3H, J = 6.8 Hz, Cp-CH_3), 1.62 (s, 3H, Cp-CH_3), 1.93 (s, 3H, S-CH_3), 2.18-2.28 (m, 1H, Cp-H), 2.45 (dd, J = 18.4, 6.8 Hz, 2H, Cp-CH_2), 6.98-7.05 (m, 4H, C_6H_4) ppm. (Minor) δ 0.75 (d, 3H, J = 6.8 Hz, Cp-CH_3), 1.61 (s, 3H, Cp-CH_3), 1.97 (s, 3H, S-CH_3), 2.32-2.40 (m, 1H, Cp-H), 2.57 (dd, J = 18.4, 6.8 Hz, 2H, Cp-CH_2), 7.06-7.05 (m, 4H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): (Major) δ 15.63, 15.96, 19.04, 37.49, 43.62, 124.88, 126.13, 128.57, 130.43, 132.60, 135.39, 138.82, 140.41, 175.57, 203.84 ppm. (Minor) 15.44, 15.65, 18.87, 37.20, 43.67, 124.97, 126.55, 128.61, 130.55, 132.87, 135.45, 138.86, 140.41, 175.48, 203.82 ppm. Anal. Calc. ($C_{14}H_{16}OS$): C, 72.37; H, 6.94%. Found: C, 72.29; H, 6.81%.

Compound 3. Compound **1** (0.90 g, 4.10 mmol) was dissolved in THF (16 mL) and added into a Schlenk flask inside a glove box. The flask was brought out and the solution was cooled to −78 °C. MeLi (3.3 mL, 5.32 mmol, 1.6 M solution in diethyl ether w/o LiBr) was added to the reaction mixture using syringe. The mixture was stirred for 2 h at −78 °C, and then slowly increased the temperature to room temperature. The reaction mixture was transferred to a separatory funnel containing H_2O (10 mL) and ethyl acetate (20 mL). The organic phase was collected and shaken vigorously with aqueous HCl (2 *N*, 25 mL) for 2 min. Aqueous saturated $NaHCO_3$ (30 mL) was added carefully to neutralize the solution. The collected organic phase was dried with anhydrous $MgSO_4$ and the removal of solvent by rotary evaporator gave a residue which was purified by column chromatography on silica gel eluting with hexane/toluene (v/v, 5:1). The product obtained as colorless oil. Yield was 60%. ^{1}H NMR (C_6D_6): δ 1.90 (s, 3H, Cp-CH_3), 1.94 (s, 3H, Cp-CH_3), 1.95 (s, 3H, S-CH_3), 2.82 (dd, J = 22.4, 2.00 Hz, 1H, Cp-CH_2), 2.93 (dd, J = 22.4, 2.00 Hz, 1H, Cp-CH_2), 5.98 (d, J = 2.0 Hz, 1H, Cp-H), 7.01 (dt, J = 8.8, 2.0 Hz, 2H, C_6H_4), 7.07 (dd, J = 7.6, 2.0 Hz, 1H, C_6H_4), 7.11 (dt, J = 7.6, 2.0 Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 14.70, 14.73, 14.82, 44.42, 124.11, 124.38, 124.40, 127.90, 130.14, 136.02, 139.49, 141.33, 141.78, 143.69 ppm. Anal. Calc. ($C_{14}H_{16}S$): C, 77.72; H, 7.45%. Found: C, 77.58; H, 7.51%.

Compound 4. The compound was synthesized according to same conditions and procedure as that of **3** using **2** (0.92 g, 3.96 mmol). The product was obtained as colorless oil.

Yield was 65% (0.60 g). ^{1}H NMR (C_6D_6): δ 1.77 (s, 3H, Cp-CH_3), 1.87 (s, 3H, Cp-CH_3), 1.88 (s, 3H, Cp-CH_3), 1.97 (s, 3H, S-CH_3), 2.82 (dd, J = 22.4, 2.00 Hz, 1H, Cp-CH_2), 2.70 (dd, J = 22.4, 2.00 Hz, 1H, Cp-CH_2), 7.00-7.04 (m, 2H, C_6H_4), 7.06-7.14 (m, 2H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 11.91, 13.54, 14.45, 14.73, 48.85, 124.36, 127.51, 128.51, 130.16, 132.44, 135.93, 136.62, 136.81, 139.47, 142.21 ppm. Anal. Calc. ($C_{15}H_{18}S$): C, 78.21; H, 7.88%. Found: C, 78.08; H, 7.73%.

Compound 5. 2-bromothioanisole (0.50 g, 2.46 mmol) was weighed in to a one-neck flask and added ether (12 mL). The flask was attached with a schlenk connector and then taken out from the glove box and connected to the schlenk line. The reaction mixture was cooled to −40 °C and added BuLi (1.6 mL, 2.58 mmol, 1.6 M solution in hexane) dropwisely. The reaction mixture then slowly warmed to room temperature and stirred for 4 h. The solution then again cooled to −40 °C and added tetramethylcyclopentenone (0.34 g, 2.46 mmol) dropwisely. The reaction mixture slowly warmed to room temperature and stirred overnight. Concentrated NH_4Cl (4 mL) was added to the reaction mixture and stirred for 5 min. After removing the aqueous layer the organic layer was treated with concentrated HCl (4 mL) three times. The organic layer was washed with water 3 times. The organic layer was dried over $MgSO_4$ and removed the solvent under vacuum. The residue was purified by column chromatography (toluene:hexane = 1:2) to obtain the product as a colorless oil. Yield was 62% (0.37 g). ^{1}H NMR (C_6D_6): δ 1.63 (d, J = 5.2 Hz, 3H, Cp-CH_3), 1.72 (s, 3H, Cp-CH3), 1.85 (s, 6H, Cp-CH_3), 1.97 (s, 3H, S-CH_3), 2.89 (q, J = 6.4 Hz, 1H, Cp-H), 7.02 (dt, J = 8.8, 2.0 Hz, 2H, C_6H_4), 7.09 (dd, J = 7.6, 2.0 Hz, 1H, C_6H_4), 7.32 (dt, J = 7.6, 2.0 Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 11.40, 12.04, 14.36, 15.17, 31.61, 49.83, 124.30, 126.15, 126.69, 127.44, 128.80, 128.93, 130.35, 132.05, 136.60, 140.25 ppm. Anal. Calc. ($C_{16}H_{20}S$): C, 78.63; H, 8.25%. Found: C, 78.59; H, 8.17%.

Compound 6. $Co_2(CO)_8$ (0.47 g, 1.35 mmol), 1,3-cyclohexadiene (0.16 g, 1.93 mmol) and CH_2Cl_2 were taken in a three-neck flask. The flask was connected with a reflux condenser, glass stopper and a rubber septum, and was brought out from the glovebox and connected to the schlenk line. Compound **3** in CH_2Cl_2 (6 mL) was added dropwisely to a magnetically stirred brown coloured solution, with venting into the atmosphere through an oil bubbler. The reaction mixture was refluxed for overnight under the weak stream of nitrogen. Solvents were removed under vacuum and CH_2Cl_2 (6 mL) was added, followed by dropwise addition of I_2 (0.69 g, 2.78 mmol) in CH_2Cl_2 (18 mL) with venting into the atmosphere through an oil bubbler. The resulting reaction mixture was refluxed for 8 h under the weak stream of nitrogen, and the color of the reaction mixture changed from dark brown to dark green. Half of the solvents were removed under vacuum and the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (v/v, 1/1). After removing the brown coloured portion completely, the eluent was changed to CH_2Cl_2 and collected the green portion. Removal of the solvent yields the product as a dark green solid. Yield was 73%. ^{1}H NMR (C_6D_6/CD_2Cl_2): δ 1.82 (s, 6H, Cp-CH_3), 2.41 (s, 3H, S-CH_3), 4.91 (s, 2H, Cp-H), 6.80 (t, J = 7.6 Hz, 1H, C_6H_4), 6.94 (t, J = 8.0 Hz, 1H, C_6H_4), 6.99-7.08 (m, 2H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6/CD_2Cl_2): δ 12.68, 28.40, 81.70 (br), 93.75, 111.64, 129.81, 130.63, 131.90, 133.84, 147.94 ppm.

Compound 7. The compound was synthesized according to same conditions and procedure as that of **6** using **4** (0.45 g, 1.95 mmol). Yield was 78%. ^{1}H NMR (C_6D_6): δ 1.71 (s, 3H, Cp-CH_3), 1.79 (s, 3H, Cp-CH_3), 2.07 (s, 3H, Cp-CH_3), 2.36 (s, 3H, S-CH_3), 4.78 (s, 1H, Cp-H), 6.82 (dt, J = 6.4 Hz, 1H, C_6H_4), 6.75 (dt, J = 6.8 Hz, 1H, C_6H_4), 6.91 (dd, J = 8.0 Hz, 1H, C_6H_4), 6.93 (dd, J = 8.0 Hz, 1H, C_6H_4) ppm, ^{13}C{^{1}H} NMR (C_6D_6/CD_2Cl_2): δ 11.27, 11.61, 14.26, 27.67, 84.60, 88.23, 93.77, 95.35, 108.74, 128.24, 129.36, 130.40, 131.73, 134.15, 148.61 ppm.

Compound 8. The compound was synthesized according to same conditions and procedure as that of **6** using **5** (0.35 g, 1.41 mmol). Yield was 40%. ^{1}H NMR (C_6D_6/CD_2Cl_2): δ 1.69 (s, 6H, Cp-CH_3), 1.94 (s, 6H, Cp-CH_3), 2.38 (s, 3H, S-CH_3), 6.83 (dt, J = 6.8 Hz, 1H, C_6H_4), 6.86 (dt, J = 7.2 Hz, 1H, C_6H_4), 7.00 (dd, J = 3.2 Hz, 1H, C_6H_4), 7.02 (dd, J = 3.6 Hz, 1H, C_6H_4) ppm, ^{13}C{^{1}H} NMR (C_6D_6/CD_2Cl_2): δ 10.78, 13.17, 20.09, 89.12, 96.21, 105.99, 128.12, 129.46, 130.43, 131.75, 134.30, 148.39 ppm.

Compound 9. Compound **6** (0.30 g, 0.57 mmol) was taken in a vial, added diethyl ether (2 mL). The solution was cooled to −30 °C, and MeLi (0.74 mL, 1.19 mmol, 1.6 M solution in diethyl ether w/o LiBr) was added dropwisely. After the complete addition of MeLi, the reaction mixture warmed to room temperature and stirred for 2 h. Solvent was removed under vacuum, pentane was added and the reaction mixture was filtered over a celite pad. Removal of the solvent yielded the product as a dark brown colored solid. Yield was 89%. ^{1}H NMR (C_6D_6): δ 1.01 (s, 6H, Co-CH_3), 1.60 (s, 3H, S-CH_3), 1.80 (s, 6H, Cp-CH_3), 3.83 (s, 2H, Cp-CH), 6.73 (dt, J = 7.2 Hz, 1H, C_6H_4), 6.82 (td, J = 8.0 Hz, C_6H_4), 6.91 (td, J = 7.2 Hz, 1H, C_6H_4), 7.09 (dd, J = 7.6 Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ −12.78, 10.96, 19.24, 81.97 (br), 92.39, 115.76, 128.61, 129.31, 130.65, 138.98, 151.85 ppm.

Compound 10. The compound was synthesized according to same conditions and procedure as that of **9** using **7** (0.20 g, 0.37 mmol). Yield was 90%. ^{1}H NMR (C_6D_6): δ 0.78 (s, 3H, Co-CH_3), 0.88 (s, 3H, Co-CH_3), 1.35 (s, 3H, Cp-CH_3), 1.58 (s, 3H, Cp-CH_3), 1.62 (s, 3H, Cp-CH_3), 1.82 (s, 3H, S-CH_3), 3.50 (s, 1H, Cp-H), 6.77 (dd, J = 8.0 Hz, 1H, C_6H_4), 6.86 (dt, J = 7.6 Hz, 1H, C_6H_4), 6.94 (dt, J = 8.4 Hz, 1H, C_6H_4), 7.13 (dd, J = 8.0 Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ −12.24, −5.12, 8.98, 10.02, 10.84, 19.38, 81.50 (br), 90.35, 90.90, 114.90, 124.35, 128.55, 129.31, 130.67, 139.32, 151.93 ppm.

Compound 11. The compound was synthesized according to same conditions and procedure as that of **9** using **8** (0.22 g, 0.40 mmol). Yield was 89%. ^{1}H NMR (C_6D_6): δ 0.68 (s, 6H, Co-CH_3), 1.21 (s, 6H, Cp-CH_3), 1.65 (s, 3H, S-Me$_3$),

1.66 (s. 6H. Cp-CH_3), 6.77 (d, J = 8.4. 1H, phenyl-CH), 6.86 (dt. J = 1.2 and 7.6 Hz. 1H, phenyl-CH), 6.95 (t, J = 1.2 and 7.2 Hz. 1H. phenyl-CH). 7.19 (d, J = 8.0 Hz. 1H. phenyl-CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ −4.82, 8.29. 9.11. 19.60. 88.36. 89.42. 112.91. 128.08. 128.50. 129.35. 130.71. 139.44. 151.93 ppm.

Compound 12. Solid compound **9** (0.01 g. 0.04 mmol) and $HB(Ar_F)_4{\cdot}2Et_2O$ (0.04 g, 0.04 mmol) were weighed in a vial and the vial cooled to −20 °C. Chilled CD_2Cl_2 was added using a previously cooled dropper. The reaction mixture was stirred for 2 min, followed by the addition of chilled CD_3CN, the color of the reaction mixture changed from dark green to dark purple. The reaction mixture stirred for 15 min at room temperature and filtered over a celite pad. ^1H NMR (CD_2Cl_2/CD_3CN): δ 0.99 (s. 3H, Co-CH_3). 1.14 (t. J = 6.8 Hz, 12H, -CH_3). 1.74 (s, 3H, Cp-CH_3). 2.04 (s. 3H. Cp-CH_3). 2.24 (s, 3H, S-CH_3). 3.42 (q. J = 6.8 Hz. 8H. -CH_2-), 4.81 (d. J = 2.4 Hz, 1H. Cp-H). 4.85 (d, J = 2.4 Hz. 1H, Cp-H). 7.39 (t. J = 4.4 Hz. 1H, C_6H_4). 7.50-7.53 (m, 3H. C_6H_4), 7.57 (br s, 4H), 7.70 (br s. 8H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3CN): δ −2.41, 3.66 (br), 9.21. 11.73. 14.01. 14.87. 65.35, 117.03, 119.94. 122.19. 123.71. 125.34. 127.13. 127.24. 128.04, 128.37 (q, $J_{C\text{-}F}$ = 31.9 Hz), 129.33. 131.62, 134.18, 141.84 (br). 161.08 (q, $J_{C\text{-}B}$ = 49.3 Hz) ppm. $^{19}F\{^1H\}$ NMR (CD_2Cl_2/CD_3CN): δ −61.51 ppm.

Compound 13. The compound was synthesized according to same conditions and procedure as that of **12** using **10** (0.01 g. 0.04 mmol). Yield was 90%. ^1H NMR (CD_2Cl_2/CD_3CN): (Major) δ 1.00 (s. 3H. Co-CH_3), 1.14 (t, J = 6.8 Hz, 12H. -CH_3), 1.31 (s, 3H, Cp-CH_3). 1.62 (s, 3H, Cp-CH_3). 1.97 (s, 3H, Cp-CH_3). 2.30 (s, 3H. S-CH_3). 3.42 (q, J = 6.8 Hz, 8H. -CH_2-), 4.67 (s, 1H. Cp-H). 7.37 (t, J = 2.4 Hz. 1H, C_6H_4). 7.48-7.51 (m, 3H, C_6H_4). 7.54 (br s. 4H). 7.69 (br s. 8H) ppm. (Minor) δ 0.79 (s. 3H, Co-CH_3), 1.14 (t, J = 6.8 Hz, 12H. -CH_3), 1.58 (s, 3H, Cp-CH_3). 1.74 (s, 3H, Cp-CH_3). 2.05 (s, 3H, Cp-CH_3). 2.25 (s, 3H. S-CH_3). 3.42 (q, J = 6.8 Hz, 8H. -CH_2-), 4.62 (s, 1H. Cp-H). 7.40 (t, J = 3.2 Hz. 1H. C_6H_4). 7.52-7.54 (m, 3H, C_6H_4). 7.54 (br s. 4H). 7.69 (br s. 8H) ppm. In the ^{13}C spectrum. the minor set signals were too weak for analyzing. so here included only the major set signals. $^{13}C\{^1H\}$ NMR(C_6D_6): δ −6.96. 2.86 (br), 7.88, 9.43. 9.90. 10.94. 15.27. 65.71. 79.85. 81.34. 89.01. 117.46. 120.41. 123.11. 125.82. 127.81 (br). 128.52. 128.85 (q. J = 31.9 Hz). 129.17. 130.51. 130.47. 131.81. 134.65. 161.54 (q. $J_{C\text{-}B}$ = 49.3 Hz) ppm. $^{19}F\{^1H\}$ NMR (CD_2Cl_2/CD_3CN): δ −61.51 ppm.

Compound 14. The compound was synthesized according to same conditions and procedure as that **12** using **11** (0.010 g. 0.03 mmol). Yield was 90%. ^1H NMR (CD_2Cl_2/CD_3CN): δ 0.79 (s, 3H, Co-CH_3). 1.11 (t, J = 6.8 Hz, 12H. -CH_3), 1.36 (s. 3H, Cp-CH_3), 1.63 (s, 3H. Cp-CH_3). 1.96 (s. 3H, Cp-CH_3). 2.25 (s, 3H. S-CH_3), 3.40 (q, J = 6.8 Hz. 8H. -CH_2-), 7.35-7.37 (m. 1H, C_6H_4). 7.48 (t. J = 4.8 Hz, 1H. C_6H_4), 7.50 (d, J = 4.8 Hz. 1H, C_6H_4), 7.52 (d, J = 4.8 Hz. 1H, C_6H_4), 7.54 (br s. 4H), 7.67 (br s. 8H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3CN): δ 1.18. 2.07. 2.39 (br), 7.83. 8.18. 9.10, 9.17. 15.23. 65.69. 78.37, 117.49, 120.43, 123.13. 123.61 (br), 125.83. 128.52. 128.87 (q, $J_{C\text{-}F}$ = 31.9 Hz), 130.34, 130.38. 131.73. 134.66. 161.56 (q, $J_{C\text{-}B}$ = 49.3 Hz) ppm. $^{19}F\{^1H\}$ NMR (CD_2Cl_2/CD_3CN): δ −61.52 ppm.

Table 1. Crystallographic parameters for compound **6**

	6
Formula	C14 H15 Co I2 S
Fw	528.05
a, Å	22.663
b, Å	8.504
c, Å	16.829
β, deg	90.73
V, Å^3	3243.1
Crystal system	Monoclinic
Space group	C2/c
D(calc), gcm^{-1}	1.081
Z	4
No. of reflections collected	15536
No. of data/restraints/parameter	3700/0/223
Final R indices [I > 2σ(I)], R1	0.0291
wR2	0.0720
Goodness of fit	1.103

Data collected with Mo-Kα radiation (λ(Kα) = 0.7107 Å). $R(F) = \Sigma||F_o| - |F_c||/\Sigma F_o$ with $F_o > 2.0\sigma(I)$. $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

X-ray crystallography. Crystals of compound **6** coated with grease (Apiezon N) was mounted onto a thin glass fiber with epoxy glue and placed at 293(2) K on Rigaku single crystal X-ray diffractometer. The structures were solved by direct methods (SHELXL-97) and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results for **6** are summarized in Table 1. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-646533). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC. 12 Union Road. Cambridge CB2 1EZ. UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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