# Nucleophilicity of Ligated $S_2^{2-}$ Ions. Conversion of Organic Chlorides into Organosulfur Compounds in *cis*-$[(MCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2R)]^+$ (M = Rh, Ir)

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The chemically active rhodium complex *cis*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SS)]$, **1**, activated all C−Cl bonds of polychlorinated organic compounds, namely, $C_6H_5CCl_3$ and *p*-$ClC_6H_4CCl_3$ (except ring chlorine), and formed compounds *cis*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_5)][BPh_4]$, **6**, and *cis*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_4\text{-}Cl\text{-}p)][BPh_4]$, **7**, after treatment with $NaBPh_4$. Similarly, the iridium complex *cis*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SS)]$, **2**, activated C−Cl bonds of *p*-$ClC_6H_4\text{-}CCl_3$(except ring chlorine) and formed the compound *cis*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_4\text{-}Cl\text{-}p)][BPh_4]$, **5**. Compound **6** is analogous to *cis*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C{-}C_6H_5)][BPh_4]$, **3** (obtained by reaction of **2** with $C_6H_5CHCl_2$ or $C_6H_5CCl_3$); however, reaction with $C_6H_5CH_2Cl$ formed the S-benzylated product *cis*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SS\text{-}CH_2\text{-}C_6H_5)][BPh_4]$, **4**. Interestingly, compound **2** activated all the C−Cl bonds of $CCl_4$ in methanol and formed the products *cis*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2CH)][BPh_4]$, **8**, and $[Ir_4S_4(Cp^*)_4(\mu\text{-}CH_2)_4]\ [BPh_4]_2$, **9**. The unique reactivity of the bridged $S_2$-dimer is that activation of C−Cl bonds occurs at S-donor atoms and not at the usual metal centers.



## Introduction

Chlorinated organic compounds, such as chloroform, dichloromethane, carbon tetrachloride, and 1,1,1-trichloroethane, used in chemical laboratories, industries, electrical appliances, etc., are toxic, and some of them pose health hazards.[1] The activation of carbon−chlorine bonds using chemical, microbial, or thermal methods, for converting organic halides into either less toxic or industrially useful materials, is an interesting area of research activity.[1−19] Very electron rich centers are required to produce rupture of the strong C−Cl bonds, such as those of $CH_2Cl_2$[20] or $CHCl_3$,[13,21] and the oxidative addition of chlorocarbons to metal complexes is the initial step for their activation either by further transfer to organic molecules[22] or by their functionalization in possible catayltic processes.[23] Among various metals, rhodium and iridium complexes have shown good

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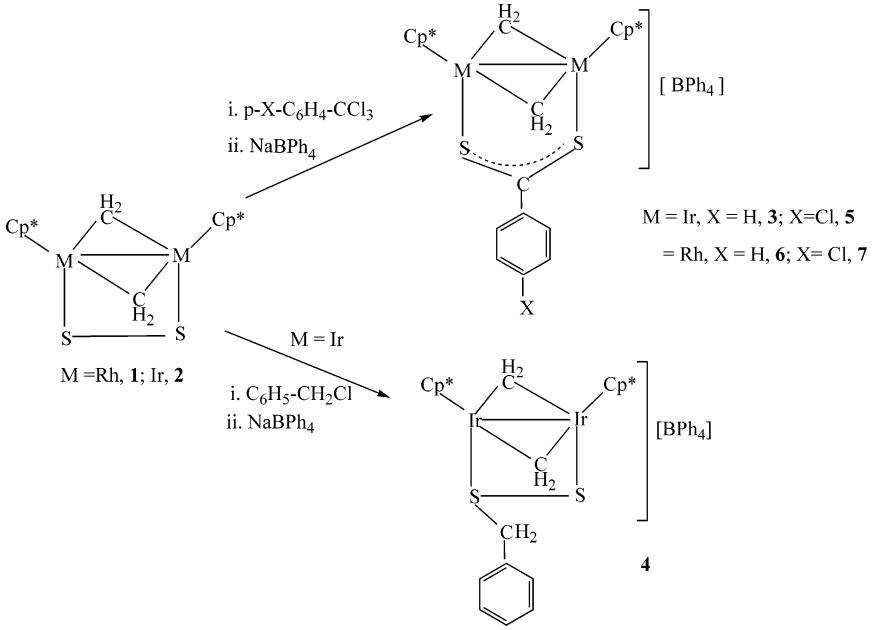
**Scheme 1**




reactivity toward chloroalkanes, for oxidative-addition reactions at their metal centers.[10−17,24−26]

Thiolate anions $S_n^{2-}$ ($n$ = 1, 2, 3) can convert alkyl chloride into dialkyl oligosulfane by activation of the C−Cl bonds.[27] Several metallosulfur systems are reported to react with chlorinated hydrocarbons;[28] however, there is no report on mono- or multi-C−Cl bond activation by the insertion to the S−S bond of the coordinated $S_2$ ligand.[1−29] The $S_2$ ligand coordinated to the metal dinuclear unit in parallel in dinuclear *cis*-[$(MCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2)$] (Scheme 1: **1**, Rh; **2**, Ir, Cp* = $C_5Me_5$) has high nucleophilicity, as noted toward dioxygen, and could be useful in activating C−Cl bonds.[30−34] Thus, using compound **2**, we have explored the novel multibond activation of C−Cl (or C−Cl and C−H) bonds in (1,1,1-trichloromethyl)benzene ($C_6H_5CCl_3$), (1,1-dichloromethyl)benzene ($C_6H_5CHCl_2$), and mono-chloromethylbenzene ($C_6H_5CH_2Cl$).[35] In this paper, we report reactions of compound **1** with $C_6H_5CCl_3$ and *p*-$ClC_6H_4CCl_3$ as well as those of compound **2** with *p*-Cl-$C_6H_4CCl_3$ and carbon tetrachloride.

## Results and Discussion

**Activation of C−Cl and C−H Bonds.** Scheme 1 summarizes the reactions of compounds **1** or **2** with a series of chlorinated toluenes. The chemically active rhodium complex *cis*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SS)$], **1**, activated all C−Cl bonds of polychlorinated organic compounds, namely, $C_6H_5CCl_3$ and *p*-$ClC_6H_4CCl_3$ (except ring chlorine), and formed compounds *cis*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_5)$][Cl], **6**·Cl, and *cis*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_4Cl\text{-}p)$][Cl], **7**·Cl. Treatment of **6**·Cl and **7**·Cl with $NaBPh_4$ formed **6** and **7**, respectively. Similarly, the iridium complex *cis*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SS)$], **2**, activated all C−Cl bonds of *p*-$ClC_6H_4CCl_3$ (except ring chlorine) and formed the compound *cis*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_4Cl\text{-}p)$][Cl], **5**·Cl, and after anion exchange it formed **5**. Compound **6** is analogous to *cis*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_5)$][$BPh_4$], **3**, obtained by reaction of **2** with $C_6H_5CHCl_2$ or $C_6H_5CCl_3$; however, reaction of **2** with $C_6H_5CH_2Cl$ formed the S-benzylated product *cis*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SS\text{-}CH_2C_6H_5)$][$BPh_4$], **4**.[35] Interestingly, compound **2** activated all the C−Cl bonds of $CCl_4$ in methanol and formed the products *cis*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2CH)$][$BPh_4$], **8**, and [$Ir_4S_4(Cp^*)_4(\mu\text{-}CH_2)_4$][$BPh_4$]$_2$, **9** (Scheme 2). Compounds **3**−**9** are stable and are not affected by air, moisture, or light under ambient conditions, unlike the chemically active species **1** and **2**, which are sensitive to air. Electron spray mass ionization spectrometry (ESI-MS) showed signals due to cations of compounds.

The formation of compounds **3**, **5**, **6**, and **7** is believed to take place as follows. In the reaction of **2** with $C_6H_5$-



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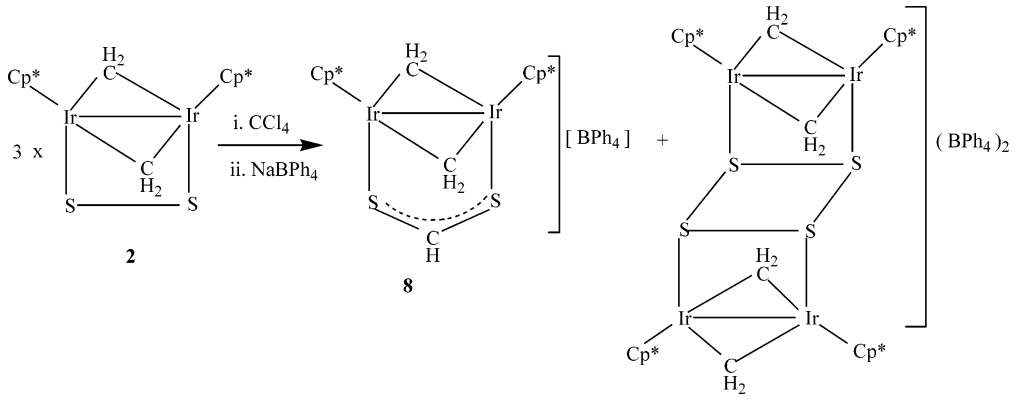
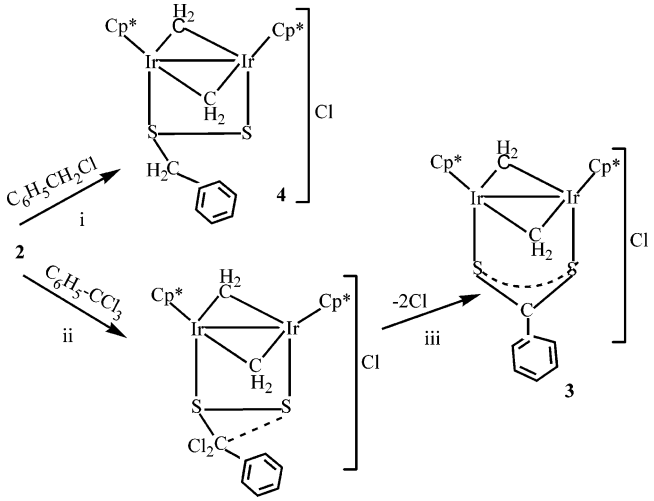
**Scheme 2**




**Scheme 3**




$CCl_3$, all C−Cl bonds are broken, while one Cl appears as an anion in *cis*-[(IrCp*)$_2$($\mu$-CH$_2$)$_2$($\mu$-S$_2$C-C$_6$H$_5$)]Cl, **3**·Cl (later replaced by $BPh_4$ anion to form **3**, Scheme 1); the fate of two other Cl atoms is not well understood, but it is likely that they may react with the solvent. The dithiobenzoate **3** is believed to be formed by an insertion of the "$CC_6H_5$" moiety from $C_6H_5CCl_3$ into the S−S bond of the disulfide ligand in **2**; similarly, compounds **5**, **6**, and **7** are believed to be formed. In the reaction of **2** with $C_6H_5CHCl_2$, activation of C−Cl and C−H bonds occurred and formed compound **3**; one Cl appears as an anion, while one H and Cl are lost or react in same manner as mentioned for $C_6H_5CCl_3$ above. The formation of **4** involves nucleophilic attack of **2** on the C−Cl bond, forming the S-benzylated product *cis*-[(IrCp*)$_2$($\mu$-CH$_2$)$_2$($\mu$-SS-CH$_2$C$_6$H$_5$)][$BPh_4$], **4**.[35] The formation of compounds **3** and **4** probably proceeds via the mechanism depicted in Scheme 3. A similar path may be followed by other reactions.

Reaction of **2** with $CCl_4$ is believed to involve the formation of the "ClCCl" moiety (species "Cl−C−Cl" exchanges one Cl atom with an H atom from MeOH to form the moiety "HCCl") and release of two chlorine atoms. The moiety "HCCl" then adds across the S−S bond of **2**, forming *cis*-[(IrCp*)$_2$($\mu$-CH$_2$)$_2$($\mu$-S$_2$CH)]Cl, **8**·Cl, which with $NaBPh_4$ formed *cis*-[(IrCp*)$_2$($\mu$-CH$_2$)$_2$($\mu$-S$_2$CH)][$BPh_4$], **8**. The origin of "CH" is doubtlessly $CCl_4$, as formation of **2** is carried out in MeOH itself.[35] The "CH" protons showed a signal at $\delta$ 9.25 (1H, s, $\mu$-S$_2$CH) in **8**·Cl, and when reaction of compound **2** was carried out in MeOH-$d_4$, the S$_2$CH proton signal disappeared due to the formation of *cis*-[(IrCp*)$_2$($\mu$-CH$_2$)$_2$($\mu$-S$_2$CD)]-Cl. The formation of compound **9** is believed to occur via oxidation of S of **2** by two chlorine atoms released as mentioned above: 2 *cis*-[(IrCp*)$_2$($\mu$-CH$_2$)$_2$($\mu$-S$_2$)] + 2 Cl → [Ir$_4$($\mu$-S)$_4$(Cp*)$_4$($\mu$-CH$_2$)$_4$]Cl$_2$, **9**·Cl$_2$, and hence [Ir$_4$S$_4$(Cp*)$_4$($\mu$-CH$_2$)$_4$][$BPh_4$]$_2$, **9**.

It may be pointed out here that the formation of **9** did not occur in other reactions, as described in this paper, under low concentration of organic chlorides used. However, to check the formation of **9** in other reactions, compound **2** was reacted with a large excess of (1,1-dichloromethyl)benzene, and it generated both **3** and **9**, but under low concentrations as mentioned above, there was no formation of **9**. The $CCl_4$ reaction is exceptional in that, as described above, both products **8** and **9** are formed, even under low concentration of $CCl_4$. The activation of bonds is suggested to involve formation of paramagnetic species, as ESR studies of a reaction mixture of solid **2** with $C_6H_5CCl_3$ showed that the rupture of C−Cl (also C−H in other substrates) bonds is probably occurring via formation of paramagnetic species ($g$ = 2.046), the exact nature of which is not understood.[35]

**NMR Spectroscopy.** The proton NMR spectrum of **5** showed one signal due to Cp* methyl protons, at $\delta$ 1.80 ppm, and two signals due to $\mu$-CH$_2$ protons, at $\delta$ 7.60 and 8.49 ppm (cf. for **2**, $\delta$ = 1.87 ppm, Cp* methyls, $\delta$ = 7.64 and 8.01 ppm, $\mu$-CH$_2$),[35] and signals due to an aromatic ring, *p*-Cl-C$_6$H$_4$CS$_2$, and $BPh_4$ anion (cf. Experimental Section). Similarly, $^{13}$C NMR signals of **5** appear at $\delta$ values of 9.40 (CH$_3$), 100.0 (C$_5$ ring of Cp*), and 100.9 ppm ($\mu$-CH$_2$) [cf. $^{13}$C NMR for **2**, $\delta$ 9.83 ppm (CH$_3$), 96.5 ppm (C$_5$ ring of Cp*), and 106.8 ($\mu$-CH$_2$)].[35] The characteristic signal due to the CS$_2$ carbon of **5** occurs at $\delta$ 208.9 ppm; this spectral behavior of **5** is analogous to that of **3**.[35] Proton NMR of **6** shows signals due to Cp* methyl protons, $\mu$-CH$_2$ protons, and the aromatic ring of C$_6$H$_5$CS$_2$ in a pattern similar to those for compound **3**;[35] however, $\mu$-CH$_2$ signals occur at low field {8.77, 9.81 ppm} vis-à-vis that of iridium complexes (**3**, 7.60, 8.50 ppm).[35] The $^{13}$C NMR signal of $\mu$-CH$_2$ of **6** appears at low field [$\delta$ = 168.7 ppm (t, $J_{Rh-C}$, 25.3 Hz)], vis-à-vis iridium compound **3** ($\delta$ 100.8 ppm, $\mu$-CH$_2$), and it shows higher lability of Rh−CH$_2$−Rh bonds. The spectral pattern of **7** is similar to that of **5** except for low-field proton and $^{13}$C NMR signals for $\mu$-CH$_2$ (cf. Experimental Section). Finally, the $^{13}$C signals for the CS$_2$ moiety for **5**, **6**, and **7** occur at, 208.9 (**5**), 222.9 (**6**), and 221.1 (**7**) ppm (cf. **3**, $\delta$ 210.8 ppm, CS$_2$). Proton NMR

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 5−7**

| | | | |
|---|---|---|---|
| **5** | | | |
| Ir(1)−Ir(2) | 2.6654(5) | Cl(1)−C(27) | 1.759(8) |
| Ir(1)−S(1) | 2.311(2) | Ir(2)−Ir(1)−S(1) | 93.90(6) |
| Ir(2)−S(2) | 2.309(2) | Ir(1)−Ir(2)−S(2) | 94.38(6) |
| Ir(1)−C(21) | 2.059(9) | Ir(1)−S(1)−C(23) | 113.0(3) |
| Ir(1)−C(22) | 2.063(9) | Ir(2)−S(2)−C(23) | 112.7(3) |
| S(1)−C(23) | 1.685(9) | S(1)−C(23)−S(2) | 125.9(5) |
| S(2)−C(23) | 1.681(9) | angle between planes of $Ir_2S_2C$ and Ph ring of $S_2CPh$ | 36.7(2) |
| **6** | | | |
| Rh(1)−Rh(2) | 2.6250(4) | Rh(2)−Rh(1)−S(1) | 94.52(4) |
| Rh(1)−S(1) | 2.318(2) | Rh(1)−Rh(2)−S(2) | 94.33(4) |
| Rh(2)−S(2) | 2.301(2) | Rh(1)−S(1)−C(23) | 111.5(2) |
| Rh(1)−C(21) | 2.040(5) | Rh(2)−S(2)−C(23) | 112.6(2) |
| Rh(1)−C(22) | 2.046(5) | S(1)−C(23)−S(2) | 127.0(4) |
| S(1)−C(23) | 1.672(6) | angle between planes of $Rh_2S_2C$ and Ph ring of $S_2CPh$ | 28.6(2) |
| S(2)−C(23) | 1.661(5) | | |
| **7** | | | |
| Rh(1)−Rh(2) | 2.6421(6) | Rh(2)−Rh(1)−S(1) | 94.79(5) |
| Rh(1)−S(1) | 2.314(2) | Rh(1)−Rh(2)−S(2) | 94.15(4) |
| Rh(2)−S(2) | 2.319(2) | Rh(1)−S(1)−C(23) | 111.6(2) |
| Rh(1)−C(21) | 2.048(7) | Rh(2)−S(2)−C(23) | 112.1(2) |
| Rh(1)−C(22) | 2.047(6) | S(1)−C(23)−S(2) | 127.2(4) |
| S(1)−C(23) | 1.679(7) | angle between planes of $Rh_2S_2C$ and Ph ring of $S_2CPhCl$ | 36.5(2) |
| S(2)−C(23) | 1.673(6) | | |
| Cl(1)−C(27) | 1.750(6) | | |

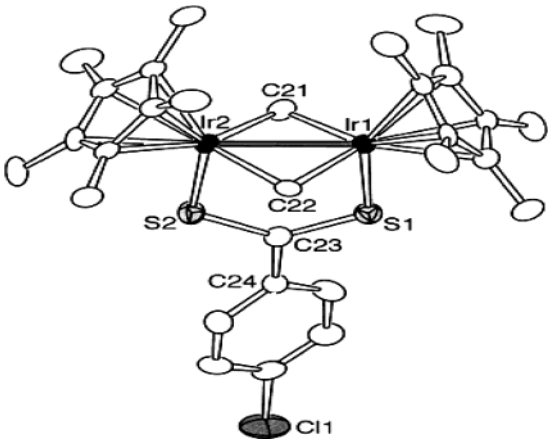



**Figure 1.** Crystal structure of the cation of **5** (H atoms and $BPh_4$ omitted for clarity).

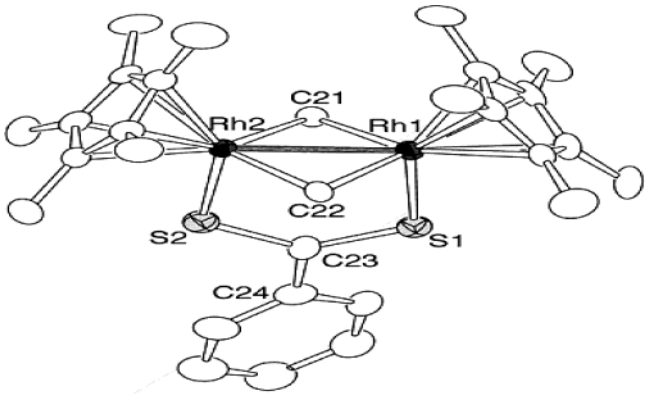



**Figure 2.** Crystal structure of the cation of **6** (H atoms and $BPh_4$ omitted for clarity).

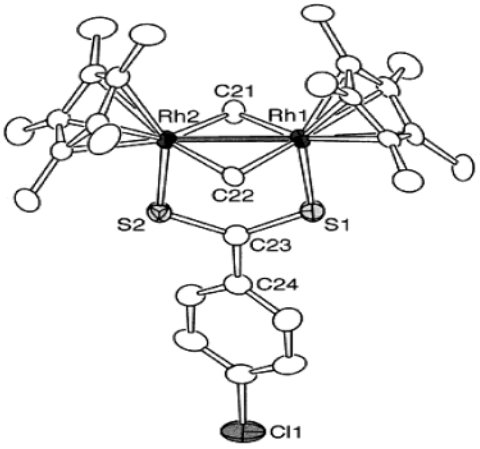



**Figure 3.** Crystal structure of the cation of **7** (H atoms and $BPh_4$ omitted for clarity).

data of compounds **8** and **9** showed peaks due to Cp* methyls and $\mu$-$CH_2$ protons (Experimental Section); **8** showed a signal due to $S_2CH$ as discussed above.

**Structures of Compounds 5−7.** The atomic numbering schemes of structures of cations of compounds **5**−**7** are shown in Figures 1−3, respectively. The bond lengths and bond angles are listed in Table 1. Compound **5** has a five-membered ring of $Ir_2S_2C$, consisting of an Ir−Ir single bond [2.6654(5) Å], two Ir−S single bonds [2.311(2), 2.309(2) Å], and two S−C bonds [1.685(9), 1.681(9) Å], being between more than a single bond and less than a double bond. This framework clearly demonstrates that two iridium atoms are coordinated to the *p*-Cl-$C_6H_4CS_2$ moiety. The S(1)−C(23)−S(2) bond angle for **5** is 125.9°, while the angle between the planes of $Ir_2S_2C$ and the aromatic ring of $S_2CC_6H_4$-Cl-*p* is 36.7(3)°, respectively. Compounds **6** and **7** have Rh−Rh bond lengths of 2.6250(4) and 2.6421(6) Å, respectively, and trends in the rest of the bond lengths and angles, are similar to those for **5** (Table 1).

**Unique Reactivity of the Bridged $S_2$ Dianion.** It is worthwhile to discuss the reactivity of $S_2$ coordinated to $Rh_2$ or $Ir_2$ bimetallic units. As mentioned in the

Introduction, activation of organic chlorides reported in the literature involves oxidative addition of chlorocarbons at the metal centers of complexes, before their transfer to organic molecules or their funcionalization in possible catalytic processes.[13,19−23] Activation of C−Cl bonds requires electron-rich centers, and thus compounds **1** and **2,** having electron-rich centers, are able to activate C−Cl bonds of organic chlorides such as chlorotoluenes or carbon tetrachloride. The activation occurs at the electron-rich sulfur donor atoms, leading to formation of S-benzylated **4**, S,S-bridged thiobenzoate complexes **3** and **5**−**7**, or thioformate complex **8**. The unique reactivity of the $S_2$ ligand coordinated to the metal dinuclear unit cannot be attributed to the ring strain of the four-membered ring formed by the $S_2$ ligand. This is supported by the formation of compound **4**, which involves nucleophilic attack of S on the C−Cl bond of $C_6H_5CH_2Cl$, and this compound is unaffected by air/moisture. The formation of **3** and **5**−**8** involves a change from four-membered to five-membered rings.

## Experimental Section

**Materials and Instruments.** All synthetic procedures were carried out using drybox or standard Schlenk techniques under dry $N_2$. Reagent grade solvents were distilled under argon from the appropriate standard drying agents. The general materials used were purchased from Wako Pure Chemical Industries, Tokyo Chemical Industies, Tokyo Kasei Kogyo, or Aldrich-Sigma Ltd. *trans*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2Me_2$] was prepared by literature methods.[36,37] *trans*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2Cl_2$] was prepared as follows. To a solution of *trans*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2Me_2$] (1.3 g, 2.4 mmol) in $CH_2Cl_2$ (30 mL) was added $CH_3COCl$ (0.5 mL, 7 mmol) at 0 °C, and the brown solution turned red. The mixture was stirred for 30 min at 0 °C, warmed to room temperature, and then refluxed for 2 h at 40 °C. To the mixture was added $CH_3OH$ (20 mL), and the reaction mixture was left for 1 h at room temperature. The mixture was concentrated to dryness under reduced pressure to leave a dark brown solid. The solid was washed with two 5 mL portions of diethyl ether, and the remaining solid was extracted with toluene (40 mL) using a Soxhlet extractor for 6 h. The extract was concentrated to obtain *trans*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2Cl_2$], which was washed with two 5 mL portions of diethyl ether. Yield: 1.2 g (84.4%). *trans*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2Me_2$] was prepared by a reported method[37] or by reaction of $Cp^*_2Ir_2Cl_4$[38,39] with $Al_2Me_6$ followed by reaction with acetyl chloride as for rhodium discussed above, and this formed *trans*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2Cl_2$]. The $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a JEOL 300 or 600 MHz at 25 °C by using TMS as the internal standard. Electron spray ionization mass spectra (ESI-MS) of the samples were measured on an Applied Biosystems Mariner mass spectrometer. The melting points of compounds were determined with a micromelting point apparatus (Yanaco, Japan). Elemental analyses were determined by the analytical center of Osaka City University, Japan. Compounds **1** and **2** were prepared as reported earlier.[35]

***cis*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_4Cl\text{-}p)$][$BPh_4$], 5.** To the flask containing *cis*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2)$], **2** (0.119 g, 0.160 mmol), were added 5 mL of MeOH and 38 $\mu$L (0.056 g, 0.240 mmol) of *p*-chloro-1,1,1-trichloromethylbenzene dissolved in 3 mL of methanol. The rest of the procedure was the same as for **3** [formation of **5**·Cl checked using $^1H$ NMR (300 MHz, $CD_3OD$, $\delta$, ppm): 1.96 (30H, s, Cp*), 7.83 (2H, s, $\mu$-$CH_2$), 8.55 (2H, s, $\mu$-$CH_2$), 7.75 {2H, d, $J$ = 8.76, o-($C_6H_4Cl$)$CS_2$}, 7.34 {2H,d, $J$ = 8.61, m-($C_6H_4Cl$)$CS_2$}]. Yield: 0.110 g, 70%. Dark red crystals (**5** as $BPh_4$ salt) were formed using $CH_2Cl_2$−toluene. Mp: 280−285 °C (dec). C, H Anal. Calcd for $C_{53}H_{58}BClIr_2S_2$: C 53.50, H 4.91. Found: C 53.30, H 4.86. $^1H$ NMR (600 MHz, $CDCl_3$, $\delta$, ppm, $J$, Hz): 1.80 (30H, s, Cp*), 7.60 (2H, s, $\mu$-$CH_2$), 8.49 (2H, s, $\mu$-$CH_2$); 7.67 {2H, dt, $J$ = 8.7, 0.4, o-($C_6H_4Cl$)$CS_2$}, 7.26 {2H, dd, $J$ = 7.6, 0.2, m-($C_6H_4Cl$)$CS_2$}, 7.42 (8H, s, br, o-$Ph_4B$), 7.03 (8H, t, $J$ = 7.4, m-$Ph_4B$), 6.87 (4H, t, $J$ = 7.2, p-$Ph_4B$). $^{13}C$ NMR (150 MHz, $CDCl_3$, $\delta$, ppm): 9.4 ($CH_3$), 100.0 ($C_5$ ring of Cp*), 100.9 ($\mu$-$CH_2$), 138.5 {i-C, ($C_6H_4Cl$)$CS_2$}, 127.5 {o-C, ($C_6H_4Cl$)$CS_2$}, 128.7 {m-C, ($C_6H_4Cl$)$CS_2$}, 138.2 {p-C, ($C_6H_4Cl$)$CS_2$}, 208.9 ($CS_2$); 164.2 (i-C, $BPh_4$), 136.3 (o-C, $BPh_4$), 125.4 (m-C, $BPh_4$), 121.5 (p-C, $BPh_4$). ESI-MS: $m/z$ 871 [$M^+$].

**Crystal data for 5:** $C_{53}H_{58}BClIr_2S_2$, $M$ = 1189.86, triclinic, $P\bar{1}$ (no. 2), $a$ = 11.608(2) Å, $b$ = 11.874(2) Å, $c$ = 17.974(3) Å, $\alpha$ = 95.436(3)°, $\beta$ = 99.040(4)°, $\gamma$ = 104.671(4)°, $V$ = 2343.2(8) Å$^3$, $Z$ = 2, $D_c$ = 1.686 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 5.871 mm$^{-1}$, $T$ = 193 K, no. of unique reflections, 10 107, $R_{int}$ 0.056, reflections with [$I > 2\sigma(I)$], 7402, final indices $R$, 0.056, $R_w$ (all data), 0.094.

***cis*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_5)$][$BPh_4$], 6.** To the flask containing *cis*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2)$], **1** (0.057 g, 0.100 mmol), were added 5 mL of MeOH and 24 $\mu$L (0.040 g, 0.200 mmol) of 1,1,1-trichloromethylbenzene dissolved in 2 mL of methanol. The rest of the procedure was the same as for **3** {**6**·Cl: $^1H$ NMR (300 MHz, $CD_3OD$, $\delta$, ppm): 1.85 (30H, s, Cp*), 8.88 (2H, s, $\mu$-$CH_2$), 9.83 (2H, s, $\mu$-$CH_2$), 7.93 (2H, m, o-$PhCS_2$), 7.76 (1H, m, p-$PhCS_2$), 7.37 (2H, m-$PhCS_2$, obscured by reagent band)}. Yield: 0.050 g, 51%. Dark red crystals of **6** were formed using $CH_2Cl_2$−toluene (or $CH_2Cl_2$−methanol). Mp: 230−235 °C (dec). C, H Anal. Calcd for $C_{53.2}H_{59.4}BCl_{0.4}Rh_2S_2\cdot(0.2CH_2Cl_2)$: C 64.30, H 6.03. Found: C 64.02, H 6.01. $^1H$ NMR (600 MHz, $CDCl_3$, $\delta$, ppm, $J$, Hz): 1.82 (30H, s, Cp*), 8.77 (2H, d, $J$ = 1.7, $\mu$-$CH_2$), 9.81 (2H, s, $\mu$-$CH_2$); 7.78 (2H, dd, $J$ = 7.3, 1.1, o-$PhCS_2$), 7.47 (1H, tt, $J$ = 5.9, 0.8, p-$PhCS_2$), 7.33 (2H, m-$PhCS_2$), 7.60 (8H, dt, $J$ = 8.1, 1.0, o-$Ph_4B$), 7.44 (8H, t, $J$ = 7.9, m-$Ph_4B$), 7.34 (4H, p-$Ph_4B$). $^{13}C$ NMR (150 MHz, $CDCl_3$, $\delta$, ppm): 9.81 ($CH_3$), 105.0 ($C_5$ ring of Cp*), 168.7 (t, $J_{Rh-C}$, 25.3, $\mu$-$CH_2$), 142.7 (i-C, $PhCS_2$), 126.5 (o-C, $PhCS_2$), 128.5 (m-C, $PhCS_2$), 132.3 (p-C, $PhCS_2$), 222.9 ($CS_2$); −, 127.2 (o-C, $BPh_4$), 128.7 (m-C, $BPh_4$) 127.5 (p-C, $BPh_4$). ESI-MS: $m/z$ 657 [$M^+$].

**Crystal data for 6:** $C_{53}H_{59}BRh_2S_2$, $M$ = 976.79, monoclinic, $P2_1$ (No. 4), $a$ = 9.889(2) Å, $b$ = 21.831(3) Å, $c$ = 11.133(2) Å, $\alpha$ = 90°, $\beta$ = 110.894(3)°, $\gamma$ = 90°, $V$ = 2245.5(6) Å$^3$, $Z$ = 2, $D_c$ = 1.445 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.862 mm$^{-1}$, $T$ = 193 K, no. of unique reflections, 9717, $R_{int}$ 0.037, reflections with [$I > 2\sigma(I)$], 9041, final indices $R$, 0.045, $R_w$ (all data), 0.119.

***cis*-[$(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_4\text{-}Cl\text{-}p)$][$BPh_4$], 7.** It was prepared by the same method as for **3** using *p*-chloro-1,1,1-trichloromethylbenzene [**7**·Cl: $^1H$ NMR (300 MHz, $CD_3OD$, $\delta$, ppm): 1.85 (30H, s, Cp*), 8.89 (2H, s, $\mu$-$CH_2$), 9.84 (2H, s, $\mu$-$CH_2$), 8.16 {2H, d, $J$ = 8.97, o-($C_6H_4Cl$)$CS_2$}, 7.82 {2H, d, $J$ = 8.80, m-($C_6H_4Cl$)$CS_2$}. Yield: 0.060 g, 59%. Dark red crystals (**7**) were formed using $CH_2Cl_2$−toluene (or $CH_2Cl_2$−methanol). Mp: 235−240 °C (dec). C, H Anal. Calcd for $C_{53}H_{58}BClRh_2S_2$: C 62.9, H 5.78. Found: C 62.5, H 5.76. $^1H$ NMR (600 MHz, $CDCl_3$, $\delta$, ppm, $J$, Hz): 1.68 (30H, s, Cp*), 8.63 (2H, d, $J$ = 1.5, $\mu$-$CH_2$), 9.76 (2H, s, $\mu$-$CH_2$); 7.74 {2H, dt, $J$ = 8.7, 1.0, o-($C_6H_4Cl$)$CS_2$}, 7.29 {2H, dt, $J$ = 8.7, 1.0, m-($C_6H_4Cl$)$CS_2$}, 7.42 (8H, s, br, o-$Ph_4B$), 7.03 (8H, t, $J$ = 7.3, m-$Ph_4B$), 6.87 (4H, t, J 7.2, p-$Ph_4B$). $^{13}C$ NMR (150 MHz, $CDCl_3$, $\delta$, ppm): 9.65 ($CH_3$), 104.9 ($C_5$ ring of Cp*), 168.7 (br, $\mu$-$CH_2$), 140.8 {i-C, ($C_6H_4Cl$)$CS_2$}, 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, $BPh_4$). ESI-MS: $m/z$ 691 [$M^+$].

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**Crystal data for 7:** $C_{53}H_{58}BClRh_2S_2$, $M = 1011.24$, triclinic, $P\bar{1}$ (No. 2), $a = 11.626(2)$ Å, $b = 11.859(2)$ Å, $c = 17.956(4)$ Å, $\alpha = 95.290(3)°$, $\beta = 99.075(4)°$, $\gamma = 104.518(4)°$, $V = 2343.9(8)$ Å$^3$, $Z = 2$, $D_c = 1.433$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.884 mm$^{-1}$, $T = 193$ K, no. of unique reflections, 10 542, $R_{int}$ 0.040, reflections with [$I > 2\sigma(I)$], 8773, final indices $R$, 0.068, $R_w$ (all data), 0.153.

**Reaction of *cis*-[(IrCp*)$_2$($\mu$-CH$_2$)$_2$($\mu$-S$_2$)], 2, with Carbon Tetrachloride: Synthesis of *cis*-[(IrCp*)$_2$($\mu$-CH$_2$)$_2$($\mu$-S$_2$CH)]-[BPh$_4$], 8, and [Ir$_4$S$_4$(Cp*)$_4$($\mu$-CH$_2$)$_4$][BPh$_4$]$_2$, 9.** To the flask containing the solid **2** (0.092 g, 0.123 mmol) were added 3 mL of methanol and 24 $\mu$L (0.038 g, 0.246 mmol) of carbon tetrachloride. The contents were stirred for 20 h at room temperature, and the color of the solution changed from dark brown to dark green. The solvent was removed using a rotary evaporator in the open atmosphere. The $^1$H NMR of an aliquot portion in $CD_3OD$ supported the formation of two different species. The solid was redissolved in 10 mL of methanol, and an excess of $NaBPh_4$ (0.050 g) in 5 mL of methanol was added. This led to the formation of precipitates, which were washed with methanol and dissolved again in dichloromethane, and an excess of methanol was layered over it. Dark green crystalline product was separated in 2 days time. The green compound was separated and washed well with methanol and dried. The $^1$H NMR of the green compound in DMSO-$d_6$ showed formation of a different compound (yield, 0.035 g, 53%, compound **9**). The mother liquor was yellow-brown, solvents were removed and dissolved in a minimum amount of dichloromethane, and methanol was diffused. No more precipitation of green compound occurred. Solvent was removed and NMR recorded, which showed a different compound (yield, 0.025 g, 37%, compound **8**).

***cis*-[(IrCp*)$_2$($\mu$-CH$_2$)$_2$($\mu$-S$_2$CH)]Cl, 8·Cl.** $^1$H NMR (300 MHz, $CD_3OD$, $\delta$, ppm, $J$, Hz): 1.93(30H, s, Cp*), 8.47 (2H, s, $\mu$-$CH_2$), 7.75 (2H, s, $\mu$-$CH_2$), 9.25 (1H, s, $\mu$-$S_2CH$). **8·BPh$_4$.** $^1$H NMR (300 MHz, $CDCl_3$, $\delta$, ppm, $J$, Hz): 1.74 (30H, s, Cp*), 8.42 (2H, s, $\mu$-$CH_2$), 7.51 (2H, s, $\mu$-$CH_2$), 8.80 (1H, s, $\mu$-$S_2CH$); 6.85 (4H, t, p-$BPh_4$), 7.01 (8H, t, m-$BPh_4$) 7.40 (8H, br, o-$BPh_4$). ESI-MS: $m/z$ 759 [M$^+$]. Anal. Found: C 53.70, H 5.25. Calcd for $Ir_2S_2BC_{47}H_{55}$·(0.3·toluene), $Ir_2S_2BC_{49.1}H_{57.1}$: C 53.30, H 5.20. Mp: 240−245 °C.

**[Ir$_4$S$_4$(Cp*)$_4$($\mu$-CH$_2$)$_4$]Cl$_2$, 9·Cl$_2$.** $^1$H NMR (300 MHz, $CD_3OD$, $\delta$, ppm, $J$, Hz): 1.88 (60H, s, Cp*), 7.83 (2H, s, $\mu$-$CH_2$), 7.72 (2H, s, $\mu$-$CH_2$), 7.48 (2H, s, $\mu$-$CH_2$, 6.53 (2H, s, $\mu$-$CH_2$). **9**·($BPh_4$)$_2$: $^1$H NMR (300 MHz, DMSO-$d_6$ $\delta$, ppm, $J$, Hz): 1.81 (60H, s, Cp*), 7.79 (2H, s, $\mu$-$CH_2$), 7.71 (2H, s, $\mu$-$CH_2$), 7.38 (2H, s, $\mu$-$CH_2$, 6.39 (2H, s, $\mu$-$CH_2$); 6.87 (4H, t, p-$BPh_4$), 7.02 (8H, t, m-$BPh_4$), 7.41 (8H, br, o-$BPh_4$). ESI-MS: $m/z$ 746 [M$^{2+}$]. Anal. Found: C 50.81, H 5.02. Calcd for [$Ir_4S_4$(Cp*)$_4$($\mu$-$CH_2$)$_4$]-($BPh_4$)$_2$·0.6$CH_2Cl_2$, $Ir_4S_4B_2C_{92}H_{108}$·0.6$CH_2Cl_2$: C 50.9, H 5.04. Mp > 290 °C.

CCDC numbers are 208 939 (**3**), 216 144 (**4**), 208 940 (**5**), 218 237 (**6**), and 218 238 (**7**).

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**Supporting Information Available:** Details about the crystal structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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