Angewandte
Chemie

Bond Activation

Activation of C$-$Cl and C$-$H Bonds by Ligated S_2^{2-} Ions: Conversion of Organic Chlorides into Organosulfur Compounds in *cis*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2R)]^+$**

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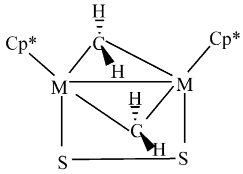
Numerous organic halides, such as 1,1,1-trichloroethane, 1,2-dichloroethane, mono-, di-, and trichloromethylbenzenes, chloroform, dichloromethane, and carbon tetrachloride are used in chemical laboratories, industries, and electrical appliances. Most of these organic halides are toxic and some find their way into the atmosphere, thus posing health hazards. As a result, various investigators are engaged in the activation of carbon–chlorine bonds using chemical, microbial, or thermal methods for converting organic halides into either less toxic or industrially useful materials.[1–7]

The activation of C$-$Cl bonds by chemical methods essentially involves reactions at a metal surface[2] or oxidative addition at the metal center of complexes.[3,4,7] Thiolate anions S_n^{2-} ($n = 1, 2, 3$) can convert alkyl chloride into dialkyl oligosulfane by activation of the C$-$Cl bond.[8] However, there is no report of multiple C$-$Cl bond activation by a coordinated S_2 ligand.[1–9] The S_2 ligand in *cis*-$[(MCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2)]$ (**1**: M = Rh, **2**: M = Ir; $Cp^* = C_5Me_5$) coordinates to the dinuclear metal unit in a parallel fashion and displays high nucleophilicity towards dioxygen.[10,11] With the electronically and structurally unique S_2 ligands in compounds **1** and **2**,[12] we have explored the multibond activation of C$-$Cl and C$-$H bonds in polychlorinated organic compounds. Herein we report the formation of dithiocarboxylate or related complexes by the reaction of **2** with a series of chlorinated organic substrates, namely, (1,1,1-trichloromethyl)benzene, (1,1-dichloromethyl)benzene, and (chloromethyl)benzene.



M = Rh (**1**), Ir (**2**)

Iridium compound **2** activates all three C$-$Cl bonds of $C_6H_5\text{-}CCl_3$ as well as the C$-$Cl and C$-$H bonds of $C_6H_5\text{-}CHCl_2$ to form the dithiobenzoate complex *cis*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_5)][BPh_4]$ (**3**; Scheme 1).[12,13] Furthermore, it activates the C$-$Cl bond of $C_6H_5\text{-}CH_2Cl$ to produce the S-benzylated compound *cis*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SS\text{-}CH_2\text{-}C_6H_5)][BPh_4]$ (**4**). This result shows that a decrease in the number of C$-$Cl bonds makes activation of C$-$H bonds more difficult, thus paving the way for the formation of **4**. Complexes **3** and **4** are stable and are not affected by air, moisture, or light under ambient conditions. This stability is in contrast to the active species **2**, which is sensitive to air. The formation of compound **4** can be described as an oxidative addition of $C_6H_5\text{-}CH_2Cl$ at one S atom, while the reactions to produce **3** involve loss of either two Cl or one Cl and one H atoms. The exact mechanism of the reaction is not yet clear.

The ^1H and ^{13}C NMR spectra of compound **3** suggest that the dinuclear unit of $\{(IrCp^*)_2(\mu\text{-}CH_2)_2\}$ remains intact in solution.[12,13] The characteristic S_2C signal of the dithiobenzoate carbon atom appears at $\delta = 210.8$ ppm. Interestingly, the S-benzyl compound **4** shows two signals for nonequivalent Cp* groups, four signals for asymmetric protons of the $\mu\text{-}CH_2$ groups, and four signals (AB quartet) for $S\text{-}CH_2$ protons.[13] The ^{13}C NMR spectrum of **4** displays one signal for the $S\text{-}CH_2$ carbon atom at $\delta = 54.2$ ppm, two signals each for the CH_3 groups, C_5 ring, and $\mu\text{-}CH_2$ carbon atoms.[13] ESI-mass spectrometry shows signals for the cations of **3** and **4**.[13]

The structures of the cations of **3** and **4** are shown in Figures 1 and 2.[14] Compound **3** has a five-membered ring of Ir_2S_2C consisting of an Ir$-$Ir single bond (2.6523(4) Å), two Ir$-$S single bonds (2.319(2), 2.304(2) Å), and two S$-$C bonds (1.667(9), 1.68(1) Å) that are intermediate between a single bond and a double bond. This framework clearly demonstrates that two iridium atoms coordinate to the dithiobenzoate which is formed by insertion of the "CC_6H_5" moiety from $C_6H_5\text{-}CHCl_2$ or $C_6H_5\text{-}CCl_3$ into the S$-$S bond of the original disulfide ligand. In contrast, compound **4** has a four-membered ring of Ir_2S_2 made up of an Ir$-$Ir single bond (2.6517(2) Å), two Ir$-$S single bonds (2.341(1), 2.368(1) Å), and a short S$-$S bond (2.091(2) Å). One of the two S atoms is bonded to the $C_6H_5\text{-}CH_2$ moiety which originates from $C_6H_5\text{-}CH_2Cl$.

The reaction of **2** with *p*-$ClC_6H_4\text{-}CCl_3$, with a chloride atom directly attached to the benzene ring, resulted in the formation of *cis*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_4\text{-}Cl\text{-}p)][BPh_4]$, which is similar to **3**.[15] From these reactions, it was noted that the ease of C$-$Cl or C$-$H bond cleavage varies in the following sequence: $p\text{-}ClC_6H_4\text{-}CCl_3 \approx C_6H_5\text{-}CCl_3 > C_6H_5\text{-}CHCl_2 > C_6H_5\text{-}CH_2Cl$. The activation of C$-$Cl bonds in $C_6H_5CCl_3$ and *p*-$ClC_6H_4CCl_3$ using rhodium compound **1** formed the analogous complexes *cis*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_5)][BPh_4]$ and *cis*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2C\text{-}C_6H_4\text{-}Cl\text{-}$

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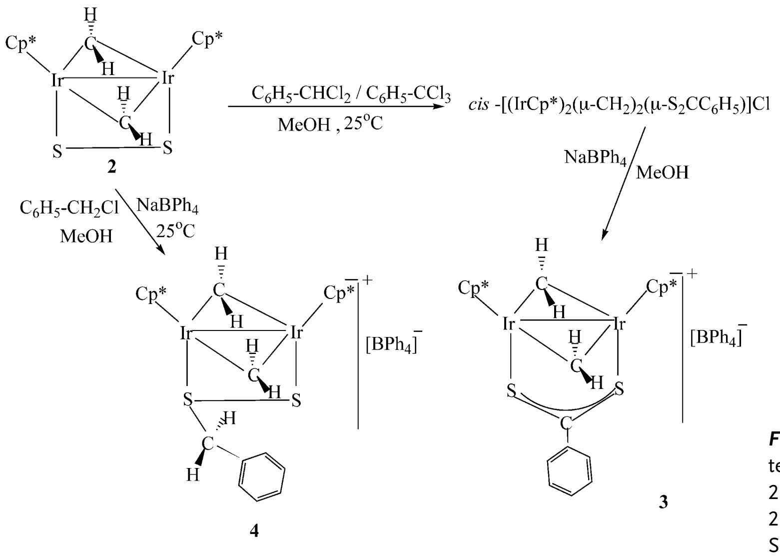
[**] We gladly acknowledge the award of an Invitation Fellowship for Professor Lobana from the Japan Society for the Promotion of Science(JSPS) and sabbatical leave by the parent university in Amritsar. $Cp^* = C_5Me_5$.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200351792



Scheme 1. Reactions of complex **2** with chlorinated organic substrates proceeds with C−Cl or C−H bond activation to provide products **3** and **4**.

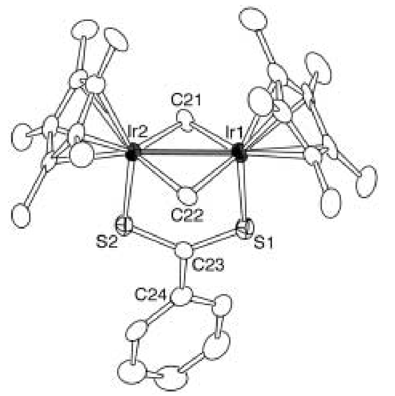


Figure 1. Structure of **3** (H atoms and the BPh_4^- counterion are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ir1-Ir2 2.6523(4), Ir1-S1 2.319(2), Ir2-S2 2.304(2), S1-C23 1.667(9), S2-C23 1.68(1), C23-C24 1.47(1); Ir2-Ir1-S1 94.18(7), Ir1-Ir2-S2 94.20(7), Ir2-S2-C23 112.7(3), Ir1-S1-C23 112.4(4), S2-C23-S1 126.5(5).

p)][BPh_4].[15] The reaction of **2** with CCl_4 is more complex, and one of the products identified by ^1H NMR spectroscopy and ESI mass spectrometry is *cis*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2CH)$][$BPh_4$].[15] Finally, compound **2** activated all three C−Cl bonds of 1,1,1-trichloroethane to form *cis*-[$(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2CCH_3)$]$^+Cl^-$. The ESR studies of a reaction mixture of **2** with $C_6H_5CCl_3$ have shown that cleavage of C−Cl bonds (as well as C−H bonds in other substrates) probably occurs with intermediate formation of paramagnetic species ($g = 2.046$), the exact nature of which is not yet understood.

The reactions described herein may lead to the development of catalytic cycles using *trans*-[$(MCp^*)_2(\mu\text{-}CH_2)_2Cl_2$] (M = Rh, Ir) as catalysts in the activation of organic chlorides via active species **1** or **2**. Further investigations are in progress.

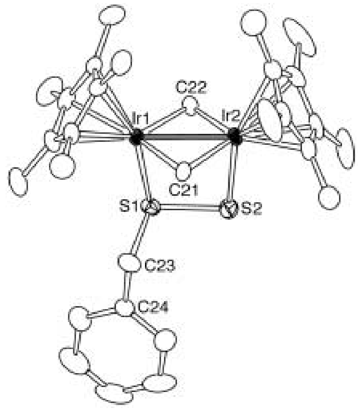


Figure 2. Structure of **4** (H atoms and the BPh_4^- counterion are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ir1-Ir2 2.6517(2), Ir1-S1 2.341(1), Ir2-S2 2.368(1), S1-C23 1.849(6), S1-S2 2.091(2), C23-C24 1.505(8);Ir2-Ir1-S1 83.22(3), Ir1-Ir2-S2 83.07(3), Ir2-S2-S1 96.21(7), Ir1-S1-S2 97.45(6), S1-C23-C24 112.7(4), S2-S1-C23 103.9(2).

Experimental Section

3: Methanol (5 mL) and (1,1,1-trichloromethyl)benzene (18 μL, 0.024 g, 0.123 mmol) dissolved in methanol (3 mL) were added to a flask containing solid **2** (0.060 g, 0.080 mmol).[12] The contents were stirred for 48 h at room temperature; the color of the solution changed from dark brown to dark red. The solvent was removed with a rotary evaporator in the open atmosphere. The ^1H NMR spectrum of a small sample in CD_3OD was recorded to confirm the formation of the cation of **3** (Cl^-).[13] The solid in the flask was redissolved in MeOH (5 mL), and an excess of $NaBPh_4$ (0.050 g, 0.160 mmol) dissolved in MeOH (5 mL) was added. The dark red precipitates formed were collected by filtration and washed with methanol (yield: 0.055 g, 60 %). The solid was redissolved in dichloromethane (5 mL), filtered, and the filtrate layered with an excess of dry toluene (50 mL). Orange crystals of **3** formed in a few days. M.p. 270–275 °C (decomp), elemental analysis calcd (%) for $C_{53}H_{59}BIr_2S_2$: C 55.10, H 5.15; found: C 54. 91, H 5.10.

4: Methanol (5 mL) and (chloromethyl)benzene (18 μL, 0.020 g, 0.160 mmol) dissolved in methanol (2 mL) were added to a flask containing solid **2** (0.060 g, 0.080 mmol). The contents were stirred for 72 h at room temperature; the color of the solution changed from dark brown to red-brown. The rest of the procedure was the same as described for compound **3**. Yield: 0.050 g, 54 %. The crystals of **4** were initially grown from CH_2Cl_2/toluene and subsequently regrown from CH_2Cl_2/methanol. M.p. 220–225 °C (decomp), elemental analysis calcd (%) for $C_{53}H_{61}BIr_2S_2$: C 54.99, H 5.31; found: C 54. 20, H 5.28.

Received: May 2, 2003
Revised: August 4, 2003 [Z51792]

Keywords: C−Cl activation · C−H activation · iridium · S ligands

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[12] Compound **2** was prepared by the reaction of *trans*- [(IrCp*)$_2$(μ-CH$_2$)$_2$Cl$_2$] (0.120 g, 0.160 mmol) with Li$_2$S$_2$ (0.030 g, 0.385 mmol) in methanol (75 mL) (method A), or by the reaction of *trans*-[(IrCp*)$_2$(μ-CH$_2$)$_2$Cl$_2$] (0.120 g, 0.160 mmol) with elemental sulfur (0.011 g, 0.344 mmol) in dry methanol (30 mL) and addition of NaBH$_4$ (0.024 g, 0.632 mmol) in 10 mL of dry THF (method B). In both cases the reactions were carried out under an atmosphere of N$_2$ and followed by removal of solvent under vacuum. ^{1}H NMR (300 MHz, CD$_3$OD): $\delta = 1.87$ (30H, s, Cp*), 7.64 (2H, s, μ-CH$_2$), 8.01 (2H, s, μ-CH$_2$); ^{13}C NMR (75 MHz, CD$_3$OD): $\delta = 9.83$ (CH$_3$), 96.5 (C$_5$ ring of Cp*), 106.8 (μ-CH$_2$); MS(ESI), $m/z = 746$ [M^+]. Compound **1** was prepared by method A with *trans*-[(RhCp*)$_2$(μ-CH$_2$)$_2$Cl$_2$] (0.060 g, 0.104 mmol) and Li$_2$S$_2$ (0.016 g, 0.205 mmol) in methanol (50 mL). ^{1}H NMR (300 MHz, CD$_3$OD): $\delta = 1.74$ (30H, s, Cp*), 9.09 (2H, s, μ-CH$_2$), 9.91 (2H, s, μ-CH$_2$).[10a,11]

[13] Compound **3**: ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 1.80$ (30H, s, Cp*), 7.60 (2H, s, μ-CH$_2$), 8.50 (2H, s, μ-CH$_2$), 7.71 (2H, dd, $J = 8.4$, 1.1 Hz, *o*-PhCS$_2$), 7.46 (1H, tt, $J = 7.4$, 0.4 Hz, *p*-PhCS$_2$), 7.29 (2H, tt, $J = 8.2$, 0.3 Hz, *m*-PhCS$_2$), 7.42 (8H, s, br, *o*-Ph$_4$B), 7.03 (8H, t, $J = 7.4$ Hz, *m*-Ph$_4$B), 6.87 (4H, t, $J = 7.1$ Hz, *p*-Ph$_4$B); ^{13}C NMR (150 MHz, CDCl$_3$): $\delta = 9.41$ (CH$_3$), 99.8 (C$_5$ ring of Cp*), 100.8 (μ-CH$_2$), 140.2 (*i*-C, PhCS$_2$), 126.3 (*o*-C, PhCS$_2$), 128.5 (*m*-C, PhCS$_2$), 132.1(*p*-C, PhCS$_2$), 210.8 (CS$_2$), 164.3 (*i*-C, BPh$_4$), 136.3 (*o*-C, BPh$_4$), 125.4 (*m*-C, BPh$_4$) 121.5 (*p*-C, BPh$_4$); MS (ESI), $m/z = 835$ [M^+]. Compound **4**: ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.77$ (15H, s, Cp*), 1.79 (15H, s, Cp*), 3.89, 3.85, 3.73, 3.69 (2H, S-CH$_2$), 7.87 (1H, s, μ-CH$_2$), 7.514 (1H, s, μ-CH$_2$), 7.509 (1H, s, μ-CH$_2$), 7.410 (1H, s, μ-CH$_2$), 7.29 (2H, *m*, *o*-PhCH$_2$), 7.24 (1H, *p*-PhCH$_2$- obscured by solvent peak), 7.12 (2H, m, *m*-PhCH$_2$), 7.41 (8H, s, br, *o*-Ph$_4$B), 7.01 (8H, t, $J = 7.3$ Hz, *m*-Ph$_4$B), 6.85 (4H, t, $J = 7.1$ Hz, *p*-Ph$_4$B); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 9.66$, 9.95 (CH$_3$), 97.2, 98.0 (C$_5$ ring of Cp*), 106.2, 109.3 (μ-CH$_2$), 132.9 (*i*-C, Ph-CH$_2$SS-), 129.1 (*o*-C, Ph-CH$_2$SS-), 128.9 (*m*-C, PhCH$_2$SS-), 128.8 (*p*-C, PhCH$_2$SS-), 54.2 (SS-CH$_2$), 164.2 (*i*-C, BPh$_4$), 136.3 (*o*-C, BPh$_4$), 125.4 (*m*-C, BPh$_4$), 121.5 (*p*-C, BPh$_4$); MS (ESI), $m/z = 837$ [M^+].

[14] Crystallography : The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) at 193 K. All calculations were performed using SGI INDY. The structure was solved by direct methods using the program SIR 92 and refined by full-matrix least-squares techniques against F^2 using the SHELXL-97 and teXsan program as a graphical interface. Crystal data for **3** (C$_{53}$H$_{59}$Ir$_2$S$_2$B): red prism, $0.10 \times 0.20 \times 0.23$ mm, $M_r = 1155.42$, monoclinic space group, $P2_1$ (no. 4); $a = 9.892$ (2), $b = 21.841(3)$, $c = 11.990(2)$ Å, $\beta = 119.715(3)°$, $V = 2249.8(6)$ Å^3; $\rho_{\text{calcd}} = 1.705$ g cm^{-3}, $Z = 2$; $F(000) = 1136$, $\mu(\text{Mo}_{K\alpha}) = 6.054$ mm^{-1}; 21941 reflections were collected, of which 8247 were unique ($R_{\text{int}} = 0.052$); $R_1 = 0.041$ (7210 reflections with $I > 2.0\sigma I$), $wR_2 = 0.080$ (all data). Crystal data for **4** (C$_{53}$H$_{61}$BIr$_2$S$_2$): orange prism, $0.15 \times 0.20 \times 0.20$ mm, $M_r = 1157.43$, monoclinic space group, $P2_1/a$ (no. 14); $a = 11.9872(5)$, $b = 28.281(1)$, $c = 13.9403(7)$ Å, $\beta = 94.231(3)°$, $V = 4713.0(4)$ Å^3; $\rho_{\text{calcd}} = 1.631$ g cm^{-3}, $Z = 4$; $F(000) = 2280.00$, $\mu(\text{Mo}_{K\alpha}) = 5.780$ mm^{-1}; 36629 reflections were collected, of which 10690 were unique($R_{\text{int}} = 0.037$); $R_1 = 0.037$ (9602 reflections with $I > 2.0\sigma I$), $wR_2 = 0.096$ (all data). Crystallographic data (excluding structure factors) for the crystal structures reported in this paper have been deposited with the Cambridge Data Centre as supplementary publication number: CCDC 208939 (**3**) and CCDC 216144 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[15] See the Supporting Information.