



Supporting Information

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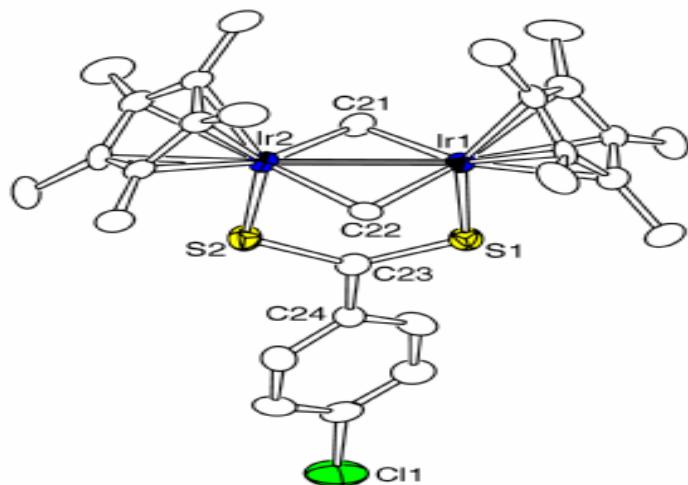
69451 Weinheim, Germany

**Activation of C–Cl and C–H bonds by Ligated S₂²⁻ in Unusual Way.
Conversion of Organic Chlorides into Organosulfur Compounds Coordinated
to Iridium Metal Atom in *cis*-[(IrCp*)₂(μ-CH₂)₂(μ-S₂R)]⁺**

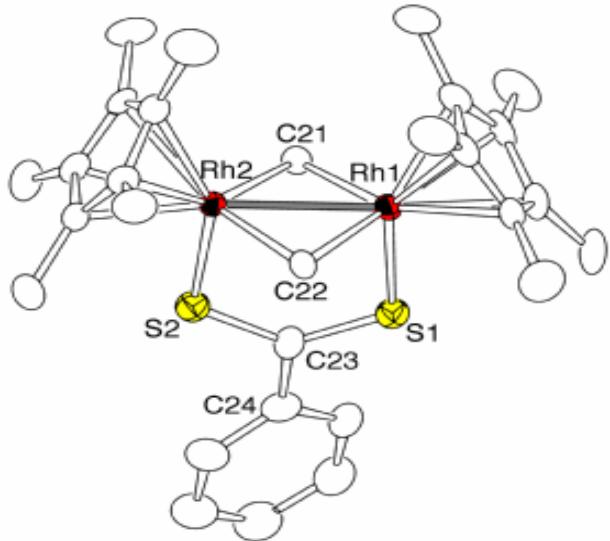
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and Isamu Kinoshita

I. Activation of C–Cl bonds of C₆H₅CCl₃ and p-ClC₆H₄CCl₃

***cis*-I[(IrCp*)₂(μ-CH₂)₂(μ-S₂C-C₆H₄-Cl-p)]/BPh₄] 5.** To the flask containing *cis*-[(IrCp*)₂(μ-CH₂)₂(μ-S₂R)] 2 (0.119 g, 0.160 mmol) was added 5 mL of MeOH and 38 μL (0.056 g, 0.240 mmol) of *p*-chloro-1, 1, 1-trichloromethylbenzene dissolved in 3 mL of methanol. The rest of procedure was same as for 3.^[13] Yield, 0.110 g, 70%. Dark red crystals (5) were formed using CH₂Cl₂-toluene. M.p. 280–285 (d). C, H analysis calcd for C₅₃H₅₈BClIr₂S₂ : C 53.50, H 4.91; found : C 53.30, H 4.86. ¹H NMR (600 MHz, CDCl₃, δ, ppm, J, Hz) : 1.80 (30H, s, Cp*), 7.60 (2H, s, μ-CH₂), 8.49 (2H, s, μ-CH₂); 7.67 {2H, dt, J = 8.7, 0.4, o-(C₆H₄Cl)CS₂}, 7.26 {2H, dd, J= =7.6, 0.2, m-(C₆H₄Cl)CS₂}, 7.42 (8H, s, br, o-Ph₄B), 7.03 (8H, t, J 7.4, m-Ph₄B), 6.87(4H, t, J 7.2, p-Ph₄B); ¹³C NMR (150 MHz, CDCl₃, δ, ppm) : 9.4 (CH₃), 100.0 (C₅ ring of Cp*), 100.9 (μ-CH₂), 138.5 {i-C, (C₆H₄Cl)CS₂}, 127.5 {o-C, (C₆H₄Cl)CS₂}, 128.7 {m-C, (C₆H₄Cl)CS₂}, 138.2 {p-C, (C₆H₄Cl)CS₂}, 208.9 (CS₂) ; 164.2 (i-C, BPh₄), 136.3 (o-C, BPh₄), 125.4 (m-C, BPh₄) 121.5(p-C, BPh₄); MS(ESI), m/z = 871[M⁺]. CCDC 208 940 .

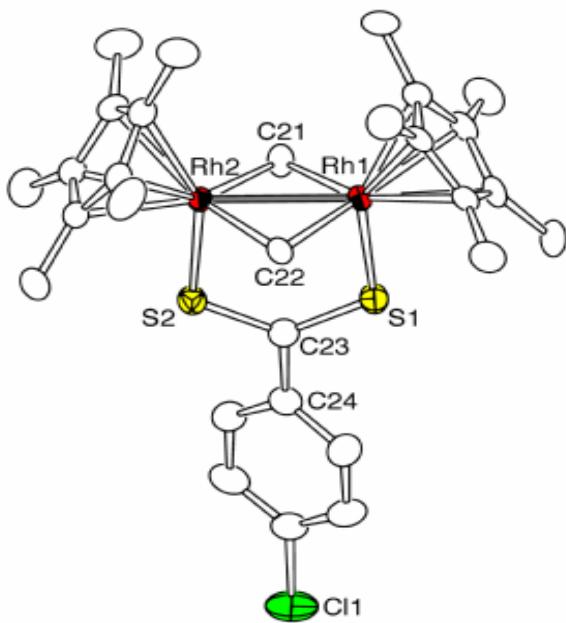


cis-[*I*(RhCp*)₂(μ-CH₂)₂(μ-S₂C-C₆H₅)]/[BPh₄] 6. To the flask containing *cis*-[(RhCp*)₂(μ-CH₂)₂(μ-S₂)] **1** (0.057 g, 0.100 mmol) prepared by method A^[12] was added 5 mL of MeOH and 24 μL (0.040 g, 0.200 mmol) of 1, 1, 1-trichloromethylbenzene dissolved in 2 mL of methanol. The rest of procedure was same as for **3**.^[13] Yield, 0.050 g, 51%. Dark red crystals (**6**) were formed using CH₂Cl₂-toluene (or CH₂Cl₂-methanol). M.p. 230–235 (d). C, H analysis calcd for C_{53.2}H_{59.4} BCl_{0.4}Rh₂S₂ (0.2CH₂Cl₂): C 64.30, H 6.03; found: C 64.02, H 6.01. ¹H NMR (600 MHz, CDCl₃, δ, ppm, J, Hz): 1.82 (30H, s, Cp*), 8.77 (2H, d, J = 1.7, μ-CH₂), 9.81 (2H, s, μ-CH₂); 7.78 (2H, dd, J = 7.3, 1.1, o-PhCS₂), 7.47 (1H, tt, J = 5.9, 0.8, p-PhCS₂), 7.33 (2H, m-PhCS₂), 7.60 (8H, dt, J = 8.1, 1.0, o-Ph₄B), 7.44 (8H, t, J = 7.9, m-Ph₄B), 7.34 (4H, p-Ph₄B); ¹³C NMR (150 MHz, CDCl₃, δ, ppm): 9.81 (CH₃), 105.0 (C₅ ring of Cp*), 168.7 (t, J_{Rh-C}, 25.3, μ-CH₂), 142.7 (i-C, PhCS₂), 126.5 (o-C, PhCS₂), 128.5 (m-C, PhCS₂), 132.3 (p-C, PhCS₂), 222.9 (CS₂); –, 127.2 (o-C, BPh₄), 128.7 (m-C, BPh₄) 127.5 (p-C, BPh₄); MS(ESI), m/z = 657[M⁺]. CCDC 218237.



cis-[*I*(RhCp*)₂(μ-CH₂)₂(μ-S₂C-C₆H₄-Cl-p)]/[BPh₄] 7. It was prepared by same method as for **6** using *p*-chloro-1, 1, 1-trichloromethylbenzene.^[13] Yield, 0.060 g, 59%. Dark red crystals (**7**) were formed using CH₂Cl₂-toluene (or CH₂Cl₂-methanol). M.p. 235–240 (d). C, H analysis calcd for C₅₃H₅₈ BClRh₂S₂: C 62.9, H 5.78; found: C 62.5, H 5.76. ¹H NMR (600 MHz, CDCl₃, δ, ppm, J, Hz): 1.68 (30H, s, Cp*), 8.63 (2H, d, J = 1.5, μ-CH₂), 9.76 (2H, s, μ-CH₂); 7.74 {2H, dt, J = 8.7, 1.0, o-(C₆H₄Cl)CS₂}, 7.29 {2H, dt, J = 8.7, 1.0, m-(C₆H₄Cl)CS₂}, 7.42 (8H, s, br, o-Ph₄B), 7.03 (8H, t, J = 7.3, m-Ph₄B), 6.87 (4H, t, J 7.2, p-Ph₄B); ¹³C NMR (150 MHz, CDCl₃, δ, ppm): 9.65 (CH₃), 104.9 (C₅ ring of Cp*), 168.7 (br, μ-CH₂), 140.8 {i-C, (C₆H₄Cl)CS₂}, 127.7 {o-C,

$(C_6H_4Cl)CS_2\}$, 128.5{m-C, $(C_6H_4Cl)CS_2\}$, 138.8{p-C, $(C_6H_4Cl)CS_2\}$, 221.1 (CS_2) ; 164.2 (i-C, BPh_4), 136.3 (o-C, BPh_4), 125.5 (m-C, BPh_4) 121.6(p-C, BPh_4); MS(ESI), m/z = 691[M⁺]. CCDC 218238.



II. Activation of Other Organic Chlorides

From the reactions of compound **2** with carbon tetrachloride and 1,1,1-trichloroethane three compounds (**8 – 10**) are identified using NMR and ESI-mass and more details are in process.

1. Reaction of cis-[$(IrCp^*)_2(\mu-CH_2)_2(\mu-S_2)$] **2** with carbon tetrachloride

To the flask containing the solid **2** (0.092 g, 0.123 mmol) was added 3 mL of methanol and 24 μ L (0.038 g, 0.246 mmol) of carbon tetrachloride. The contents were stirred for 20 h at room temperature and the colour of the solution changed from dark brown to dark green. The solvent was removed using an rotary evaporator in the open atmosphere. The ¹H NMR of an aliquot portion in CD₃OD supported the formation of two different species. The solid was redissolved in 10 mL of methanol and an excess of NaBPh₄ (0.050 g) in 5 mL of methanol was added and this led to the formation of precipitates which were washed with methanol and dissolved again in dichloromethane and excess of methanol was layered over it. Dark green crystalline product was separated in two days time. The green compound was separated and washed well with methanol and dried. The ¹H NMR in dmso-d₆ showed formation of a different compound (labelled as Compound **9**). The mother liquor was yellow-brown and solvents were

removed and dissolved in minimum amount of dichloromethane and methanol was diffused. No more precipitation of green compound occurred. Removed solvent and recorded NMR and it showed a different compound (labelled as Compound **8**). NMR data are given below and further work to crystallise and carry out other studies is in process.

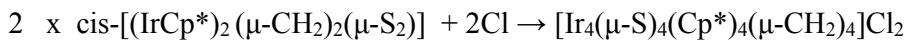
(cis-[(IrCp^{*})₂(μ-CH₂)₂(μ-S₂CH)]Cl 8.Cl : ¹H NMR (300 MHz, CD₃OD, δ, ppm, J, Hz) : 1.93(30H, s, Cp^{*}), 8.47 (2H, s, μ-CH₂), 7.75 (2H, s, μ-CH₂), 9.25(1H, s, μ-S₂CH). **8.BPh₄:** ¹H NMR (300 MHz, CDCl₃, δ, ppm, J, Hz) 1.74(30H, s, Cp^{*}), 8.42 (2H, s, μ-CH₂), 7.51(2H, s, μ-CH₂), 8.80(1H, s, μ-S₂CH); 6.85(4H, t, p-BPh₄), 7.01 (8H, t, m-BPh₄) 7.40(8H, br, o-BPh₄); MS(ESI), m/z = 759 [M⁺]. Elemental Analysis: Found C 53.70, H 5.25. Calcd for Ir₂S₂BC₄₇H₅₅.(0.3.toluene) : Ir₂S₂BC_{49.1}H_{57.1} : 53.30, 5.20 (M = 1106.56), mp 240-245 °C .

([Ir₄S₄(Cp^{*})₄(μ-CH₂)₄]Cl₂) 9.Cl₂ : ¹H NMR (300 MHz, CD₃OD, δ, ppm, J, Hz) : 1.88 (60H, s, Cp^{*}), 7.83 (2H, s, μ-CH₂), 7.72 (2H, s, μ-CH₂), 7.48 (2H, s, μ-CH₂), 6.53 (2H, s, μ-CH₂); **9.(BPh₄)₂** salt : ¹H NMR (300 MHz, dmso-d₆ δ, ppm, J, Hz) : 1.81 (60H, s, Cp^{*}), 7.79 (2H, s, μ-CH₂), 7.71 (2H, s, μ-CH₂), 7.38 (2H, s, μ-CH₂), 6.39 (2H, s, μ-CH₂); 6.87 (4H, t, p-BPh₄), 7.02 (8H, t, m-BPh₄) 7.41 (8H, br, o-BPh₄); MS(ESI), m/z = 746 [M²⁺]. Elemental analysis : found 50.81, 5.02. Calcd for [Ir₄S₄(Cp^{*})₄(μ-CH₂)₄](BPh₄)₂. 0.6 CH₂Cl₂ : Ir₄S₄B₂C₉₂H₁₀₈.0.6 CH₂Cl₂; 50.9, 5.04 mp > 290 °C.

Explanation for formation of **8 and **9**.** Due to degradation of CCl₄, three chlorine atoms appear to be released and ‘HCCl₃’ moiety is generated (H atom from solvent) which adds across S-S bond forming, (cis-[(IrCp^{*})₂(μ-CH₂)₂(μ-S₂CH)]Cl **8**.

cis-[(IrCp^{*})₂(μ-CH₂)₂(μ-S₂)] + CCl₄ (CH₃OH solvent) → cis-[(IrCp^{*})₂(μ-CH₂)₂(μ-S₂CH)]Cl . Later Cl is replaced by BPh₄ .

The formation **9** is believed to occur via oxidation of S of **2** by free radicals (Cl) :



Cl anions are replaced by BPh₄ anions.

2. Reaction of cis-[(IrCp^{*})₂(μ-CH₂)₂(μ-S₂)] **2** with 1,1,1-trichloroethane

cis-[(IrCp^{*})₂(μ-CH₂)₂(μ-S₂C-CH₃)]⁺Cl⁻ **10**

To the flask containing the solid **2** (0.120 g, 0.160 mmol) was added 2 mL of methanol followed by addition of 2 mL of 1,1,1-trichloroethane (0.020 mol). The contents were stirred for 6 d at room temperature and the colour of the solution changed from dark brown to greenish-

brown. The solvent was removed using an rotary evaporator in the open atmosphere. The ^1H NMR of an aliquot portion in CD_3OD supported the formation of $\text{cis}-[(\text{IrCp}^*)_2(\mu-\text{CH}_2)_2(\mu-\text{S}_2\text{C}-\text{CH}_3)]^+\text{Cl}^-$ and ESI-MS confirmed the formation. The attempts to grow crystals and get pure sample are in progress. : ^1H NMR (300 MHz, CD_3OD , δ , ppm, J , Hz) : 1.92 (30H, s, Cp^*), 7.79 (2H, s, $\mu\text{-CH}_2$), 8.36 (2H, s, $\mu\text{-CH}_2$) and 2.70 (C-CH_3). MS(ESI), $m/z = 773 [\text{M}^+]$.