*Organometallics* **1999,** *18,* 2843−2850

# Reactions of Alkylidene-Bridged Cobaltadithiolene Complexes with Lewis Bases. Formation of M−S Sulfur Ylide Structure

Chikako Takayama,*[,†,‡] Keiko Takeuchi,[†] Shin-ichi Ohkoshi,[§]
Gerardo C. Janairo,[||] Toru Sugiyama,[†] Masatsugu Kajitani,*[,†] and
Akira Sugimori*[,†]

*Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1, Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan, and Department of Chemistry, De La Salle University, 2401 Taft Avenue, 1104 Manila, Philippines*

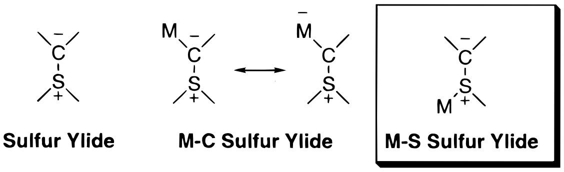
*Received March 1, 1999*

The reactions of a malonate ($C(COOMe)_2$)-bridged complex with Lewis bases give novel sulfur ylide (M−S sulfur ylide) complex due to the cleavage of Co−C bond as determined by X-ray sturucture analysis. Acetate (CHCOOEt)- and methylene-bridged complexes, on the other hand, reacted with Lewis bases via an $S_N2$ type reaction to give unstable M−S sulfur ylide complexes and stable six-membered-ring complexes.

## Introduction

The sulfur ylides have been extensively studied as reaction intermediates.[1] In general, these intermediates are unstable but can be isolated as delocalized carbanion.

It is known that for some sulfur ylide complexes, the carbanions directly bonded to metals (M−C sulfur ylide) can delocalize to the metal.[2,3]



So far we have synthesized many alkylidene-bridged complexes[4] through the reactions of metalladithiolene complexes[5−7] with diazo compounds. In these complexes, their properties as metallacycles are controlled by changing the substituents. The thermal, photochemical, and electrochemical[8] behavior of these complexes has been previously reported. We also reported the reactions of these complexes with Lewis bases to give the first types of sulfur ylide (M−S sulfur ylide) complexes.[9]

In the present paper, we report the synthesis of M−S sulfur ylide complexes from the reactions of three kinds of alkylidene-bridged cobaltadithiolene complexes with trimethyl phosphite and trimethylphosphine. We investigated the thermal and electrochemical properties according to the substituent effects of alkylidene moieties and Lewis bases and revealed that there are two types of reaction mechanisms for the formation of M−S sulfur ylide complexes.

## Experimental Section

**Reactions of Alkylidene-Bridged Complexes with Lewis Bases.** Trimethyl phosphite or trimethylphosphine ($4 \times 10^{-4}$ mol) was added to solutions of **1c**, **1b**, and **1a** ($2 \times 10^{-4}$ mol) in $CH_2Cl_2$. The suspensions were vigorously stirred under argon atmosphere for 30 min at ambient temperature, except for the reaction of complex **1a** with trimethylphosphine, which was treated at 0 °C. After the reactions, the solvents were removed under an reduced pressure and the residue was recrystallized from $CH_2Cl_2$/hexane (v/v 1:1).

**In Situ $^1H$ NMR Spectral Measurement of the Reactions of Alkylidene-Bridged Complexes with Lewis Bases.** Five molar equivalents of trimethyl phosphite or trimethylphosphine was added to $CDCl_3$ (0.5 mL) solutions of **1a**, **1b**,

---

* Corresponding author: (e-mail) kajita-m@hoffman.cc.sophia.ac.jp.

[†] Sophia University.

[‡] Present address: The Institute of Physical and Chemical Research (RIKEN), 2−1 Hirosawa, Wako-shi, Saitama 351-0198, Japan.

[§] Present address: Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan.

[||] De La Salle University.

(1) (a) Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylides*; Academic Press: New York, 1975. (b) Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179.

(2) Review: Weber, L. *Angew. Chem., Int. Ed. Engl.*, **1983**, *22*, 516.

(3) (a) Seyferth, D.; Womack, G. B.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 1696. (b) McCrindle, R.; Ferguson, G.; McAlees, A. J.; Arsenault, G. J.; Gupta, A.; Jennings, M. C. *Organometallics* **1995**, *14*, 2741. (c) Werner, H.; Mahr, N.; Frenking, G.; Jonas, V. *Organometallics* **1995**, *14*, 619. (d) Lin, I. J. B.; Liu, C. W.; Liu, L.-K.; Wen, Y.-S. *Organometallics* **1992**, *11*, 1447. (e) Wu, R. F. Lin, I. J. B. Lee, G. H. Cheng, M. C. Wang, Y. *Organometallics* **1990**, *9*, 126. (f) Lai, J. S.; Wu, R. F.; Lin, J. B.; Cheng, M. C.; Wang, Y. *J. Organomet. Chem.* **1990**, *393*, 341. (g) Holy, N.; Nalesnik, T.; Warfield, L.; Mojesky, M. *J. Coord. Chem.* **1983**, *12*, 157.

(4) (a) Sakurada, M.; Kajitani, M.; Dohki, K.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *423*, 144. (b) Werner, H.; Xiaolan, L. Peters, K. von Schnering H. G. *Chem. Ber./Rec.* **1997**, *130*, 871.

(5) Review: (a) McCleaverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (b) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303. (c) Schrauzer, G. N. *Transition Met. Chem.* **1968**, *4*, 299. (d) Schrauzer, G. N. *Acc. Chem. Res.* **1969**, *2*, 72. (e) Hoyer, E.; Dietzsch, W. *Z. Chem.* **1971**, *11*, 41.

(6) (a) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1587. (b) Dessy, R. E.; Kormann, R.; Smith, C.; Haytor, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001.

(7) Fourmigue, M. *Coord. Chem. Rev.* **1998**, *178−180*, 823.

(8) Takayama, C.; Kajitani, M.; Sugiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1998**, ***563***, 161.

(9) Takayama, C.; Sakamoto, N.; Harada, T.; Kajitani, M.; Sugiyama, T.; Akiyama, T.; Sugimori, A. *Organometallics* **1996**, *15*, 5077.

10.1021/om990139m CCC: $18.00

and **1c** (~10 mg) with a small scrap of durene as the internal standard in the NMR sample tubes at ambient temperature. The reaction of complex **1a** with trimethylphosphine was also treated at 0 °C. The yields were determined by the integral of the Cp ring proton peak.

**CV Measurement.** All electrochemical measurements were done in 1 mmol dm$^{-3}$ acetonitrile solutions containing 0.1 mol dm$^{-3}$ tetraethylammonium perchlorate (TEAP) at 25 °C. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode. A coiled platinum wire served as a counter electrode. The reference electrode is Ag|AgNO$_3$ corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc|Fc$^+$) couple. Complexes **2a** and **4a** were also prepared in situ in an electrochemical cell by the addition of a slight excess of trimethyl phosphite or trimethylphosphine to complex **1a**. In the case of complex **5b**, we measured the CV of the isolated complex **5b**, together with that of the prepared one in situ from complex **1b** with trimethylphosphine.

**X-ray Diffraction Study.** All measurement was made on a Rigaku AFC5S diffractometer with graphite-monochromated Mo Kα radiation. Each structure was solved by direct methods and expanded using Fourier techniques.[10] The non-hydrogen atoms were refined anisotropically. Idealized positions were used for the teXsan crystallographic software package of Molecular Structure Corp.[11]

**ESR Spectral Measurement.** ESR spectra were obtained for ~1 mmol dm$^{-3}$ solutions of complex **2a** with excess NaBH$_4$. Anisotropic spectra were obtained from frozen solutions of an ethanol and toluene 1:1 mixture at 77 K. Spectra were recorded on a JEOL X-band JES-3X ESR spectrometer. Microwave frequencies and the magnetic field were directly determined by using a microwave counter, ADVANTEST TR5212, and a field measurement unit, JEOL NMR field meter ES-FC-5, respectively.

**[CpCo(S$_2$C$_2$(COOMe)$_2$(COOMe)$_2$)(P(OMe)$_3$)], 2a.** mp: 79−81 °C (dec). $^1$H NMR (270 MHz, CDCl$_3$, TMS): $\delta$ 3.63 (s, 3H, OC$H_3$), 3.74 (s, 3H, OC$H_3$), 3.76 (s, 3H, OC$H_3$), 3.83 (s, 3H, OC$H_3$), 3.92 (d, 9H, $J_{PH}$ = 11.0 Hz, P(OC$H_3$)$_3$), 5.22 (s, 5H, C$_5H_5$). $^{13}$C NMR (67.94 MHz, CDCl$_3$, TMS, −10 °C): $\delta$ 14.25 (alkylidene carbon), 49.97 (O$C$H$_3$), 50.37 (O$C$H$_3$), 51.59, 52.24 (O$C$H$_3$), 54.17 ($J_{PC}$ = 7.3 Hz, P(O$C$H$_3$)$_3$), 90.96 ($J_{PC}$ = 12.4 Hz, $C_5$H$_5$), 120.13 ($J_{PC}$ = 6.1 Hz, dithiolene ring carbon), 160.66, 166.62, 165.69, 165.86, 166.07. MS (FAB$^+$) $m/z$: 585 (M$^+$ + 1), 584 (M$^+$). UV−vis (benzene): $\lambda_{max}$ ($\epsilon$) 288 (14260), 368 (7460), 584 (3700) nm. IR (KBr): 1736, 1697, 1620, 1528, 1248, 1182, 1126, 1082, 1028 cm$^{-1}$.

**Crystal Structure Data for 2a.** A dark-purple prismatic crystal of C$_{19}$H$_{26}$O$_{11}$PS$_2$Co (FW = 584.43), monoclinic, space group $P2_1/a$ (No. 14), $a$ = 9.816(3) Å, $b$ = 17.271(4) Å, $c$ = 14.689(3) Å, $\beta$ = 93.57(2)°, $V$ = 2485(1) Å$^{-3}$, $Z$ = 4, $D_c$ = 1.562 g cm$^{-3}$, $\mu$(Mo Kα) = 9.78 cm$^{-1}$, $F_{000}$ = 1208.00, $R$ = 0.042 ($R$w = 0.030) on 2528 intensities ($|F_o| > 3.00\sigma|F_o|$).

**[CpCo(S$_2$C$_2$(COOMe)$_2$(CHCOOEt))(P(OMe)$_3$)], 3b.** mp: 136−138 °C (dec). Anal. Calcd for C$_{18}$H$_{26}$O$_9$P$_1$S$_2$Co$_1$: C, 40.01; H, 4.85. Found: C. 40.09; H, 5.02. $^1$H NMR (270 MHz, CDCl$_3$, TMS): $\delta$ 1.34 (t, 3H, $J_{HH}$ = 7.3 Hz, CH$_2$C$H_3$), 3.05 (d, 1H, $J_{PH}$ = 7.3 Hz, C$H$), 3.74 (d, 9H, $J_{PH}$ = 10.4 Hz, P(OC$H_3$)$_3$), 3.75 (s, 3H, OC$H_3$), 3.87 (s, 3H, OC$H_3$), 4.15~4.34(m, 2H, C$H_2$CH$_3$), 4.94 (s, 5H, C$_5H_5$). $^{13}$C NMR (67.94 MHz, CDCl$_3$, TMS): $\delta$ 14.50 (CH$_2$$C$H$_3$, $J_{CH}$ = 127 Hz), 28.04 (alkylidene carbon, $J_{PC}$ = 25.6 Hz, $J_{CH}$ = 58.1 Hz), 52.36 (O$C$H$_3$, $J_{CH}$ = 147.7 Hz), 53.05 (O$C$H$_3$, $J_{CH}$ = 147.7 Hz), 54.31 (P(O$C$H$_3$)$_3$, $J_{PC}$ = 8.5 Hz, $J_{CH}$ = 147.7 Hz), 60.52 ($C$H$_2$CH$_3$, $J_{CH}$ = 294.2 Hz), 91.21 ($C_5$H$_5$, $J_{PC}$ = 2.4 Hz, $J_{CH}$ = 180.7 Hz), 122.53 (dithiolene ring carbon, $J_{PC}$ = 6.1 Hz), 146.27 ($J_{PC}$ = 4.9 Hz), 164.69, 169.84 ($J_{PC}$ = 3.7 Hz), 180.15 ($J_{PC}$ = 2.5 Hz). MS (FAB$^+$) $m/z$: 541 (M$^+$ + 1), 540 (M$^+$). UV−vis (benzene): $\lambda_{max}$ ($\epsilon$): 300 (10 225), 345 (12 299), 520 (974) nm. IR (KBr): 1722, 1699, 1679, 1288, 1219, 1047, 1014 cm$^{-1}$.

**Crystal Structure Data for 3b.** A brown prismatic crystal of C$_{18}$H$_{26}$O$_9$PS$_2$Co (FW = 540.42), monoclinic, space group $P21/n$ (No. 14), $a$ = 12.961(4) Å, $b$ = 8.085(3) Å, $c$ = 22.111(2) Å, $\beta$ = 90.48(1)°, $V$ = 2316(1) Å$^{-3}$, $Z$ = 4, $D_c$ = 1.549 g cm$^{-3}$, $\mu$(Mo Kα) = 10.36 cm$^{-1}$, $F_{000}$ = 1120.00, $R$ = 0.049 ($Rw$ = 0.031) on 2228 intensities ($|F_o| > 3.00\sigma|F_o|$).

**[CpCo(S$_2$C$_2$(COOMe)$_2$(CH$_2$))(P(OMe)$_3$)], 3c.** mp: 141−145 °C (dec). $^1$H NMR (CDCl$_3$): $\delta$ 1.96 (1H, t, $^2J_{HH}$ = 8.5 Hz, $^3J_{PH}$ = 8.5 Hz, C$H$), 3.68 (9H, d, $^3J_{PH}$ = 11.0 Hz, P(OC$H_3$)$_3$), 3.75, 3.86 (3H, s, C$H_3$), 4.86 (1H, dd, $^2J_{HH}$ = 8.5 Hz, $^3J_{PH}$ = 5.5 Hz, C$H$), 4.93 (5H, s, C$_5H_5$). $^{13}$C NMR (125.77 MHz, CDCl$_3$, TMS): $\delta$ 10.80 (alkylidene carbon, $^2J_{PC}$ = 31.0 Hz), 52.28 (O$C$H$_3$), 52.95 (O$C$H$_3$), 53.50 (P(O$C$H$_3$)$_3$, $^2J_{PC}$ = 6.2 Hz), 90.57 ($C_5$H$_5$, $^2J_{PC}$ = 3.1 Hz), 124.31 (dithiolene ring carbon), 146.02 (dithiolene ring carbon, $^3J_{PC}$ = 5.2 Hz), 164.81 ($C$OOMe), 169.94 ($C$OOMe, $^5J_{PC}$ = 3.1 Hz). MS (FAB$^+$) $m/z$: 469 (M$^+$ + 1), 468 (M$^+$). HR MS (FAB$^+$) $m/z$: calcd for C$_{15}$H$_{23}$O$_7$P$_1$S$_2$Co$_1$, 468.9955; found, 468.9954 (M$^+$ + 1).

**[CpCo(S$_2$C$_2$(COOMe)$_2$(C(COOMe)$_2$)(PMe$_3$)], 4a.** $^1$H NMR (270 MHz, CDCl$_3$, TMS): $\delta$ 1.58 (d, 9H, $J_{PH}$ = 14.0 Hz, P(C$H_3$)$_3$), 3.62 (s, 3H, OC$H_3$), 3.74 (s, 3H, OC$H_3$), 3.78 (s, 3H, OC$H_3$), 3.83 (s, 3H, OC$H_3$), 5.09 (s, 5H, C$_5H_5$). MS (FAB$^+$) $m/z$: 537 (M$^+$ + 1), 536 (M$^+$). UV−vis (C$_6$H$_6$): $\lambda_{max}$ ($\epsilon$) 282 (14 101), 367 (7675), 570 (4070) nm.

**[CpCo(S$_2$C$_2$(COOMe)$_2$(CHCOOEt))(PMe$_3$)], 5b.** mp: 161−163 °C (dec). Anal. Calcd for C$_{18}$H$_{26}$O$_6$PS$_2$Co: C, 43.91; H, 5.32; S, 13.02. Found: C, 43.58; H, 5.26; S, 13.24. $^1$H NMR (CDCl$_3$): $\delta$ 1.40 (3H, t, C$H_3$), 1.41 (9H, d, $^2J_{P-H}$ = 10.4 Hz, P(C$H_3$)$_3$), 2.49 (1H, d, $^3J_{PH}$ = 6.7 Hz, C$H$), 3.76, 3.88 (3H, s, C$H_3$), 4.1−4.5 (2H, m, C$H_2$), 4.81 (5H, s, C$_5H_5$). $^{13}$C NMR (CDCl$_3$): $\delta$ 14.72 (CH$_2$$C$H$_3$), 15.24 ($J$ = 31.8 Hz, P($C$H$_3$)$_3$), 26.32 ($J$ = 17.1 Hz, alkylidene carbon), 52.39 (O$C$H$_3$), 53.09 (O$C$H$_3$), 60.69 ($C$H$_2$CH$_3$), 90.14 ($J$ = 2.4 Hz, $C_5$H$_5$), 122.09 (dithiolene ring carbon), 147.12 ($J$ = 4.9 Hz, dithiolene ring carbon), 164.69, 170.51 ($C$OOMe), and 180.15 ($C$OOEt). MS (FAB$^+$) $m/z$: 493 (M$^+$ + 1), 492 (M$^+$). UV−vis (C$_6$H$_6$): $\lambda_{max}$ ($\epsilon$) 283 (14 973), 332 (10 716) nm. IR (KBr): 1722, 1703, 1693, 1236, 1205, 953 cm$^{-1}$.

**Crystal Structure Data for 5b.** A brown prismatic crystal of C$_{18}$H$_{26}$O$_6$PS$_2$Co (FW = 492.43), orthorhombic, space group $P2_12_12_1$ (No. 19), $a$ = 12.38(2) Å, $b$ = 20.24(2) Å, $c$ = 8.71(2) Å, $V$ = 2183(6) Å$^{-3}$, $Z$ = 4, $D_c$ = 1.498 g cm$^{-3}$, $\mu$(Mo Kα) = 10.81 cm$^{-1}$, $F_{000}$ = 1024.00, $R$ = 0.055 ($Rw$ = 0.051) on 2875 intensities ($|F_o| > 3.00\sigma|F_o|$).

**[CpCo(S$_2$C$_2$(COOMe)$_2$(CH$_2$))(PMe$_3$)], 5c.** mp: 169−171 °C (dec). Anal. Calcd for C$_{15}$H$_{22}$O$_4$PS$_2$Co: C, 42.86; H, 5.28; S, 15.25. Found: C, 42.73; H, 5.23; S, 15.20. $^1$H NMR (CDCl$_3$): $\delta$ 1.32 (9H, d, $^3J_{PH}$ = 11.0 Hz, P(C$H_3$)$_3$), 1.46 (1H, d, $^2J_{HH}$ = 8.6 Hz, C$H$), 3.75, 3.83 (3H, s, C$H_3$), 4.67 (1H, dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{PH}$ = 4.3 Hz, CH), 4.81 (5H, s, C$_5H_5$). $^{13}$C NMR (CDCl$_3$): $\delta$ 16.25 (P($C$H$_3$)$_3$), 29.33 ($C$H$_2$), 52.24 (O$C$H$_3$), 52.92 (O$C$H$_3$), 89.60 ($C_5$H$_5$), 124.28, 145.46 (dithiolene ring carbon), 164.92, 169.97 ($C$OOCH$_3$). MS (EI$^+$) $m/z$ (relative intensity): 420 (0.45, M$^+$), 344 (100.00, M$^+$ − PMe$_3$), 330 (27.04, M$^+$ − PMe$_3$ − CH$_2$), 188 (41.40, CpCoS$_2^+$), 124 (46.30, CpCo$^+$). MS (FAB$^+$) $m/z$: 493 (M$^+$ + 1), 492 (M$^+$). UV−vis (C$_6$H$_6$): $\lambda_{max}$ ($\epsilon$) 284 (16 571), 373 (8180), 571 (582) nm. IR (KBr): 1711, 1693, 1047, 1016, 949 cm$^{-1}$.

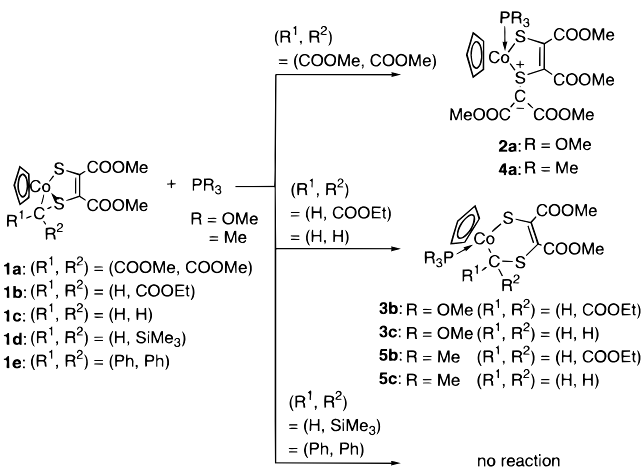
**Crystal Structure Data for 5c.** A brown prismatic crystal of C$_{15}$H$_{22}$O$_4$PS$_2$Co (FW = 420.36), orthorhombic, space group $Pbca$ (No. 61), $a$ = 17.920(3) Å, $b$ = 14.785(4) Å, $c$ = 14.180(4) Å, $V$ = 3756(2) Å$^{-3}$, $Z$ = 8, $D_c$ = 1.486 g cm$^{-3}$, $\mu$(Mo Kα) = 12.35 cm$^{-1}$, $F_{000}$ = 1744.00, $R$ = 0.055 ($Rw$ = 0.031) on 4814 intensities ($|F_o| > 3.00\sigma|F_o|$).

---

(10) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykala, C. The DIRDIF Program System. Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

(11) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corp., The Woodlands, TX, 1985, 1992.

### Scheme 1



## Results and Discussion

**Reaction of Alkylidene-Bridged Complexes with Trimethyl Phosphite and Trimethylphosphine.** The reactions of the five alkylidene-bridged complexes [$CpCoS_2C_2(COOMe)_2(CR^1R^2)$] (Cp = $\eta^5$-$C_5H_5$, ($R^1$, $R^2$) = (COOMe, COOMe) **1a**; (H, COOEt) **1b**; (H, H) **1c**; (H, $SiMe_3$) **1d**; and (Ph, Ph) **1e**) with excess trimethyl phosphite gave varying results. For complexes **1d** and **1e**, no reaction was observed. However, the alkylidene-bridged complexes **1a**, **1b**, and **1c** reacted easily with trimethyl phosphite and gave good yields of the products. In the reaction of complex **1a**, the color of the solution was changed from brown to dark-purple. The resulting product (**2a**) was determined to have an M−S sulfur ylide structure. On the other hand, for complexes **1b** and **1c**, the change of color of the solution from brown to light brown was evident. The products (**3c** and **3b**) had the ring-expanded six-membered-ring structures (Scheme 1). Likewise, in the reactions with trimethylphosphine, similar results were obtained.

Single crystals of the ylide complex **2a** as well as those of the six-membered-ring complexes **3b**, **5c**, and **5b** were prepared, and X-ray crystal structure analyses were done. The molecular structure of **2a** is shown in Figure 1. Selected bond lengths and bond angles are given in the caption. In complex **2a**, the almost planar five-membered cobaltadithiolene ring is retained. Coordination of trimethyl phosphite to the cobalt atom causes the cleavage of the Co−C bond of the alkylidene moiety to give the sulfonium ylide structure. As predicted from the structure of **1a**, the phosphite is situated perpendicular to the dithiolene ring and on the opposite side of the alkylidene moiety, $C(COOMe)_2$. The bond length of C(1)−C(2) (1.331(6) Å) is slightly shorter than the corresponding value of the original complex **1a** (1.361(3) Å) and agrees with normal C=C bond lengths (1.337 ± 0.006 Å). In addition, Co−S bond lengths (2.248(1) and 2.215(1) Å) are normal for $Co^{III}-SR_2$ bond. Thus, it can be concluded that the dithiolene ring has an olefinic structure. The bond length of S(1)−C(7) (1.730(4) Å) is shorter than the corresponding value of the original complex **1a** (1.794(3) Å) and a value between the normal C−S single bond length (1.81 Å) and the normal C=S double bond length (1.66 Å).[12] The S(1)−C(7)−C(8)−C(10) atoms are found to be planar, and the sulfur atom shows the pyramidal structure (see Figure 2).[13]

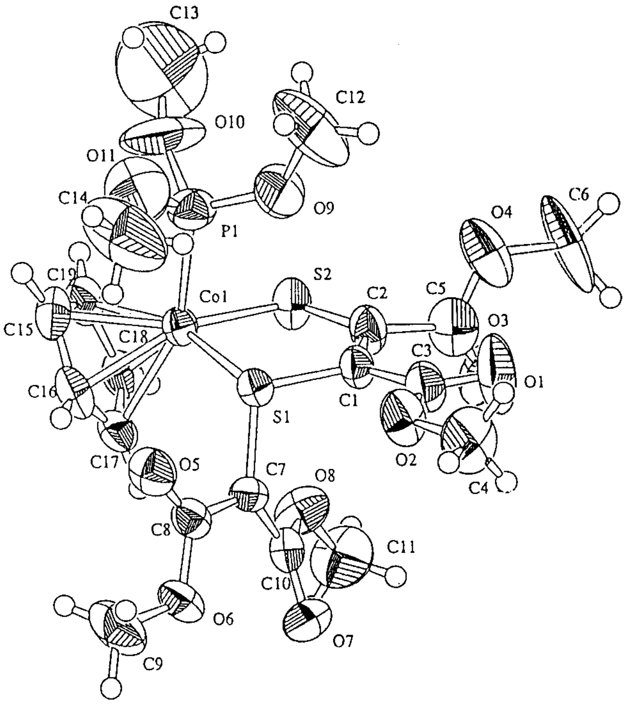


**Figure 1.** Molecular structure of **2a**. Selected bond lengths (Å) and angles (deg) are as follows: Co−S(1), 2.248(1); Co−S(2), 2.215(1); S(1)−C(1), 1.770(4); S(2)−C(2), 1.714(5); C(1)−C(2), 1.331(6); S(1)−C(7), 1.730(4); Cp−Co, 1.707; S(1)−Co−S(2), 90.26(5); Co−S(1)−C(1), 102.8(1); Co−S(2)−C(2), 102.2(2); S(1)−C(1)−C(2), 118.1(4); S(2)−C(2)−C(1), 125.4(4); Co−S(1)−C(7), 116.7(1); C(1)−S(1)−C(7), 105.7(2); S(1)−C(7)−C(8), 111.4(3); S(1)−C(7)−C(10), 123.7(4); C(8)−C(7)−C(10), 124.4(4).

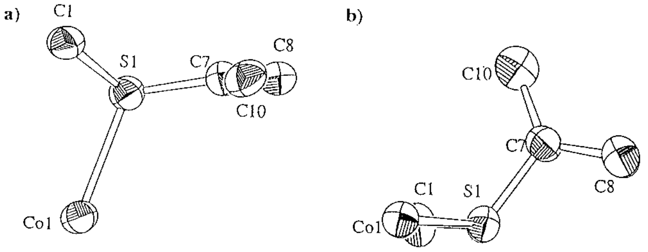
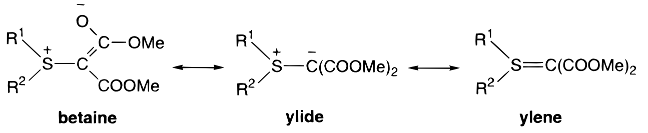


**Figure 2.** Structures of the sulfonium ylide moiety: (a) around the carbon atom (planar); (b) around the sulfur atom (pyramidal).

### Scheme 2



The above results suggest that the ylide structure is a resonance hybrid between betaine and ylene structures. The extensive charge delocalization of the carbanion in the C−S bond of the sulfonium ylide contribute to its stability (Scheme 2).

The molecular structures of **3b**, **5b**, and **5c** are shown in Figures 3−5, respectively. Selected bond lengths and bond angles are given in the captions. Complexes **3b**, **5b**, and **5c**, in which trimethyl phosphite or trimeth-

---

(12) Christensen, A. T.; Whitmore, W. G. *Acta Crystallogr.* **1969**, *25*, 73 and references therein.

(13) Ando, W. *Acc. Chem. Rec.* **1977**, *10*, 179.

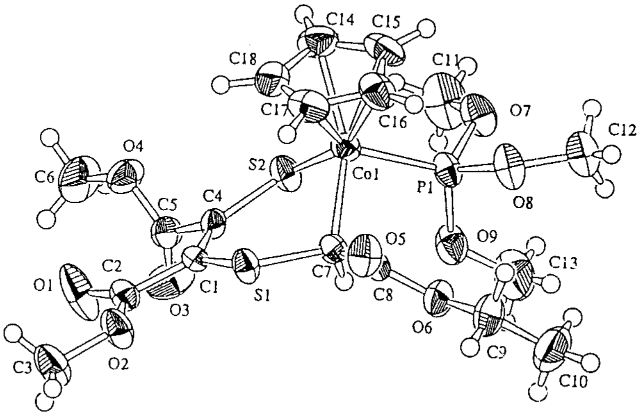


**Figure 3.** Molecular structure of **3b**. Selected bond lengths (Å) and angles (deg) are as follows: Co−S(2), 2.234(2); Co−C(7), 2.019(6); S(1)−C(7), 1.799(5); S(1)−C(1), 1.751(6); S(2)−C(4), 1.721(6); Co−P, 2.155(2); Cp−Co, 1,693; S(2)−Co−C(7), 87.7(2); C(1)−S(1)−C(7), 103.6(3); Co−S(2)−C(4), 111.8(2); Co−C(7)−S(1), 112.3(3); S(2)−Co−P(1), 94.67(7); P(1)−Co−C(7), 92.3(2).

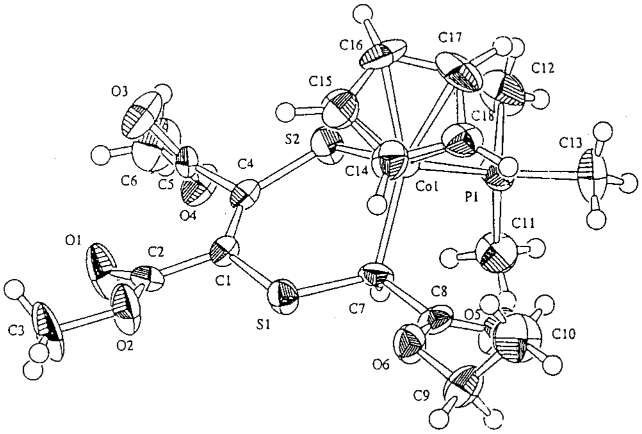


**Figure 4.** Molecular structure of **5b**. Selected bond lengths (Å) and angles (deg) are as follows: Co−S(2), 2.216(3); Co−C(7), 2.02(1); S(1)−C(7), 1.79(1); S(1)−C(1), 1.759(9); S(2)−C(4), 1.72(1); C(1)−C(4), 1.36(1); Co−P, 2.209(3); Cp−Co, 1.707; S(2)−Co−C(7), 88.0(3); S(1)−C(1)−C(4), 126.2(8); S(2)−C(4)−C(1), 132.2(8); C(1)−S(1)−C(7), 104.0(5); Co−S(2)−C(4), 110.8(4); Co−C(7)−S(1), 114.8(5); S(2)−Co−P(1), 87.1(1); P(1)−Co−C(7), 94.6(3).

ylphosphine is coordinated to the cobalt atom, have a six-membered ring. This is due to the Co−S bond cleavage. The six-membered ring is not planar. The phosphite or phosphine is situated on the side of the S(1) atom opposite to the Co−S(1)−C(7) planar. The cobalt atom can be described as being in a three-legged piano stool environment. The Co−S(2) bond lengths (2.206−2.234 Å) are close to the normal $Co^{III}$-$SR_2$ bond length (2.25−2.48 Å).[14] These structures are the same as that of the previously reported complex.[15]

The sulfonium ylide complexes are obtained selectively in the case of $R^1 = R^2 =$ COOMe. This fact provides the evidence for the extensive delocalization of the negative charge caused by the electron-withdrawing methoxycarbonyl group; this leads to the predominance of a betaine structure stabilizing the ylide structure. The stabilization of the sulfonium ylide structure is attributed to the stability of the carbanion which in turn is stabilized by two ester groups in the alkylidene moieties.

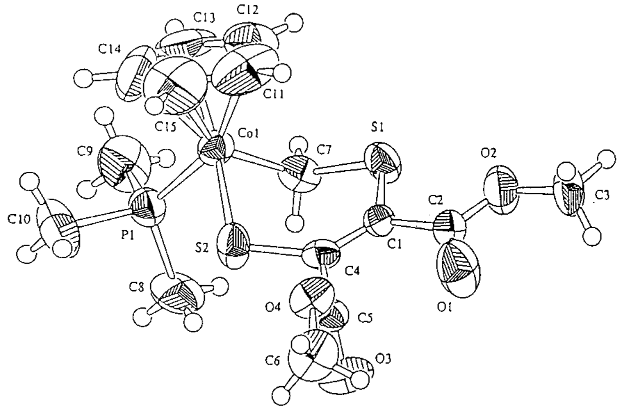
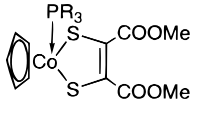


**Figure 5.** Molecular structure of **5c**. Selected bond lengths (Å) and angles (deg) are as follows: Co−S(2), 2.206(3); Co−C(7), 1.970(9); S(1)−C(7), 1.770(9); S(1)−C(1), 1.756(9); S(2)−C(4), 1.707(8); C(1)−C(4), 1.34(1); Co−P, 2.164(3); Cp−Co, 1,714; S(2)−Co−C(7), 88.6(3); S(1)−C(1)−C(4), 126.3(7); S(2)−C(4)−C(1), 132.4(7); C(1)−S(1)−C(7), 104.1(4); Co−S(2)−C(4), 109.5(3); Co−C(7)−S(1), 115.8(5); S(2)−Co−P(1), 89.5(1); P(1)−Co−C(7), 90.7(3).

**Table 1. Yields of the Products**

| starting complex | 2/% | 3/% | 4/% | 5/% |
|---|---|---|---|---|
| **1a** | 61 | 0 | 12 | 0 |
| **1b** | 0 | 37 | 0 | 72 |
| **1c** | 0 | 6 | 0 | 100 |

Table 1 shows the yields of the reaction using ∼10 molar equiv of Lewis bases for 30 min. In the reactions of complex **1a**, it yielded dithiolene complex **6** and **2a** and **4a** together with the original complex **1a**. In the reaction of complex **1a** with trimethylphosphine, the presence of $Me_3P{=}C(COOMe)_2$ was detected by GC−MS. Therefore it can be concluded that the ylide complexes **2a** and **4a** were broken by the excess Lewis bases and formed Lewis base adducts **7** and **8**[16] which in turn gave dithiolene complex **6**. Furthermore, the isolated complexes **2a** and **4a** were observed to have slowly formed the alkylidene-bridged complex **1a** and the dithiolene complex **6** at ambient temperature. It is probable that **2a** and **4a** slowly eliminated the Lewis bases and regenerated the alkylidene-bridged complex **1a**. Then the eliminated bases reacted with ylide complexes **2a** and **4a** and gave the original dithiolene complex **6** via adducts **7** and **8** (Scheme 3).



**7**; R = OMe
**8**; R = Me

In the reaction of complexes **1b** and **1c** with a large excess of trimethyl phosphite, products **3b** and **3c** were obtained in quantitative yield. When trimethylphosphine was used as a Lewis base, the reactions proceeded faster than with trimethyl phosphite. The expected

---

[14] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

[15] Sakurada, M.; Kajitani, M.; Hatano, H.; Matsudaira, Y.; Suetsugu, T.; Ono, S.; Akiyama, T.; Sugimori, A. *Organometallics* **1992**, *11*, 2337.

[16] Kajitani, M.; Igarashi, A.; Hatano, H.; Akiyama, T.; Sugimori, A.; Matsumoto, S.; Iguchi, Y.; Bönnemann, H.; Shimizu, K.; Sato, G. P. *J. Organomet. Chem.* **1995**, *485*, 31.

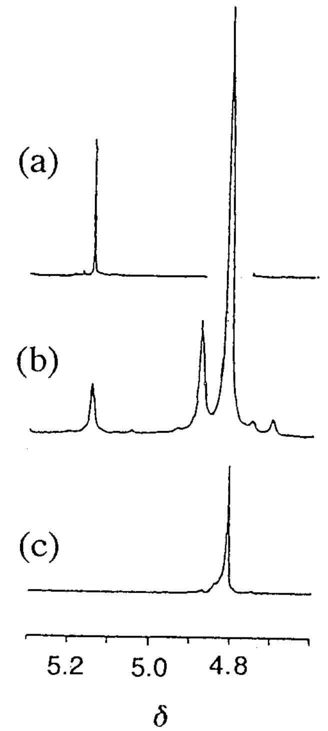
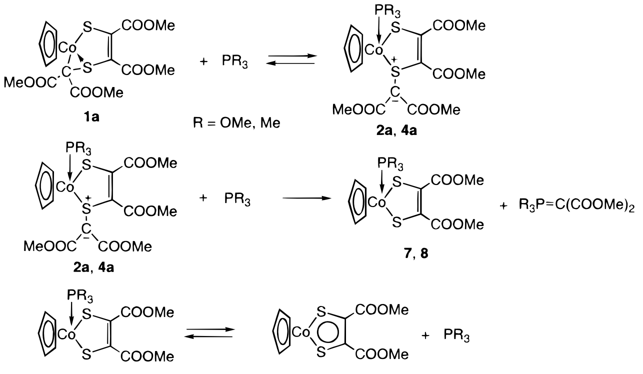


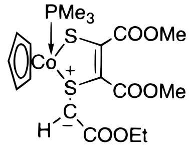
**Figure 6.** $^1$H NMR spectra of (a) purified **1b**, (b) **1b** with trimethylphosphine, and (c) purified **5b**.

**Scheme 3**



order of reactivity of alkylidene-bridged complexes is **1a** > **1b** > **1c**. But in the reaction of complex **1b** with trimethylphosphine, it needed a longer period of time to obtain product **5b** in quantitative yield.

Thus, we tried an in situ NMR spectral measurement of the reaction of complex **1b** with trimethylphosphine. The $^1$H NMR spectra of the reaction of complex **1b** with trimethylphosphine are shown in Figure 6, together with those of the isolated complexes **1b** and **5b**. We were able to confirm that two products were formed. The signal at δ 4.81 (Cp ring proton) is assigned to the six-membered ring complex **5b**. The other signal at δ 4.88 (Cp ring proton) most likely belongs to the ylide complex [CpCo($S_2C_2$(COOMe)$_2$(CHCOOEt))(PMe$_3$)] (**4b**) (Scheme 4). This result is supported by CV measurement, which is described later.



**4b**

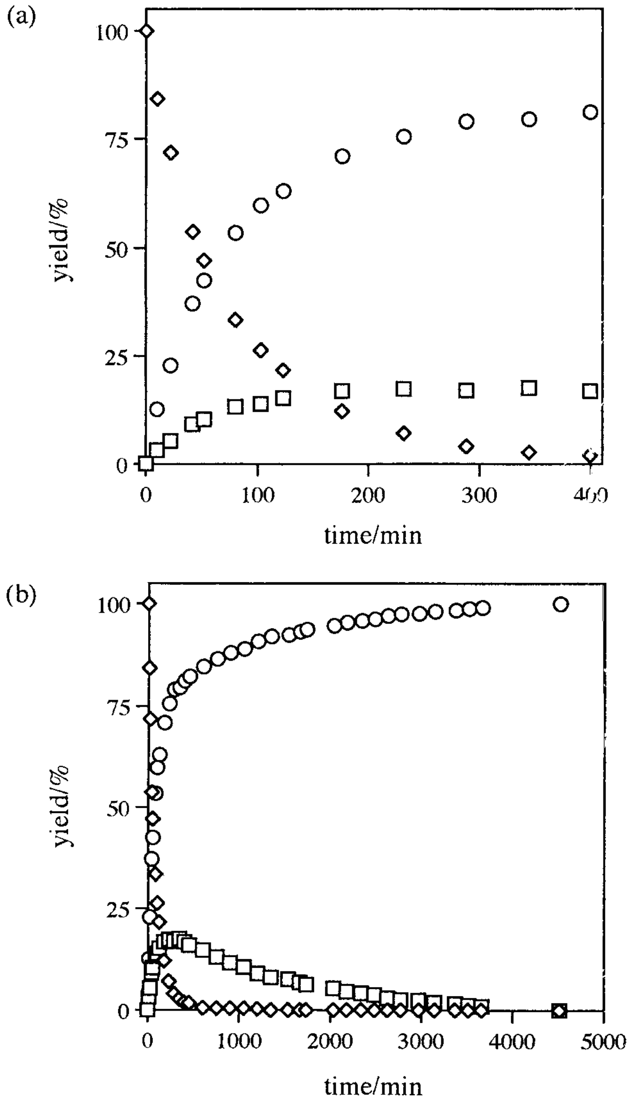
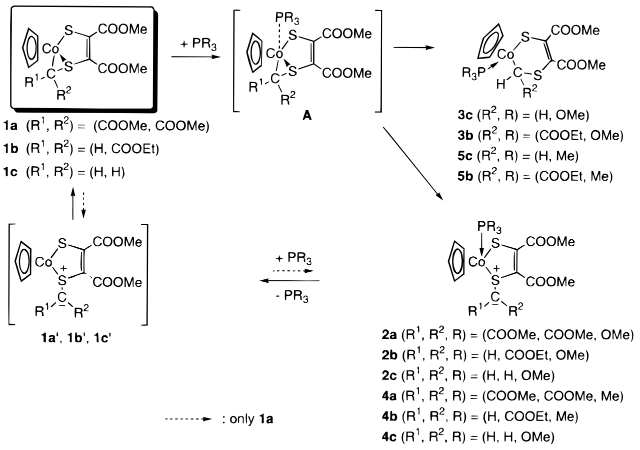


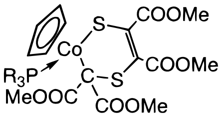
**Figure 7.** Time dependence of the yields (○, **5b**; □, **4b**; ◇, recovery **1b**) between (a) 0–399 (b) 0–4508 min.

**Scheme 4**



Furthermore, the changes of yields against time are worth mentioning (Figure 7). The yields of complexes **5b** (six-membered ring) and **4b** (ylide) became higher along with the decrease of the original complex **3b** (Figure 7 (a)). Six hours after the start of the reaction, it was observed that the amount of complex **4b** decreases and only complex **5b** increases. At the end, we observed only the signal of complex **5b** (Figure 7b). These results show that complex **4b** is not so stable and is converted to complex **5b**.

The ester groups make the ylide structures stable.[17−19] When the ylide compounds are unstable, 1,2-rearrangement often occurs.[20−22] The 1,2-rearrangement reaction in the cyclic ylides causes ring expansion. Namely, a five-membered-ring ylide compound becomes a six-membered ring.Here, we examined the thermal behavior of ylide complexes **2a** and **4a** to confirm the formation of six-membered-ring complexes **3a** and **5a**, via 1,2-rearrangement. However, when the solutions of these complexes were heated at 40 °C, it accelerated the elimination of Lewis bases and gave complexes **1a** and **6** instead of **3a** and **5a**.



**3a** R = OMe
**5a** R = Me

On the other hand, the six-membered-ring complexes **3b**, **3c**, **5b**, and **5c** upon heating at 80 °C eliminated the Lewis bases and regenerated the alkylidene-bridged complexes **1b** and **1c** quantitatively. The combined results of the reactions of the alkylidene-bridged complexes with Lewis bases led us to postulate two types of mechanism as shown below: Complex **1a** exists in equilibrium with ylide structure **1a′**.[23] The measured reduction potentials (**1a′**, $E_p = -0.9$ V; **1a**, $E_p = -1.3$ V vs Fc|Fc$^+$) suggest that Lewis bases react more readily with **1a′** than **1a**. As a result, trimethyl phosphite and trimethylphosphine react with **1a′** to form ylide complexes **2a** and **4a**, respectively (Scheme 4).

In complexes **1b** and **1c**, the equilibrium with **1b′** and **1c′** does not exist. Lewis bases react with complexes **1b** and **1c** to form seven-coordinated transition states (**A**). Transition states **A** cleaves the Co−S bond or the Co−C bond immediately (S$_N$2 reaction mechanism). Complexes **2b**, **2c**, **4b**, and **4c** seemed to be unstable, because it is difficult for them to have betaine structures. The six-membered-ring complexes **3** and **5** are more favored than the corresponding ylide complexes **2** and **4**, especially when the starting complex is **1c**. The normal ylide compounds undergo 1,2-rearrangement via diradicals.[24] In these complexes, Co−P bond cleavage (elimination of Lewis bases) occurs more rapidly than Co−S bond cleavage (1,2-rearrangement) and the alkylidene complex is regenerated. Complexes **3b**, **3c**, **5b**, and **5c** eliminated Lewis bases when they were heated and regenerated alkylidene complexes **1b** and **1c** (Scheme 5).

**Scheme 5**

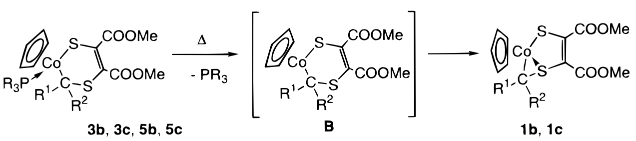


**Table 2. Redox Potentials (vs Fc|Fc$^+$)**

| | $E_{1/2}{}^a$/V | |
|---|---|---|
| | reduction | oxidation |
| **2a** | −1.01 | 0.45 |
| **3b** | −1.61 | 0.30 |
| **3c** | −1.74 | 0.19 |
| **4a** | −1.20 | 0.43 |
| **4b** | −1.31 | |
| **5b** | −1.63 | 0.29 |
| **5c** | −1.82 | 0.11 |

[a] $E_{1/2} = (E_p + E_{p/2})/2$, as half-wave potential.

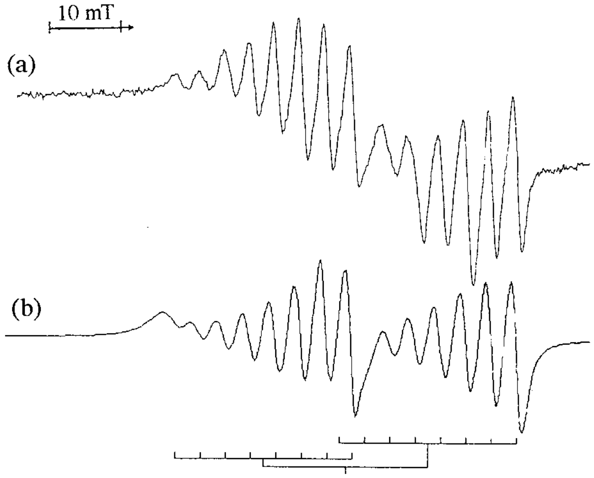


**Figure 8.** ESR spectra (a) immediately after reduction of **2a**; (b) simulation of (a).

We also examined the electrochemical behavior of the products. The redox potentials of all the products are shown in Table 2.

Although the electrochemical behavior of complex **2a** has been reported previously,[23] we examined its ESR in more detail. In the ethanol/benzene 1:1 solution, the reductant **2a**$^-$ exhibited isotropic ESR signals at 20 °C. This spectrum shows hyperfine splittings of both cobalt ($I = {}^7/_2$) and phosphorus ($I = {}^1/_2$) (Figure 8 a) ($g_{iso} = 2.065$, $A_{iso(Co)} = 3.6$ mT, $A_{iso(P)} = 23.5$ mT).

Complex **4a** showed the same behavior as complex **2a**. The reduction potential of complex **4a** is more positive than that of original complex **1a**, and the oxidation potential is more negative than that of original complex **1a**. The reduction is reversible, and the oxidation is irreversible and eliminates the trimethylphosphine cation to regenerate alkylidene-bridged complex **1a** via ylide complex **1a′** (Scheme 6).

The central metal cobalt, which is the reduction site, is electron poor because of the neighboring ylide sulfur. And because of this, it causes complexes **2a** and **4a** to be reduced at a more positive potential than the alkylidene-bridged complex **1a** and makes the reductants stable. On the other hand, these complexes were

---

(17) Ando, W.; Yagihara, T.; Migita, T. *Tetrahedron Lett.* **1969**, 1983.

(18) Ando, W.; Yagihara, T. Tozune, I.; Imai, I.; Suzuki, J.; Toyama, T.; Nakaido, S.; Migita, T. *J. Org. Chem.* **1972**, *37*, 1721.

(19) Ando, W.; Yagihara, T. Kondo, S.; Nakayama, K.; Yamamoto, H.; Nakaido, S.; Migita, T. *J. Org. Chem.* **1971**, *36*, 1732.

(20) Ando, W.; Yagihara, T.; Tozune, S.; Migita, T. *J. Am. Chem. Soc.* **1969**, *91*, 2786.

(21) Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Yamamoto, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.* **1972**, *94*, 3870.

(22) Ando, W.; Yagihara, T. Tozune, I.; Imai, I.; Suzuki, J.; Toyama, T.; Nakaido, S.; Migita, T. *J. Org. Chem.* **1972**, *37*, 1721.

(23) Takayama, C.; Kajitani, M.; Sugiyama, T.; Akiyama, T.; Shimizu, K.; Sugimori, A. *Organometallics* **1997**, *16*, 3498.

(24) Schöllkopf, U.; Ostermann, G.; Schossig, J. *Tetrahedron Lett.* **1969**, 2619. (b) Schöllkopf, U.; Schossig, J.; Osterman, G. *Liebigs Ann. Chem.* **1970**, *737*, 158. (c) Immur, H.; Iwamura, M.; Nishida, T.; Yoshida, M.; Nakayama, J. *Tetrahedron Lett.* **1971**, 63.

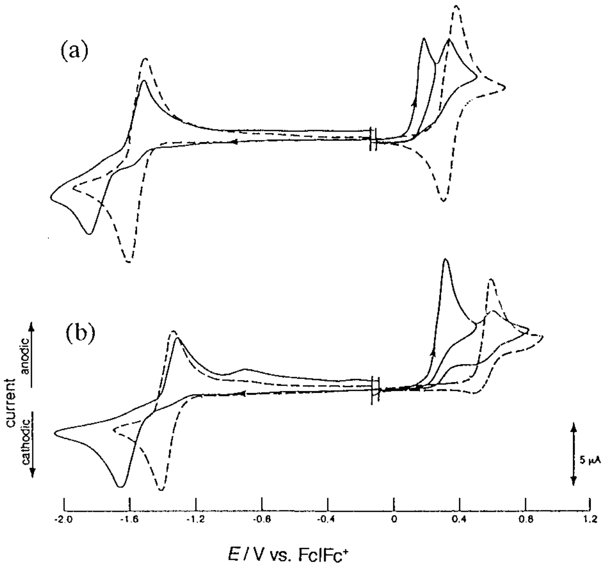
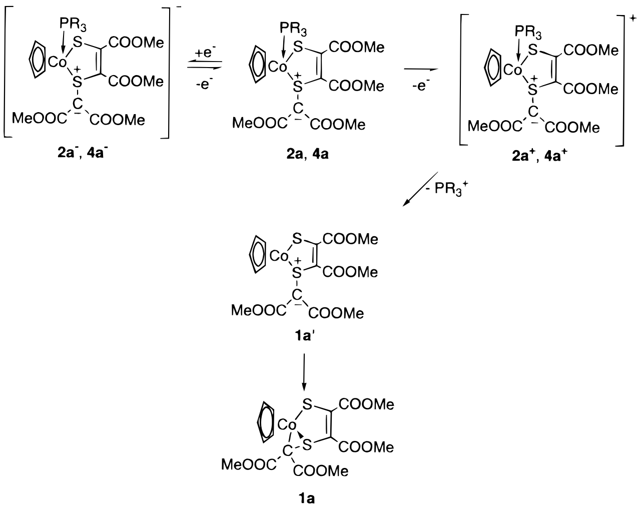


**Figure 9.** Cyclic voltammograms ($v$ = 100 mV s$^{-1}$,$\Phi$ = 1.6-mm Pt disk) of 1 mM (a) **3c** (—) and **1c** (- - -) and (b) **3b**(—) and **1b** (- - -) in $CH_3CN$ containing 0.1 M TEAP.

**Scheme 6**



oxidized at a potential more negative than that of **1a**. The oxidation site seemed to be sulfur, which does not have the ylide structure. This sulfur became electron rich because of the addition of Lewis bases. And, the electron density of the dithiolene ring seemed to be slanted.

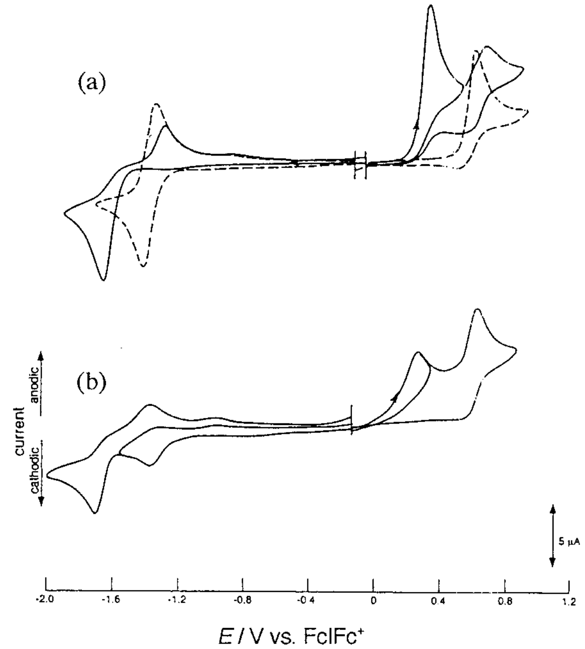
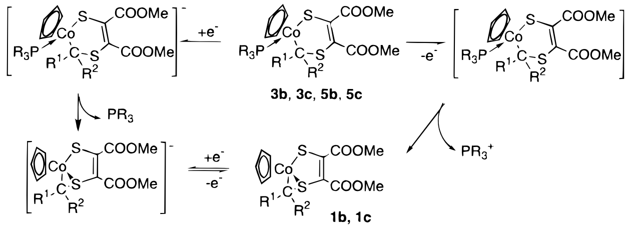


**Figure 10.** Cyclic voltammograms ($v$ = 100 mV s$^{-1}$,$\Phi$ = 1.6-mm Pt disk) of 1 mM (a) isolated **5b** (—) and **1b** (- - -) and (b) in situ measurement of **1b** with trimethylphosphine in $CH_3CN$ containing 0.1 M TEAP.

**Scheme 7**



Cyclic voltammograms of six-membered-ring complexes **3b** and **3c** (solid line) are shown in Figure 9, together with those of **1b** and **1c** (broken line). Complexes **3b** and **3c** displayed irreversible reduction and oxidation waves. The reduction potentials of **3b** and **3c** are more negative than those of the corresponding alkylidene-bridged complexes **1b** and **1c**. When the potential was reversed after reduction, a reoxidation wave that agrees with that of the corresponding alkylidene-bridged complex appeared. On the other hand, the oxidation potentials of **3b** and **3c** are also more negative than those of the corresponding alkylidene-bridged complexes **1b** and **1c**. When the potential scan was continued to a more positive range, an oxidation wave corresponding to the oxidation of alkylidene-bridged complex appeared. Namely, the reductants **3b**$^-$ and **3c**$^-$ formed the corresponding reductants of the alkylidene-bridged complexes along with the elimination of the neutral trimethyl phosphite. On the other hand, the oxidants formed neutral alkylidene-bridged complexes along with an elimination of the trimethyl phosphite cation (Scheme 7).

Complexes **5b** and **5c** also showed behavior similar to that of the corresponding trimethyl phosphite adducts **3b** and **3c**. Here, we tried an in situ measurement of complex **1b** with trimethylphosphine and the CVs are shown in Figure 10, together with those of the isolated complex **5b**. In the reduction, two reduction waves appeared. The more negative one is the reduction wave of complex **5b**. Here, we tried a differential pulse voltammetry (DPV) measurement and the in situ DPV of complex **1b** with trimethylphosphine is shown in Figure 11, together with that of complex **6**. These DPVs also show two reduction waves. The more negative one is the reduction wave of complex **5b**. But the other wave is not that of complex **6**. Judging from the tendency of the reduction potential, this negative wave is the reduction wave of the ylide complex **4b**.

Both reduction and oxidation potentials of the six-membered-ring complexes shifted to a more negative site than those of alkylidene-bridged complexes. That is, both metal and sulfur atoms became electron rich by the addition of Lewis bases. Furthermore, both reduction and oxidation showed irreversible behavior;

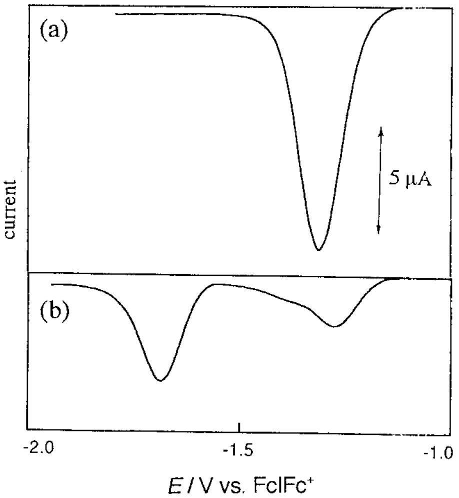


**Figure 11.** Differential pulse polarograms of (a) **6** and (b) in situ measurement of **1b** with trimethylphosphine.

six-membered-ring structures are less stable than five-membered-ring dithiolene complexes, which show aromaticity.

## Conclusion

The reactions of an alkylidene-bridged complex **1a** with trimethyl phosphite and trimethylphosphine result in the formation of novel M−S sulfonium ylide complexes **2a** and **4a**. In these reactions, Lewis bases react with unstable ylide complex **1a′** to form stable ylide complexes **2a** and **4a**. On the other hand, alkylidene-bridged complexes **1b** and **1c** gave six-membered-ring complexes **3b**, **3c**, **5b**, and **5c**. In these reactions, Lewis bases react via an $S_N2$ type of reaction to form seven-coordinated transition states (**A**), which immediately caused the cleavage of the Co−S bond or the Co−C bond. The ylide complexes **2b**, **2c**, **4b**, and **4c** were too unstable to detect and Co−P bond cleavage occurs.

The reductants of ylide complexes **2a** and **4a** are stable on the CV time scale and we observed reversible redox couples. However, oxidants are too unstable and give the original alkylidene-bridged complex **1a** with $PR_3^+$ (R = OMe and Me). On the other hand, six-membered-ring complexes are not stable in either reduction or oxidation and regenerate the corresponding alkylidene-bridged complexes with free $PR_3$ or $PR_3^+$.

The metalladithiolene rings have both aromatic properties[25,26] and unsaturated properties.[27] The nature of the dithiolene complex may be regarded as either a 16e or 18e complex, depending upon the absence or presence of lone pair donations from the sulfurs to the metal center.[28] When they react with the ligand like a Lewis base, they behave as an 18e complex. These rings are very stable; however, they are also very reactive. In this work, the dithiolene ring had made it possible to form the first M−S sulfur ylide complexes This can be achieved by controlling the electron density of the dithiolene ring by changing the substituent, thus making it a very good reaction site.

**Acknowledgment.** This study was supported by the Hayashi Memorial Foundation for Female Natural Scientists and by Grants-in-Aid for Scientific Research Nos. 09440247 and 09640673 and Grant-in-Aid on Priority Area-Researches on “Inter-element” No. 0923-9246 from the Ministry of Education, Science, Sports and Culture of Japan.

**Supporting Information Available:** Tables giving crystal data and refinement details, positional and thermal parameters, and bond distances and angles for complexes **2a**, **3b**, **5b**, and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990139M

---

(25) Kajitani, M.; Hagino, G.; Tamada, M.; Fujita, T.; Sakurada, M.; Akiyama, T.; Sugimori, A. *J. Am. Chem. Soc.* **1996**, *118*, 489.

(26) (a) Ohkoshi, S.; Ohba, Y.; Iwaizumi, M.; Yamauchi, S.; Ohtani, M.; Tokuhisa, K.; Kajitani, M.; Akiyama, T.; Sugimori A. *Inorg. Chem.* **1996**, *35*, 4569. (b) Sugimori, A.; Tachiya, N.; Kajitani, M.; Akiyama, T. *Organometallics* **1996**, *15*, 5664.

(27) (a) Sakurada, M.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Chem. Exp.* **1991**, *6*, 759. (b) Katsuta, H.; Noguchi, N.; Inomata, Y.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1994**, *1165*. (c) Takayama, C.; Takeuchi, K.; Kajitani, M.; Sugiyama, T.; Sugimori, A. *Chem. Lett.* **1998**, 241.

(28) Don, M.-J.; Yang, K.; Bott, S. G.; Richmond, M. G. *J. Organomet. Chem.* **1997**, *554*, 15.