Reactions of 16-Electron Iridium(III) Dithiolene Complexes with Diazoalkanes: Formation and Properties of Novel Mononuclear and Binuclear Alkylidene Adducts of Iridium Dithiolene Complexes

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Some 16-electron pentacoordinated iridium dithiolene complexes were synthesized by the reactions of $[Cp*Ir(Cl)(\mu\text{-}Cl)]_2$ ($Cp* = C_5Me_5$) with 1,3-dithiol-2-one derivatives. The iridium dithiolene complex $[Cp*Ir\{S_2C_2(COOMe)_2\}]$ (**1**) reacted with ethyl diazoacetate or (trimethylsilyl)diazomethane to give the 1:1 alkylidene adducts of iridium dithiolene complexes $[Cp*Ir\{S_2C_2(COOMe)_2\}(CHR)]$ (R = COOEt (**3a**), SiMe$_3$ (**3b**)), respectively. The structures of complexes **3a**,**b** were determined by X-ray crystal structure analyses: the COOEt unit of complex **3a** is located at the exo position with respect to the iridadithiolene ring, and the SiMe$_3$ group of complex **3b** is located at the corresponding endo position with respect to the same ring. In solution, the endo (**3b-1**) and exo (**3b-2**) isomers of complex **3b** were observed. In an electrochemical investigation, the oxidized species of the exo isomer (**3b-2**$^+$) was isomerized to the stable endo isomer (**3b-1**$^+$). The reaction of complex **1** with diazomethane gave the novel 2:2 methylene adduct of a binuclear iridium dithiolene complex $[Cp*Ir\{S_2C_2(COOMe)_2\}(CH_2)][Cp*Ir\{SC_2(COOMe)_2S\}(CH_2)]$ (**4**). This complex **4** has a five-membered iridadithiolene ring and a six-membered iridacycle. The dimeric complex **4** was also formed from the desilylation of the monomeric complex **3b** with TBAF. The complex (**5a**) that includes a six-membered iridacycle $[Cp*Ir\{SC_2(COOMe)_2S\}(CHCOOEt)(P(OMe)_3)]$ was obtained by the reaction of the alkylidene-bridged complex **3a** with trimethyl phosphite. The reactions of complex **3b** with HCl gave $[Cp*Ir(Cl)\{S(SCH_2SiMe_3)C_2(COOMe)_2\}]$ (**6b**) due to Ir−C bond cleavage.

Introduction

Alkylidene complexes are useful organometallic complexes for metathesis reactions,[1] olefin cyclopropanations,[2] and C−H activations of an alkane.[3] One of the synthetic methods for an alkylidene complex is the reaction of a diazoalkane with a metal complex.[4] This reaction includes the N$_2$ loss of a diazoalkane, and then

various alkylidene complexes are obtained (Figure 1): (1) the metal carbene complex having a M=C bond (type 1),[5,6] (2) the complex in which an alkylidene group is bridging into two metal atoms (type 2),[7,8] and (3) the complex in which an alkylidene group is bridging between a metal and the coordination atom (type 3).[9] On the other hand, an alkylidene group occasionally

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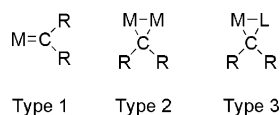
Figure 1.

undergoes an addition reaction to a ligand (e.g. coordinated alkyne[10]).

The reaction of a diazoalkane with a metal complex does not always give alkylidene complexes directly.[11] In some cases, a diazoalkane reacts with a metal complex without N_2 loss. One such case is the reaction where the terminal nitrogen atom of a diazoalkane coordinates a metal center[12] or bridges two metal atoms,[13] and another such reaction involves two nitrogen atoms coordinating to a metal center.[14] In most cases, these diazoalkane complexes cause N_2 elimination in the diazoalkane ligand to form alkylidene complexes;[15] however, it has been also reported that an alkylidene moiety is eliminated to give a N_2-bound complex.[16]

We have studied the chemistry of the metalladithiolene ring,[17] which consists of one metal, two sulfur atoms, and two unsaturated carbons. Coordinatively unsaturated species of metal dithiolene complexes are well-known, because the π-electron donation of the dithiolate ligand alleviates the electron deficiency and the coordinative unsaturation around the transition-metal center. In such complexes, a Lewis base (e.g. PR_3) is added to the unsaturated metal center,[18] and in the solid state, these often form the dimers of a metal dithiolene complex.[19] We have focused on the reactions of metal dithiolene complexes with nucleophiles such

Scheme 1
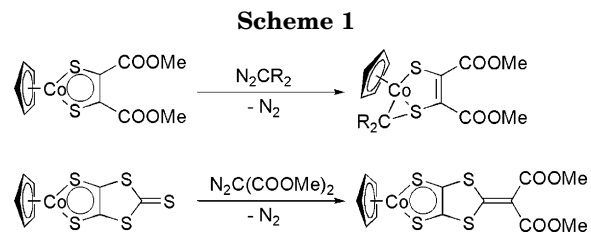
as 1,3-dipoles: for example, the cyclopentadienylcobalt or -rhodium dithiolene complex $[CpM^{III}(S_2C_2Y_2)]$ (M = Co, Rh) reacts with diazoalkane to give the coordinatively saturated adduct in which an alkylidene bridges into the metal–sulfur bond of the metalladithiolene ring (Scheme 1).[20] Therefore, this alkylidene complex is classified into type 3, as noted above (Figure 1). Similar reactions have been reported by Kang et al. in their studies of *o*-carborane dithiolato complexes.[21] In addition, dimethyl diazomalonate ($N_2C(COOMe)_2$) reacts with [CpCo(dmit)] (dmit = $S_2C_2S_2C{=}S$) to form [CoCo-$\{S_2C_2S_2C{=}C(COOMe)_2\}$] by the substitution of a terminal sulfur atom (Scheme 1).[22] The square-planar nickel dithiolene complex $[Ni(S_2C_2Ph_2)_2]$ reacts with diazomethane to cause the elimination of a central nickel atom, and then the methylene-bridged macrocycle is formed.[23]

We report here on the reactions of diazoalkanes with coordinatively unsaturated iridium dithiolene complexes $[Cp^*Ir(S_2C_2Y_2)]$ to give the alkylidene adducts of iridium dithiolene complexes. The stereoisomers of alkylidene adducts were selectively synthesized, and the isomerizations of the alkylidene moiety were observed. In addition, we report on the reaction of diazomethane with iridium dithiolene complexes. This reaction included unique alkylidene addition and resulted in an unprecedented binuclear complex.

Results and Discussion

1. Preparations of Iridium Dithiolene Complexes. Dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate, $[O{=}C\{S_2C_2(COOMe)_2\}]$, was treated with 2 equiv of sodium methoxide in methanol, and the colorless solution changed to yellow. After the iridium complex $[Cp^*Ir(Cl)(\mu{-}Cl)]_2$ ($Cp^* = C_5Me_5$) was added into the

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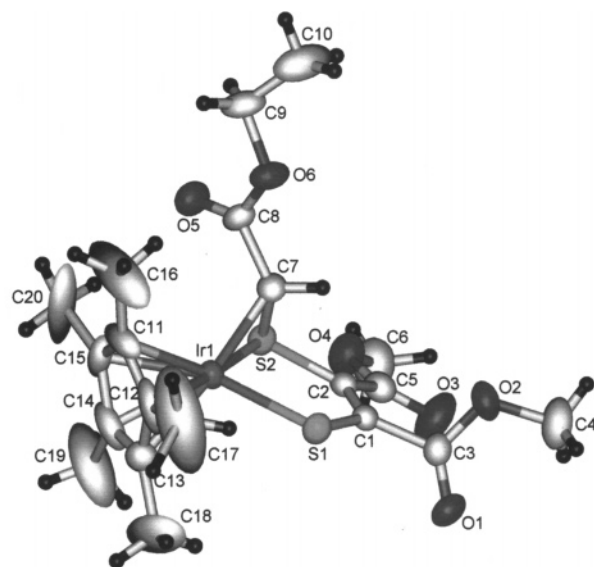
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Scheme 2

Scheme 3
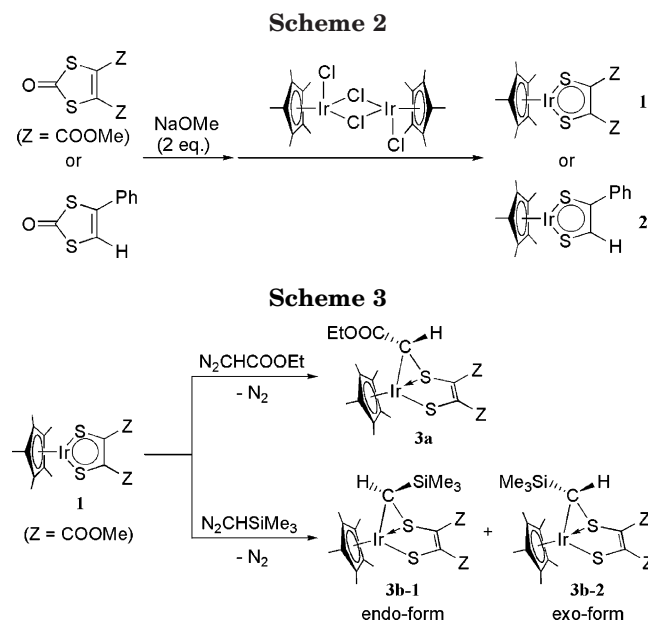
yellow solution, the reaction mixture was stirred at room temperature. After the products were separated by column chromatography, the red solid of the iridium dithiolene complex [Cp*Ir{S$_2$C$_2$(COOMe)$_2$}] (**1**) was obtained in 73% yield. Whereas the synthetic procedure for complex **1** previously reported[24] is inefficient, our synthetic route is efficient enough to synthesize complex **1**. Similarly, the iridium complex [Cp*Ir{S$_2$C$_2$(Ph)(H)}] (**2**), having a phenyl substituent, was obtained from 4-phenyl-1,3-dithiole-2-one, [O=C{S$_2$C$_2$(Ph)(H)}], in 70% yield (Scheme 2). The ^{1}H NMR spectrum of complex **2** showed the signal of a dithiolene proton at 8.49 ppm, a location whose value is more downfield than that of a typical olefin proton. This provides some evidence for the ring current[25] on the iridadithiolene ring.

2. Reactions of Iridium Dithiolene Complexes with Diazoalkanes. The reaction of complex **1** with ethyl diazoacetate (N$_2$CHCOOEt) or (trimethylsilyl)-diazomethane (N$_2$CHSiMe$_3$) gave the alkylidene-bridged adduct [Cp*Ir{S$_2$C$_2$(COOMe)$_2$}(CHR)] (R = COOEt (**3a**), SiMe$_3$ (**3b**)) in 68% or 81% yield, respectively (Scheme 3). The elemental analyses and spectroscopic data of complexes **3a** and **3b** revealed that these complexes were the 1:1 adducts of complex **1** with an alkylidene (=CHR) moiety. In the ^{1}H NMR spectrum of complex **3b**, two geometrical isomers were observed. We previously reported two geometrical isomers in the CHSiMe$_3$ adducts of the cobalt dithiazole complex [CpCo{S$_2$NC(Ph)}(CHSiMe$_3$)].[26] According to this report, in the major addition product, the SiMe$_3$ group is located at the exo position with respect to the cobaltadithiazole ring, and in the minor product, the SiMe$_3$ group is placed at the endo position. The δ value of the endo-SiMe$_3$ group (δ(^{1}H) 0.045 ppm) is more upfield than that of the exo-SiMe$_3$ group (δ(^{1}H) 0.19 ppm).[26] In this case

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Figure 2. ORTEP drawing of [Cp*Ir{S$_2$C$_2$(COOMe)$_2$}-(CHCOOEt)] (**3a**). Selected bond lengths (Å): Ir1−S1 = 2.317(1), Ir1−S2 = 2.339(2), S1−C1 = 1.699(8), S2−C2 = 1.781(6), C1−C2 = 1.354(9), Ir1−C7 = 2.088(7), S2−C7 = 1.820(7). Selected bond angles (deg): S1−Ir1−S2 = 86.48-(6), Ir1−S1−C1 = 104.9(2), Ir1−S2−C2 = 104.3(3), S1−C1−C2 = 124.8(5), S2−C2−C1 = 118.7(6), Ir1−C7−S2 = 73.2(2), Ir1−S2−C7 = 58.7(2), S2−Ir1−C7 = 48.1(2).

of the iridium dithiolene adduct **3b**, when the molar ratio of stereoisomers was determined by ^{1}H NMR, the endo isomer (**3b-1**) was richer than the exo isomer (**3b-2**) (Scheme 3). Moreover, the molar ratio of isomers depended on temperature (**3b-1**:**3b-2** = 2:1 (80 °C), 4.5:1 (40 °C), 12.5:1 (0 °C), 13:1 (−40 °C) in toluene-d_8). On the other hand, the acetate adduct **3a** was only one isomer.

The X-ray structures of complexes **3a**,**b** are shown in Figures 2 and 3, respectively. These alkylidene complexes have a three-legged piano-stool geometry and coordinatively saturated metal centers. The five-membered iridadithiolene rings are planar: mean deviation from iridadithiolene plane 0.0595 Å (**3a**), 0.0771 Å (**3b**). The three-membered ring of the bridging alkylidene moiety (iridathiirane ring) is extremely distorted (e.g. the bond angles of S2−Ir1−C7 are 48.1° in **3a** and 51.9° in **3b**), and the iridathiirane ring is located at a position almost perpendicular to the iridadithiolene ring, because of the dihedral angles between the iridadithiolene and the iridathiirane rings being 92.374° in **3a** and 92.413° in **3b**. In complex **3a**, the COOEt unit is located at the exo position with respect to the iridadithiolene ring. On the other hand, the SiMe$_3$ group of complex **3b** is located at the endo position. We assume that the major endo isomer **3b-1** in solution was well crystallized. We did not find any single crystals of the exo isomer **3b-2**. Such an endo type complex is the first case in the alkylidene-bridged adducts of metal dithiolene complexes formulated as [(C$_n$R$_n$)M(S$_2$C$_2$Y$_2$)(CHR′)] (M = Co, Rh (n = 5)[20] and M = Ru (n = 6);[27] R′ = SiMe$_3$, COOEt).
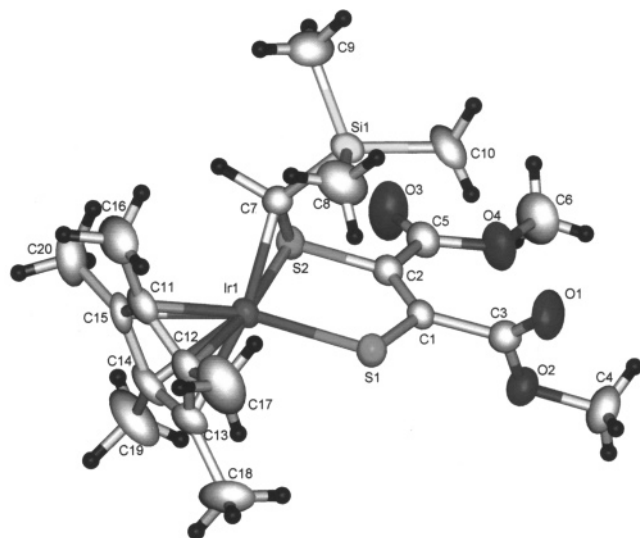
The reaction of complex **1** with diazomethane did not produce a 1:1 alkylidene adduct such as that of the

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Figure 3. ORTEP drawing of [Cp*Ir{S₂C₂(COOMe)₂}-(CHSiMe₃)] (**3b**). Selected bond lengths (Å): Ir1−S1 = 2.340(1), Ir1−S2 = 2.2325(8), S1−C1 = 1.646(4), S2−C2 = 1.766(5), C1−C2 = 1.363(5), Ir1−C7 = 2.029(4), S2−C7 = 1.875(4). Selected bond angles (deg): S1−Ir1−S2 = 88.84(4), Ir1−S1−C1 = 103.1(2), Ir1−S2−C2 = 102.1(1), S1−C1−C2 = 122.5(4), S2−C2−C1 = 122.6(3), Ir1−C7−S2 = 69.6(2), Ir1−S2−C7 = 58.4(1), S2−Ir1−C7 = 51.9-(1).
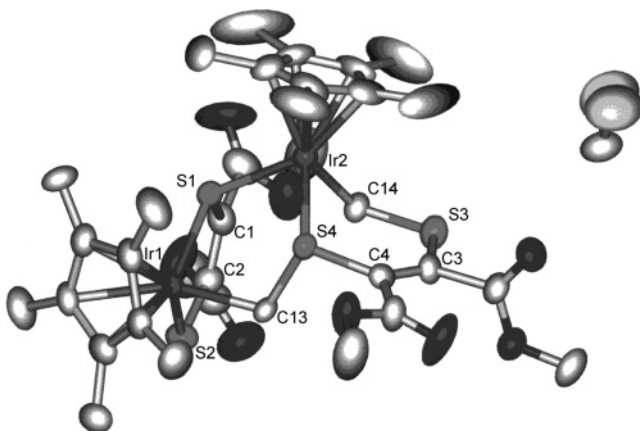
Figure 4. ORTEP drawing of [Cp*Ir{S₂C₂(COOMe)₂}-(CH₂)][Cp*Ir{SC₂(COOMe)₂S}(CH₂)](CH₂Cl₂) (**4**). The hydrogen atoms are not shown for the sake of simplicity. Selected bond lengths (Å): Ir1−S1 = 2.252(1), Ir1−S2 = 2.2451(6), S1−C1 = 1.735(3), S2−C2 = 1.742(4), C1−C2 = 1.338(5), Ir1−C13 = 2.08(1), Ir2−S1 = 2.388(3), Ir2−S4 = 2.301(3), S3−C3 = 1.72(1), S4−C4 = 1.76(1), C3−C4 = 1.32(2), Ir2−C14 = 2.08(1), S3−C14 = 1.77(1), S4−C13 = 1.79(2). Selected bond angles (deg): S1−Ir1−S2 = 86.98-(3), Ir1−S1−C1 = 106.0(1), Ir1−S2−C2 = 106.3(1), S1−C1−C2 = 120.9(3), S2−C2−C1 = 119.9(2), S4−Ir2−C14 = 86.9(4), Ir2−S4−C4 = 109.5(5), Ir2−C14−S3 = 118.8-(8), S4−C4−C3 = 129(1), S3−C3−C4 = 130(1), C3−S3−C14 = 108.1(6).

alkylidene complexes **3a,b**. The spectroscopic data of this reaction product showed the signals of a dimeric iridium dithiolene complex. The X-ray structure analysis (Figure 4) revealed the structure of a 2:2 methylene-bridged adduct of the dimeric iridium dithi-
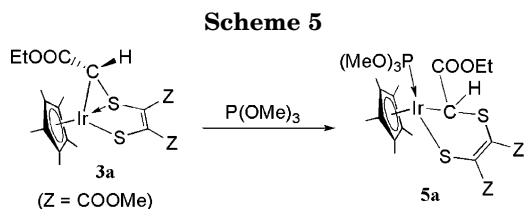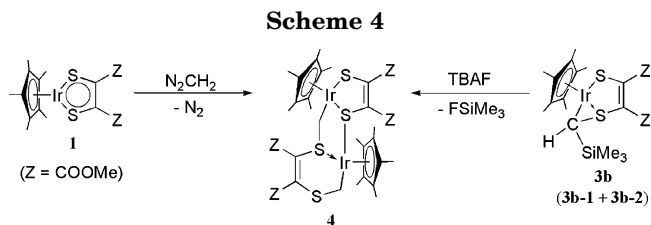
Scheme 4

Scheme 5

olene complex [Cp*Ir{S₂C₂(COOMe)₂}(CH₂)][Cp*Ir{SC₂(COOMe)₂S}(CH₂)] (**4** in Scheme 4). The complex **4** has an asymmetric binuclear structure, which has a five-membered iridadithiolene ring and a six-membered iridacycle formulated as Ir(CH₂)S₂C₂. One methylene carbon (C14) is inserted into the Ir2−S3 bond of the iridadithiolene ring to make the six-membered iridacycle, and another methylene carbon (C13) bridges between Ir1 and the S4 atom. The five-membered iridadithiolene ring is extremely planar (mean deviation 0.0167 Å). Although the six-membered iridacycle itself is not planar, the C14−S3−C3−C4−S4 plane excluding Ir2 is planar (mean deviation 0.0477 Å).
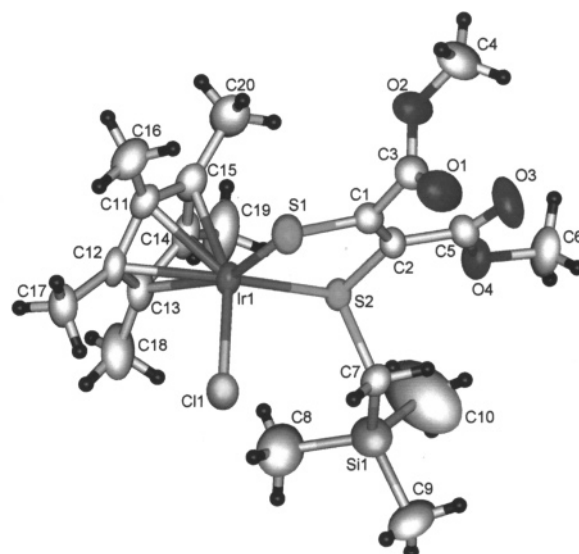
3. Reactivities of the Alkylidene Adduct of the Iridium Dithiolene Complex. The synthesis of a monomeric methylene-bridged adduct was attempted by another route. The reaction of complex **3b** with tetrabutylammonium fluoride (TBAF) aimed for the desilylation reaction. However, a monomeric methylene-bridged adduct was not found; rather, the dimeric complex **4** was unexpectedly obtained in 80% yield (Scheme 4). We propose that the monomeric methylene-bridged adduct is very unstable and, thus, is rapidly dimerized to form the dimeric complex **4**. In cobalt and rhodium dithiolene complexes, in contrast, such methylene-bridged adducts are stable and can be isolated as monomeric complexes.[20]

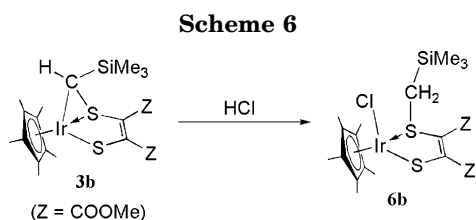The alkylidene-bridged adduct **3a** reacted with trimethyl phosphite to undergo the ring expansion of the iridadithiolene ring, and then the six-membered-ring complex [Cp*Ir{SC₂(COOMe)₂S}(CHCOOEt)(P(OMe)₃)] (**5a**) was obtained in 52% yield (Scheme 5). The structure of complex **5a** was determined by X-ray structure analysis (Figure 5). Trimethyl phosphite coordinates to the iridium center. The Ir1 and the S2 atoms are not combined thus, the C7 atom inserts between the Ir1 and S2 atoms. Therefore, the Ir−S bond of complex **3a** is cleaved by the nucleophilic attack of trimethyl phosphite at the iridium center. The structure of the six-membered iridacycle of complex **5a** is similar to that of complex **4** (Figure 4). After studying the formation of complex **4**, we conclude that when a monomeric methylene-bridged adduct is dimerized, a ring expansion of the iridadithiolene ring is produced by a nucleophilic attack of sulfur atom at the iridium center.
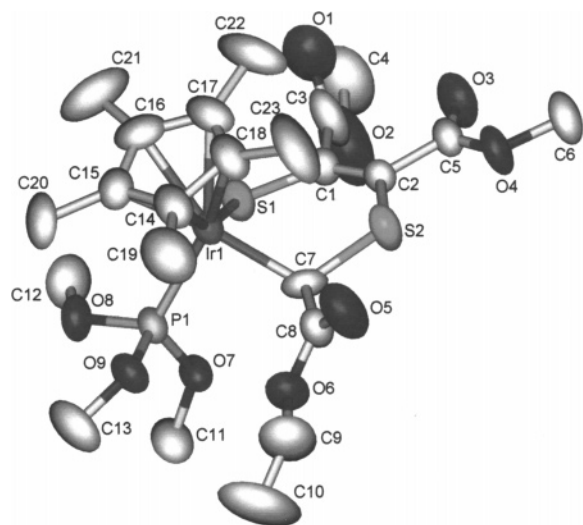
Figure 5. ORTEP drawing of [Cp*Ir{SC₂(COOMe)₂S̄}-(CHCOOEt)(P(OMe)₃)] (**5a**). The hydrogen atoms are not shown for the sake of simplicity. Selected bond lengths (Å): Ir1−S1 = 2.351(2), Ir1−C7 = 2.101(7), Ir1−P1 = 2.206(2), S1−C1 = 1.738(7), S2−C2 = 1.757(7), C1−C2 = 1.35(1), S2−C7 = 1.861(7). Selected bond angles (deg): S1−Ir1−C7 = 83.6(2), Ir1−S1−C1 = 110.5(3), Ir1−C7−S2 = 114.9(4), S1−C1−C2 = 130.3(6), S2−C2−C1 = 129.1(5), C2−S2−C7 = 105.0(3).
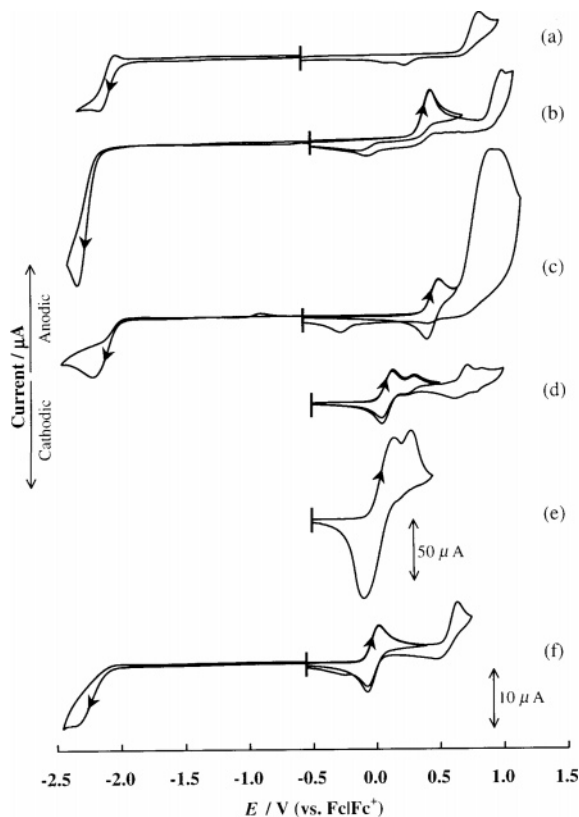
Scheme 6

(Z = COOMe)

The reaction of complex **3b** with hydrochloric acid caused the Ir−C bond cleavage on the alkylidene-bridged moiety (Scheme 6). The structure of the product [Cp*Ir(Cl){S(SCH₂SiMe₃)C₂(COOMe)₂}] (**6b**) was determined by X-ray structure analysis (Figure 6). Complex **6b** has a structure similar to that of cobalt dithiolene complexes previously reported.[28] The chloride coordinates to the iridium center, and the CH₂SiMe₃ group binds to the sulfur atom. We have observed two geometrical isomers of such cobalt dithiolene complexes. In one, the halide and alkyl groups are located at the same side of the cobaltadithiolene ring (syn form), and in the other, the groups take the anti form. Complex **6b** has the syn form, as shown in Figure 6. The alkylidene complex **3a** reacted with hydrochloric acid to give a similar product, formulated as [Cp*Ir(Cl)-{S(SCH₂COOEt)C₂(COOMe)₂}] (**6a**). Complex **6a** was identified by elemental analysis and spectroscopic data.

4. Electrochemical Behavior of Iridium Dithiolene Complexes. Cyclic voltammetry was performed on iridium dithiolene complexes. The cyclic voltammograms (CV) and their redox potentials are indicated in Figure 7 and Table 1, respectively. The CV of complex **1** showed a reversible reduction wave at −2.11 V and

(28) (a) Harada, T.; Takayama, C.; Kajitani, M.; Sugiyama, T.; Akiyama, T.; Sugimori, A. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2645. (b) Takayama, C.; Takeuchi, K.; Ohkoshi, S.; Kajitani, M.; Sugimori, A. *Organometallics* **1999**, *18*, 4032.

Figure 6. ORTEP drawing of [Cp*Ir(Cl){S(SCH₂SiMe₃)-C₂(COOMe)₂}] (**6b**). Selected bond lengths (Å): Ir1−S1 = 2.346(1), Ir1−S2 = 2.3421(8), S1−C1 = 1.719(4), S2−C2 = 1.772(4), C1−C2 = 1.340(6), Ir1−Cl1 = 2.392(1), S2−C7 = 1.832(4). Selected bond angles (deg): S1−Ir1−S2 = 85.78(3), Ir1−S1−C1 = 102.8(1), Ir1−S2−C2 = 103.6(1), S1−C1−C2 = 124.6(3), S2−C2−C1 = 119.4(3).

Figure 7. Cyclic voltammograms of 1 mM solutions in dichloromethane containing 0.1 M TBAP of (a) complex **1**, (b) complex **2**, (c) complex **3a**, (d) complex **3b**, and (f) complex **4** (v = 100 mV s⁻¹, 1.6 mm i.d. Pt disk) and (e) complex **3b** (v = 5 mV s⁻¹, Pt mesh in an OTTLE cell).

an irreversible oxidation wave at 0.78 V (vs Fc/Fc⁺). The redox potentials of complex **2** and those of the alkylidene complexes **3a**−**c** were more negative than those of complex **1**, but the reduction wave of complex **3b** was not found in the potential window for these measure-

Table 1. Redox Potentials of Iridium Dithiolene Complexes[a]

| complex	first redn			first oxidn		
	$E_{1/2}$/V	ΔE/mV	ΔE_p/mV	$E_{1/2}$/V	ΔE/mV	ΔE_p/mV
1	−2.11 r	94	134	0.78 ir	78	
2	−2.29 ir	88		0.41 ir	68	
3a	−2.15 ir	126		0.46 r	70	94
3b	b			0.10 r	68	88
4	−2.15 ir	134		−0.02 r	68	94

[a] Legend: r, reversible wave; ir, irreversible wave. $E_{1/2} = (E_p + E_{p/2})/2$, $\Delta E = |E_p − E_{p/2}|$, $\Delta E_p = |E_{pc} − E_{pa}|$. [b] Not observed in the potential window of TBAP−CH_2Cl_2.

ment conditions. In complexes **3a**−**c**, complex **3a** was the easiest one to be reduced and was the hardest one to be oxidized. The CV of complex **3b** resulted in an oxidation wave of four steps; the first and third oxidation currents were larger than the second and fourth ones. From these results, we conclude that (1) the redox potentials of iridium dithiolene complexes can be controlled by the substituent effects on the iridadithiolene ring and on the alkylidene moiety, (2) the 16-electron complex has lower redox potentials than those of the corresponding 18-electron alkylidene adducts, and (3) in complex **3b**, the oxidation waves of the endo isomer **3b-1** and the exo isomer **3b-2** are observed, and the first and third waves correspond to the first and second oxidations of the major isomer **3b-1**.

The oxidation behavior of complex **3b** was investigated in detail. Figure 7e is the CV of complex **3b** measured by a slow scan rate (v = 5 mV s^{-1}) in an optically transparent thin-layer electrode (OTTLE) cell. The first oxidation wave of the endo isomer **3b-1** showed a reversible response, but the second wave of the exo isomer **3b-2** was irreversible. This result suggests that the oxidized species of the isomer **3b-2** is unstable on the time scale of the slow scan. Figure 8 shows the visible absorption spectral changes during electrolysis of complex **3b** using the OTTLE cell. When a mixture of the isomers **3b-1** and **3b-2** was oxidized at +0.4 V, the spectrum was remarkably changed and did not show an isosbestic point (Figure 8a). The reason for the absence of an isosbestic point is a chemical reaction of the unstable cation **3b-2**$^+$ after the electrochemical oxidation. However, when the stable cation **3b-1**$^+$ was rereduced at −0.5 V, the spectrum recovered the original absorbance before electrolysis; moreover, these spectral changes showed an isosbestic point (at 520 nm in Figure 8b). We propose that the oxidant of the exo isomer (**3b-2**$^+$) is quantitatively converted to the oxidized endo isomer (**3b-1**$^+$) and, when it is rereduced, the neutral endo isomer **3b-1** is formed electrochemically (Scheme 7).

Conclusion

In this work, we carried out the reactions of the 16-electron coordinatively unsaturated iridium dithiolene complex **1** with diazoalkanes. These reactions resulted in the formations of 18-electron alkylidene adducts of iridium dithiolene complexes. This is a reaction based on the unsaturation of the iridadithiolene ring. On the other hand, the iridadithiolene ring proton ($\delta(^1H)$ 8.49 ppm in complex **2**) provided some evidence for the ring current of an aromatic ring. Therefore, the iridadithi-
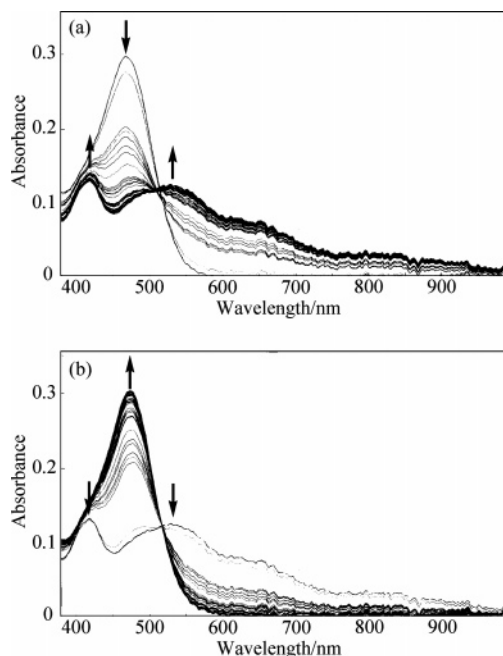
Figure 8. Spectral changes in the visible region of complex **3b** during (a) oxidation (+0.40 V, sampling time 2 min, sampling interval 4 s) and (b) rereduction after oxidation (−0.50 V, sampling time 2 min, sampling interval 4 s) using an OTTLE cell.

Scheme 7
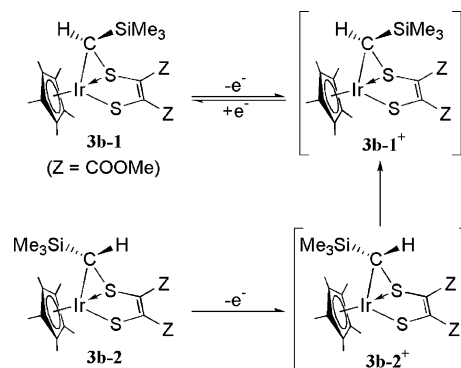
olene ring has both aromaticity and unsaturation, like cobalta- and rhodadithiolene rings.

When diazoacetate or (trimethylsilyl)diazomethane was used for the synthesis of the alkylidene adduct, the alkylidene-bridged complex **3a** or **3b** was obtained, respectively. The alkylidene groups were bridging into the Ir−S bond of the iridadithiolene ring, and this case is classified as type 3 in Figure 1. In such alkylidene adducts [Cp*Ir{$S_2C_2(COOMe)_2$}(CHR)], the stereoisomer of exo (R = COOEt in Figure 2) or endo (R = SiMe$_3$ in Figure 3) form could be selectively synthesized. Especially, the endo type of alkylidene adduct is the first example found for a Cp metal dithiolene complex. If we were to use such alkylidene complexes as a catalyst or a carbene source, stereoselective reactions could be expected for metathesis reactions[1] and olefin cyclopropanations.[2]

The reaction of a iridium dithiolene complex with diazomethane gave the novel binuclear iridium dithiolene adduct **4** (Figure 4). Complex **4** is a novel alkylidene complex, which cannot be classified into any of the types 1−3 noted in Figure 1.

Experimental Section

General Remarks. All reactions were carried out under an argon atmosphere by means of standard Schlenk techniques. All solvents for reactions were purified by Na–benzophenone or CaH_2 before use. The precursor of complexes **1** and **2**, $[Cp^*Ir(Cl)(\mu\text{-}Cl)]_2$, was synthesized by literature methods.[29] Dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate (O=C$\{S_2C_2(COOMe)_2\}$) was obtained from the reaction of dimethyl 1,3-dithiol-2-thione-4,5-dicarboxylate (from Tokyo Kasei Kogyo Co., Ltd.) with $Hg(OAc)_2$.[30] (Trimethylsilyl)diazomethane in *n*-hexane solution and TBAF in THF solution were produced by Sigma-Aldrich Fine Chemicals. Silica gel (Wakogel C-300) was obtained from Wako Pure Chemical Industries, Ltd. Mass and IR spectra were recorded on JEOL JMS-D300 and Shimadzu Model FTIR 8600PC instruments, respectively. NMR spectra were measured with a JEOL LA500 spectrometer. UV–vis spectra were recorded on a Hitachi Model UV-2500PC spectrometer. Elemental analyses were determined by using a Shimadzu PE2400-II instrument.

Preparations of the Iridium Dithiolene Complexes $[Cp^*Ir\{S_2C_2(COOMe)_2\}]$ (1) and $[Cp^*Ir\{S_2C_2(Ph)(H)\}]$ (2). Dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate (1.62 mmol; O=C$\{S_2C_2(COOMe)_2\}$) was treated with 2 equiv of sodium methoxide in methanol solution (50 mL) at room temperature. The color of the initial solution changed to yellow after 1 h. When the iridium complex dimer $[Cp^*Ir(Cl)(\mu\text{-}Cl)]_2$ (0.62 mmol) was added into this solution, the yellow solution changed to brown. The reaction mixture was stirred at room temperature for 24 h. After the solvent was removed under reduced pressure, the residue was extracted by dichloromethane/water and the organic layer was purified by column chromatography (silica gel, eluent dichloromethane). Complex **1** was obtained as a brown solid in 80% yield. Complex **2** was obtained from 4-phenyl-1,3-dithiol-2-one (O=C$\{S_2C_2(Ph)(H)\}$) with $[Cp^*Ir(Cl)(\mu\text{-}Cl)]_2$ in 70% yield.

$[Cp^*Ir\{S_2C_2(COOMe)_2\}]$ (1). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm (ϵ) 305 (16 000), 416 (8000). Anal. Calcd for $C_{16}H_{21}O_4S_2Ir$: C, 36.01; H, 3.97. Found: C, 36.19; H, 3.95. The mass, NMR, and IR spectral data of complex **1** are given in the literature previously reported.[24b]

$[Cp^*Ir\{S_2C_2(Ph)(H)\}]$ (2). Mass (EI$^+$, 70 eV): *m/z* (relative intensity) 494 ([M$^+$], 100), 392 ([C$_5$Me$_5$IrS$_2^+$], 30.4). ^{1}H NMR (CDCl$_3$, 500 MHz, vs TMS): δ 2.19 (s, 15H, C$_5Me_5$), 7.20–7.23 (tt, J = 1.81, 7.39 Hz, 1H, Ph), 7.30–7.33 (m, 2H, Ph), 7.76–7.78 (m, 2H, Ph), 8.49 (s, 1H, dithiolene proton). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm (ϵ) 295 (14 700), 450 (8800). IR (KBr disk): 2960.5, 2912.3, 1591.1, 1504.4, 1438.8, 1380.9, 1261.4, 1215.1, 1031.8, 796.5, 761.8, 696.3 cm^{-1}. Anal. Calcd for $C_{18}H_{21}S_2Ir$: C, 43.79; H, 4.29. Found: C, 43.83; H, 4.21.

Reactions of Complex 1 with Ethyl Diazoacetate. Ethyl diazoacetate was prepared by a literature method.[31] A solution of complex **1** (0.23 mmol) and ethyl diazoacetate (2.0 mmol) in benzene (90 mL) was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, eluent dichloromethane). The orange residue was purified by recrystallization (*n*-hexane/dichloromethane). Adduct **3a** was obtained as an orange solid in 94% yield.

$[Cp^*Ir\{\overline{S_2C_2(COOMe)_2\}(CHCOOEt)}]$ (3a). Mass (FAB$^+$, 70 eV, NBA): *m/z* (relative intensity) 621 ([M$^+$ + 1], 68.9), 547 ([M$^+$ − COOMe], 100). ^{1}H NMR (CDCl$_3$, 500 MHz, vs TMS): δ 1.27 (t, J = 7.26 Hz, 3H, CH$_2Me$), 1.96 (s, 15H, C$_5Me_5$), 2.86 (s, 1H, CH), 3.73 (s, 3H, COOMe), 3.85 (s, 3H, COOMe), 4.07–

4.21 (m, 2H, CH_2Me). ^{13}C NMR (CDCl$_3$, 125 MHz, vs TMS): δ 9.1 (C$_5Me_5$), 14.5 (COOCH$_2Me$), 29.3 (CH), 52.2, 53.1, 60.5 (COOMe or COOCH_2Me), 92.7 (C$_5$Me$_5$), 113.0, 163.0 (dithiolene carbon), 169.0, 170.1, 175.3 (COOMe or COOEt). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm (ϵ) 346 (5500), 397 (5000), 443 (6000). IR (KBr disk): 1730.0, 1697.2, 1469.7, 1423.4, 1380.9, 1363.6, 1298.0, 1230.5, 1153.4, 1085.8, 1026.1, 759.9 cm^{-1}. Anal. Calcd for $C_{20}H_{27}O_6S_2Ir$: C, 38.76; H, 4.39. Found: C, 38.76; H, 4.40.

Reaction of Complex 1 with (Trimethylsilyl)diazomethane. A 2.0 mmol dm^{-3} *n*-hexane solution of (trimethylsilyl)diazomethane (1.9 mL, 3.8 mmol) was added into a benzene solution (20 mL) of complex **1** (100 mg, 0.26 mmol). The reaction mixture was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, eluent dichloromethane). The orange residue was purified by recrystallization (*n*-hexane/dichloromethane). Adduct **3b** was obtained as an orange solid in 78% (94 mg, 0.20 mmol) yield.

$[Cp^*Ir\{\overline{S_2C_2(COOMe)_2\}(CHSiMe_3)}]$ (3b). Mass (EI$^+$, 70 eV): *m/z* (relative intensity) 620 ([M$^+$], 35.1), 605 ([M$^+$ − Me], 100). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm (ϵ) 469.5 (5590). ^{1}H NMR (CDCl$_3$, 500 MHz, vs TMS): major isomer, δ 0.04 (s, 9H, SiMe_3), 1.96 (s, 15H, C$_5Me_5$), 2.11 (s, 1H, CH), 3.73 (s, 3H, COOMe), 3.83 (s, 3H, COOMe); minor isomer, δ 0.11 (s, 9H, SiMe_3), 2.00 (s, 15H, C$_5Me_5$), 2.13 (s, 1H, CH), 3.72 (s, 3H, COOMe), 3.85 (s, 3H, COOMe). IR (KBr disk): 2949.0, 2333.7, 1732.0, 1676.0, 1477.4, 1259.4, 1230.5, 1026.1, 871.8, 833.2 cm^{-1}. Anal. Calcd for $C_{20}H_{31}O_4SiS_2Ir$: C, 38.75; H, 5.04. Found: C, 38.72; H, 5.05.

Reaction of Complex 1 with Diazomethane. Diazomethane was prepared by a literature method.[20c] Excess diazomethane gas was blown into a dichloromethane solution of complex **1** (98 mg, 0.254 mmol) at 0 °C. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, eluent dichloromethane). The orange residue was purified by recrystallization (*n*-hexane/dichloromethane). Adduct **4** was obtained as an orange solid in 80% yield (81 mg, 0.203 mmol).

$[Cp^*Ir\{\overline{S_2C_2(COOMe)_2\}(CH_2)}][Cp^*Ir\{\overline{SC_2(COOMe)_2S}\text{-}}$ $(CH_2)]$ (4). Mass (FAB$^+$, 70 eV, NBA): *m/z* (relative intensity) 1096 ([M$^+$], 39.1), 548 ([M$^+$]/2, 100). ^{1}H NMR (CDCl$_3$, 500 MHz, vs TMS): δ 1.71 (s, 15H, C$_5Me_5$), 1.72 (s, 15H, C$_5Me_5$), 2.71 (q, J = 5.03 Hz, 2H, CH$_2$), 2.96 (q, J = 6.77 Hz, 2H, CH$_2$), 3.64 (s, 3H, COOMe), 3.73 (s, 3H, COOMe), 3.81 (s, 6H, COOMe). ^{13}C NMR (CDCl$_3$, 125 MHz, vs TMS): δ 8.3, 8.4 (C$_5Me_5$), 10.5, 36.7 (CH$_2$), 52.1, 52.4, 52.5, 52.8 (COOMe), 92.0, 93.4 (C$_5$Me$_5$), 111.8, 121.8, 157.9, 159.4 (dithiolene carbon), 165.9, 166.8, 167.0, 168.2 (COOMe). IR (KBr disk): 2947.0, 2906.5, 1732.0, 1701.1, 1508.2, 1456.2, 1431.1, 1230.5, 1070.4, 1022.2, 748.3 cm^{-1}. Anal. Calcd for $[C_{17}H_{23}O_4S_2Ir]_2(CH_2Cl_2)$: C, 35.61; H, 4.10. Found: C, 35.59; H, 4.03.

Reaction of Complex 3b with Tetrabutylammonium Fluoride (TBAF). The 2.0 mmol dm^{-3} THF solution of TBAF (30 μL, 0.107 mmol) was added into a THF solution (2 mL) of complex **3b** (10 mg, 0.016 mmol). The reaction mixture was stirred at room temperature for 10 min, and then a few drops of water were added. The reaction mixture was separated by column chromatography (silica gel, eluent dichloromethane). The adduct **4** was formed in 80% yield.

Reaction of Complex 3a with Trimethyl Phosphite. A solution of complex **3a** (53.7 mg, 0.087 mmol) and trimethyl phosphite (110 μL, 0.87 mmol) in dichloromethane (5 mL) was stirred at room temperature for 3 days. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, eluent dichloromethane). The orange residue was purified by recrystallization (*n*-hexane/dichloromethane). Complex **5a** was obtained as a yellow solid in 52% yield.

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(31) Womack, E. B.; Nelson, A. B. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 392.

Table 2. Crystallographic Data of Iridium Dithiolene Complexes 3a,b, 4, 5a, and 6b

	3a	3b	4·CH$_2$Cl$_2$	5a	6b
formula	C$_{20}$H$_{27}$IrO$_6$S$_2$	C$_{20}$H$_{31}$IrO$_4$S$_2$Si	C$_{35}$H$_{48}$Cl$_2$Ir$_2$O$_8$S$_4$	C$_{23}$H$_{36}$IrO$_9$PS$_2$	C$_{20}$H$_{32}$ClIrO$_4$S$_2$Si
formula wt	619.77	619.89	1180.35	743.85	656.35
cryst color	orange	orange	orange	yellow	yellow
cryst habit	block	platelet	block	block	block
cryst size (mm)	0.15 × 0.12 × 0.10	0.15 × 0.15 × 0.10	0.15 × 0.15 × 0.15	0.15 × 0.12 × 0.06	0.09 × 0.09 × 0.06
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	8.5846	10.90150(10)	17.9309(5)	8.1750(8)	7.8461(4)
b (Å)	10.7532	11.1238(2)	13.0331(4)	31.572(3)	10.8280(5)
c (Å)	14.1927	11.3765(4)	20.1731(7)	11.2418(10)	16.3196(9)
α (deg)	70.386(9)	89.846(5)			100.320(2)
β (deg)	73.927(10)	70.899(4)	106.1368(5)	103.0624(11)	103.658(2)
γ (deg)	71.420(9)	67.032(3)			97.870(2)
V (Å^{-3})	1148.434 89(10)	1187.83(5)	4528.6(2)	2826.5(4)	1301.97(11)
Z	2	2	4	4	2
D_{calcd} (g cm^{-3})	1.792	1.733	1.731	1.748	1.674
μ(Mo Kα) (cm^{-1})	60.43	58.84	62.32	49.88	54.72
$2\theta_{max}$ (deg)	54.9	55.0	55.0	55.0	55.0
no. of unique data (R_{int})	4993 (0.030)	5028 (0.022)	10 240 (0.020)	6267 (0.048)	5674 (0.019)
no. of observns	3757	4320	7580	3222	4741
no. of variables	289	284	508	361	294
R1, wR2 ($I > 3.00\sigma(I)$)	0.030, 0.029	0.023, 0.025	0.056, 0.096	0.032, 0.028	0.024, 0.025
goodness of fit on F_2	1.049	1.121	1.437	0.862	1.322

[Cp*Ir{SC$_2$(COOMe)$_2$S}(CHCOOEt)(P(OMe)$_3$)] (5a). Mass (EI$^+$, 70 eV) *m/z* (relative intensity) 744 ([M$^+$], 12.6), 559 ([M$^+$ − OOEt − P(OMe)$_3$], 24.1), 547 ([M$^+$ − COOEt − P(OMe)$_3$], 100), 484 ([Cp*IrS$_2$C$_3$(CO)$_2$$^+$], 18.4). ^{1}H NMR (CDCl$_3$, 500 MHz, vs TMS): δ 1.25 (t, *J* = 7.23 Hz, 3H, CH$_2$*Me*), 1.74 (d, *J* = 3.16 Hz, 15H, C$_5$*Me$_5$*), 3.68 (s, 3H, COO*Me*), 3.69 (d, *J* = 10.29 Hz, 9H, P(O*Me*)$_3$), 3.83 (s, 3H, COO*Me*), 3.95−3.98 (m, 1H, *CH$_2$*Me), 4.18−4.22 (m, 1H, *CH$_2$*Me), 4.61 (d, *J* = 4.69 Hz, 1H, CH). UV−vis (CH$_2$Cl$_2$): λ_{max}/nm (ϵ) 285 (14 000), 379 (4600). IR (KBr disk): 2989.4, 2949.0, 2896.9, 1716.5, 1693.4, 1508.2, 1429.2, 1232.4, 1141.8, 1029.9 cm^{-1}. Anal. Calcd for C$_{23}$H$_{36}$O$_9$-PS$_2$Ir: C, 37.14; H, 4.88. Found: C, 37.32; H, 4.54.

Reaction of Complex 3a or 3b with Hydrochloric Acid. Excess hydrochloric acid (a few drops) was added into the dichloromethane (10 mL) solution of complex **3a** (12 mg, 0.019 mmol) or **3b** (20 mg, 0.032 mmol). The reaction mixture was reacted at room temperature for 10 min; then the solution was extracted by dichloromethane/H$_2$O, and the organic layer was dried with MgSO$_4$. After the solvent was removed under reduced pressure, the yellow residue was purified by recrystallization (*n*-hexane/dichloromethane). Complex **6a** or **6b** was obtained as a yellow solid in 96% or 97% yield, respectively.

[Cp*Ir(Cl){S(SCH$_2$COOEt)C$_2$(COOMe)$_2$}] (6a). Mass (EI$^+$, 70 eV): *m/z* (relative intensity) 656 ([M$^+$], 42.6), 569 ([M$^+$ − CH$_2$COOEt], 80.1), 534 ([M$^+$ − CH$_2$COOEt − Cl], 100). ^{1}H NMR (CDCl$_3$, 500 MHz, vs TMS): δ 1.27 (t, *J* = 7.25 Hz, 3H, CH$_2$*Me*), 1.79 (s, 15H, C$_5$*Me$_5$*), 3.51 (d, *J* = 15.8 Hz, 1H, CH), 3.74 (s, 3H, COO*Me*), 3.86 (s, 3H, COO*Me*), 4.14−4.18 (m, 2H, *CH$_2$*Me), 4.62 (d, *J* = 15.8 Hz, 1H, CH). UV−vis (CH$_2$Cl$_2$): λ_{max}/nm (ϵ) 357 (7700). IR (KBr disk): 2993.3, 2979.8, 2948.9, 1737.7, 1699.2, 1685.7, 1508.2, 1249.8, 1182.3, 1026.1 cm^{-1}. Anal. Calcd for C$_{20}$H$_{28}$ClO$_6$S$_2$Ir: C, 36.60; H, 4.30. Found: C, 36.51; H, 4.10.

[Cp*Ir(Cl){S(SCH$_2$SiMe$_3$)C$_2$(COOMe)$_2$}] (6b). Mass (EI$^+$, 70 eV): *m/z* (relative intensity) 656 ([M$^+$], 100), 621 ([M$^+$ − Cl], 17.1), 569 ([M$^+$ − CH$_2$SiMe$_3$], 62.9), 534 ([M$^+$ − CH$_2$SiMe$_3$ − Cl], 93.5). ^{1}H NMR (CDCl$_3$, 500 MHz, vs TMS): δ = 0.17 (s, 9H, Si*Me$_3$*), 1.33 (d, *J* = 13.3 Hz, 1H, CH), 1.73 (s, 15H, C$_5$*Me$_5$*), 3.50 (d, *J* = 13.3 Hz, 1H, CH), 3.73 (s, 3H, COO*Me*), 3.85 (s, 3H, COO*Me*). UV−vis (CH$_2$Cl$_2$): λ_{max}/nm (ϵ) 359 (9300). IR (KBr disk): 2956.7, 2894.9, 2883.4, 1737.7, 1699.2, 1517.9, 1236.3, 1029.9 cm^{-1}. Anal. Calcd for C$_{20}$H$_{32}$ClO$_4$S$_2$SiIr: C, 36.60; H, 4.91. Found: C, 36.90; H, 4.75.

X-ray Diffraction Study. Single crystals of complexes **3a,b**, **4**, **5a**, and **6b** were obtained by recrystallization from the dichloromethane solutions and then vapor diffusion of *n*-hexane into those solutions. Measurements were made on a Rigaku MERCURY diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All the calculations were carried out using the Crystal Structure crystallographic software package. Crystallographic data are summarized in Table 2.

Electrochemical Measurements. All electrochemical measurements were performed under an argon atmosphere. Solvents for electrochemical measurements were dried by molecular sieve 4A before use. A platinum wire served as a counter electrode, and the reference electrode is Ag/AgCl, corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc/Fc$^+$) couple. Cyclic voltammograms were measured with a Model CV-50W instrument from BAS Co. Visible and near-IR absorption spectra during electrolysis were measured with Model MCPD-7000 and MC-2530 instruments from Otsuka Electronics Co. Ltd.

CV Measurements. CV measurements were done in 1 mmol dm^{-3} dichloromethane solutions of complexes containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) at 25 °C. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode.

Visible Absorption Spectral Measurements during Electrolysis. The visible absorption spectra during electrolysis were obtained for 1 mmol dm^{-3} dichloromethane solutions of complexes containing 0.1 mol dm^{-3} TBAP at 25 °C in an optically transparent thin-layer electrode (OTTLE, thin-layer thickness 0.4 mm) cell by using a Photal MCPD-7000 rapid scan spectrometer. The working electrode was stationary platinum mesh in thin-layer form.