Electrochemistry and Reactivity of Cobaltadithiolene Complexes Having Sulfilimine Structures: Effect of Phosphorus Ligand Basicity and Cone Angle on the Electrochemical Behavior and on the Imido Migration to the Cp Ring

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Various types of cobaltadithiolene complexes having the sulfilimine structure CpCo[S(NTs)-$SC_2(COOMe)_2$](PR_3) were newly synthesized. The lifetimes of the sulfilimine complexes are influenced by the basicities and by the cone angles of PR_3 ligands used. Some of the sulfilimine complexes rapidly eliminate PR_3 ligands by a one-electron reduction (PR_3 = PPh_3, $P(OPh)_3$, $P(p\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4Cl)_3$, PCy_3, $P(p\text{-}C_6H_4OMe)_3$) to give the precursor of the sulfilimine complex, the imido-bridged cobaltadithiolene adduct [CpCo{$S_2C_2(COOMe)_2$}(NTs)]. On the other hand, the complexes of PBu_3 and $P(OMe)_3$ were stable during a one-electron reduction. The elimination of the imido group (NTs) by a second reduction was confirmed in all of the sulfilimine complexes. The investigation of the reactivity of the sulfilimine complexes showed that some of the sulfilimine complexes were the intermediates in the imido migration to the Cp ring (PR_3 = PPh_3, $P(OPh)_3$, $P(p\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4Cl)_3$). The basicities (or nucleophilicities) of PR_3 were important parameters for the imido migration. Sulfilimine complexes containing strongly nucleophilic PR_3 ligands (PR_3 = $P(p\text{-}C_6H_4OMe)_3$, PBu_3, $P(OMe)_3$) did not undergo migration of the imido group. In the formation of the disubstituted Cp complex [{C_5H_3(NTs)(PR_3)}Co{$S_2C_2(COOMe)_2$}], the basicity (or nucleophilicity) of PR_3 ligands is also an important parameter (PR_3 = PPh_3, $P(p\text{-}C_6H_4Me)_3$).

Introduction

The metalladithiolene ring,[1] which consists of one metal, two sulfur atoms, and two unsaturated carbon atoms, exhibits both aromaticity and unsaturation. Electrophilic and radical substitution reactions[2] due to the aromaticity of the metalladithiolene ring have been reported. This metal chelate ring has six delocalized π electrons and has $\pi-\pi^*$ transitions in the visible and near-IR regions.[3]

The metalladithiolene ring shows unsaturation when the metal in the ring is coordinatively unsaturated. Thus, addition reactions often occur between the metal and the sulfur bond. We have reported the addition reactions of cyclopentadienyl (Cp) metalladithiolene complexes [$CpM(S_2C_2Z_2)$] (M = Co, Rh).[4−7] The reactions of the Cp metalladithiolene complexes with diazo compounds ($R^1R^2CN_2$) and tetracyanoethylene oxide (TCNEO) yield alkylidene-bridged metalladithiolene adducts.[4] The corresponding alkene-[5] and norbornene-bridged[6] adducts can be obtained by reactions with alkyne and quadricyclane, respectively. Furthermore, imido-bridged adducts are formed by reaction with (*N*-tosylimino)phenyliodinane (PhI═NTs) or sulfonyl azides.[7] Recently, *o*-carboranedithiolato complexes have been

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(1) Reviews: (a) Schrauzer, G. N. *Acc. Chem. Res.* **1969**, *2*, 72. (b) McCleverty, J. A. *Prog. Inorg. Chem.* **1969**, *10*, 49. (c) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303. (d) Kisch, H. *Coord. Chem. Rev.* **1993**, *125*, 155.

(2) (a) Kajitani, M.; Hagino, G.; Tamada, M.; Fujita, T.; Sakurada, M.; Akiyama, T.; Sugimori, A. *J. Am. Chem. Soc.* **1996**, *118*, 489. (b) Sugimori, A.; Tachiya, N.; Kajitani, M.; Akiyama, T. *Organometallics* **1996**, *15*, 5664. (c) Sugimori, A.; Akiyama, T.; Kajitani, M.; Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 879.

(3) Schrauzer, G. N.; Meyweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 1483.

(4) (a) Kajitani, M.; Sakurada, M.; Dohki, K.; Suetsugu, T.; Akiyama, T.; Sugimori, A. *J. Chem. Soc., Chem. Commun.* **1990**, 19. (b) Sakurada, M.; Kajitani, M.; Dohki, K.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *423*, 144. (c) Kajitani, M.; Kawakita, F.; Chikuma, E.; Sakurada, M.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1995**, 85. (d) Takayama, C.; Sakamoto, N.; Harada, T.; Kajitani, M.; Sugiyama, T.; Akiyama, T.; Sugimori, A. *Organometallics* **1996**, *15*, 5077. (e) Takayama, C.; Kajitani, M.; Sugiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1998**, *563*, 161. (f) Takayama, C.; Kajitani, M.; Sugiyama, T.; Sugimori, A. *Chem. Lett.* **1998**, 241.

(5) (a) Kajitani, M.; Suetsugu, T.; Wakabayashi, R.; Igarashi, A.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1985**, *293*, C15. (b) Kajitani, M.; Hisamatsu, N.; Takehara, M.; Mori, Y.; Sugiyama, T.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1994**, 473. (c) Kajitani, M.; Suetsugu, T.; Takagi, T.; Akiyama, T.; Sugimori, A.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1995**, *487*, C8.

(6) (a) Kajitani, M.; Eguchi, Y.; Abe, R.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1990**, 359. (b) Kajitani, M.; Hatano, H.; Fujita, T.; Okumachi, T.; Nagao, H.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *430*, C64.

(7) Nomura, M.; Yagisawa, T.; Takayama, C.; Sugiyama, T.; Yokoyama, Y.; Shimizu, K.; Sugimori, A.; Kajitani, M. *J. Organomet. Chem.* **2000**, *611*, 376.

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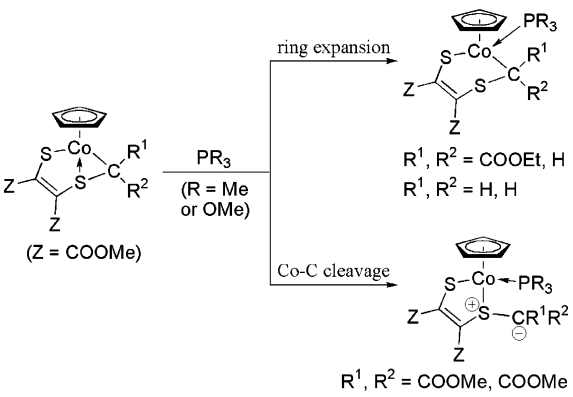
Scheme 1



developed, and various addition and isomerization reactions have been reported by Kang[8] and by Herberhold et al.[9]

We have studied the reactivities of metalladithiolene adducts: the alkylidene-, alkene-, norbornene-, and imido-bridged adducts dissociate by thermal, photochemical, and electrochemical redox reactions,[4−7] and the corresponding original metalladithiolene complexes are regenerated. We have also developed a novel reaction between the metalladithiolene adducts with nucleophiles. For example, the reaction of the alkylidene-bridged adduct with PR_3 undergoes two types of structural changes[10] (Scheme 1). One is the ring expansion of the five-membered metalladithiolene ring to form a six-membered ring by the nucleophilic attack of PR_3 at the metal. The other reaction is metal−carbon bond cleavage to form a sulfonium ylide structure. In addition, both complexes undergo redox-induced structural changes.[11]

Recently, we have continued the study of the imido-bridged adduct [CpCo{$S_2C_2(COOMe)_2$}(NTs)] (**1**). Complex **1** reacts with PR_3 to form complexes having a sulfilimine structure, CpCo[S(NTs)$SC_2(COOMe)_2$](PR_3) (PR_3 = PPh_3 (**2a**), $P(OPh)_3$ (**2b**)), by metal−nitrogen bond cleavage[7,12] (Scheme 2). We have new investigated the effects of the basicities and the cone angles[13] of PR_3 ligands on the electrochemical behavior of the sulfilimine complexes.

We have found that the sulfilimine complexes **2a** and **2b** are intermediates in the novel imido migration reaction to the Cp ring[7,12] (Scheme 2). The migration of a monodentate ligand from the central transition metal to the Cp ring can be classified into four main categories: (1) base-induced migration from the metal to the Cp ring;[14−17] (2) migration by ligand(metal)/H(Cp) exchange;[18] (3) migratory insertion into the C−H bond of the Cp ring;[19] (4) ligand migration to the Cp ring induced by a photoreaction.[20] Our work belongs in the third category. These four types of migrations may find use in the generation of functionally substituted Cp ligands. The effects of the basicities and the cone angles[13] of phosphine and phosphite in the imido migration reaction shown in Scheme 2 have been examined.

Results and Discussion

1. Preparations and Spectroscopic Properties of the Sulfilimine Complexes. The imido-bridged adduct **1** was prepared from the cobaltadithiolene complex [CpCo{$S_2C_2(COOMe)_2$}] (**5**) by reaction with tosyl azide.[7] When complex **1** reacted with 2 equiv of PR_3 in dichloromethane at room temperature, the solution color rapidly changed from green to brown. The sulfilimine complexes CpCo[S(NTs)$SC_2(COOMe)_2$](PR_3) (**2c**−**h**) were

(8) (a) Kim, D.-H.; Ko, J.; Park, K.; Cho, S.; Kang, S. O. *Organometallics* **1999**, *18*, 2738. (b) Bae, J.-Y.; Park, Y.-I.; Ko, J.; Park, K.-I.; Cho, S.; Kang, S. O. *Inorg. Chim. Acta* **1999**, *289*, 141. (c) Bae, J.-Y.; Lee, Y.-J.; Kim, S.-J.; Ko, J.; Cho, S.; Kang, S. O. *Organometallics* **2000**, *19*, 1514. (d) Won, J.-H.; Lim, H.-G.; Kim, B. Y.; Lee, J.-D.; Lee, C.; Lee, Y.-J.; Cho, S.; Ko, J.; Kang, S. O. *Organometallics* **2002**, *21*, 5703.

(9) (a) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **2000**, *604*, 170. (b) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Chem. Soc., Dalton Trans.* **2001**, 1782. (c) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem. Eur. J.* **2002**, *8*, 388.

(10) Takayama, C.; Takeuchi, K.; Ohkoshi, S.; Janairo, G. C.; Sugiyama, T.; Kajitani, M.; Sugimori, A. *Organometallics* **1999**, *18*, 2843.

(11) (a) Takayama, C.; Kajitani, M.; Sugiyama, T.; Akiyama, T.; Shimizu, K.; Sugimori, A. *Organometallics* **1997**, *16*, 3498. (b) Takayama, C.; Takeuchi, K.; Ohkoshi, S.; Kajitani, M.; Sugimori, A. *Organometallics* **1999**, *18*, 4032.

(12) Nomura, M.; Takayama, C.; Janairo, G. C.; Sugiyama, T.; Yokoyama, Y.; Kajitani, M. *Organometallics* **2003**, *22*, 195.

(13) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956. (b) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953. (c) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (c) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981. (d) Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758 and references therein.

(14) (a) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194. (b) Heah, P. H.; Gladysz, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 7636. (c) Abbott, S.; Baird, G. J.; Davies, S. G.; Dordor-Hedgecock, I. M.; Maberly, T. R.; Walker, J. C.; Warner, P. *J. Organomet. Chem.* **1985**, *289*, C13. (d) Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185. (e) Akita, M.; Kondoh, A. *J. Organomet. Chem.* **1986**, *299*, 369. (f) Melletti, M. C.; Fenske, R. F. *Organometallics* **1989**, *8*, 420. (g) Liu, L.-K.; Chang, K.-Y.; Wen, Y.-S. *J. Chem. Soc., Dalton Trans.* **1998**, 741. (h) Berryhill, S. R.; Sharenow, B. *J. Organomet. Chem.* **1981**, *221*, 143. (i) Thum, G.; Ries, W.; Greissinger, D.; Malisch, W. *J. Organomet. Chem.* **1983**, *252*, C67. (j) Berryhill, S. R.; Clevenger, G. L.; Burdurlu, F. Y. *Organometallics* **1985**, *4*, 1509. (k) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (l) Pasman, P.; Snel, J. J. M. *J. Organomet. Chem.* **1986**, *301*, 329. (m) Pannell, K. H.; Vicenti, S. P.; Scott, R. C., III. *Organometallics* **1987**, *6*, 1593. (n) Crocco, G. L.; Young, C. S.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1988**, *7*, 2158. (o) Pannell, K. H.; Rozell, J. M.; Lii, J.; Tien-Mayr, S.-Y. *Organometallics* **1988**, *7*, 2524. (p) Pannell, K. H.; Cervantes, J.; Parkanyi, L.; Cervantes-Lee, F. *Organometallics* **1990**, *9*, 859. (q) Sharma, S.; Cervantes, J.; Mata-Mata, J. L.; Brun, M.-C.; Cervantes-Lee, F.; Pannell, K. H. *Organometallics* **1995**, *14*, 4269. (r) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875. (s) Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1061. (t) Cervantes, J.; Vicenti, S. P.; Kappor, R. N.; Pannell, K. H. *Organometallics* **1989**, *8*, 744.

(15) (a) Davis, S. G.; Felkin, H.; Watts, O. *J. Chem. Soc., Chem. Commun.* **1980**, 159. (b) Merrifield, J. H.; Gladysz, J. A. *Organometallics* **1983**, *2*, 782. (c) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 283. (d) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110.

(16) (a) Nakazawa, H.; Sone, M.; Miyoshi, K. *Organometallics* **1989**, *8*, 1564. (b) Kubo, K.; Nakazawa, H.; Kawamura, K.; Mizuta, T.; Miyoshi, K. *J. Am. Chem. Soc.* **1998**, *120*, 6715. (c) Nakazawa, H.; Kawamura, K.; Kubo, K.; Miyoshi, K. *Organometallics* **1999**, *18*, 4518.

(17) Pannell, K.; Castillo-Ramirez, J.; Cervantes-Lee, F. *Organometallics* **1992**, *11*, 3139.

(18) (a) Baya, M.; Crochet, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 240. (b) Ortmann, D. A.; Weberndörfer, B.; Schöneboom, J.; Werner, H. *Organometallics* **1999**, *18*, 952. (c) Ortmann, D. A.; Weberndörfer, B.; Ilg, K.; Laubender, M.; Werner, H. *Organometallics* **2002**, *21*, 2369. (d) Herber, U.; Bleuel, E.; Gevert, O.; Laubender, M.; Werner, H. *Organometallics* **1998**, *17*, 10. (e) Hofmann, W.; Buchner, W.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 795. (f) Werner, H.; Hofmann, W. *Chem. Ber.* **1981**, *114*, 2681.

(19) (a) Bleuel, E.; Laubender, M.; Weberndörfer, B.; Werner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 156. (b) Hubbard, J. L.; McVicar, W. K. *J. Am. Chem. Soc.* **1986**, *108*, 6422.

(20) (a) Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694. (b) Carpenter, N. E.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1999**, *18*, 1569.

Scheme 2

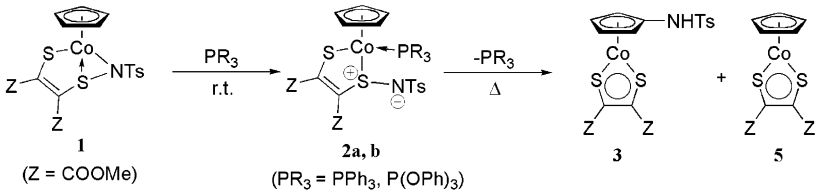


Table 1. Yields and Spectroscopic Data of the Sulfilimine Complexes $CpCo[S(NTs)SC_2(COOMe)_2](PR_3)$ (2a−h)

				^{31}P NMR (δ/ppm)	
complex	PR_3	yield/%	IR (ν_{S-N}/cm^{-1})	complex	corresponding free P ligand
2a	PPh_3	95[a]	922	35.2	−5.0
2b	$P(OPh)_3$	80[b]	932[b]	126.6	128.4[b]
2c	$P(p\text{-}C_6H_4Me)_3$	96	920	33.2	−7.6
2d	$P(p\text{-}C_6H_4Cl)_3$	95	922	35.6	−7.9
2e	PCy_3	90	932	32.5	11.9
2f	$P(p\text{-}C_6H_4OMe)_3$	98	935	32.0	−9.7
2g	PBu_3	92	928	49.4	−30.3
2h	$P(OMe)_3$	95	932	122.8	141.5

[a] Reference 7. [b] Reference 12.

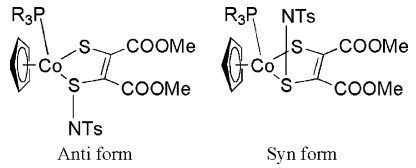


Figure 1.

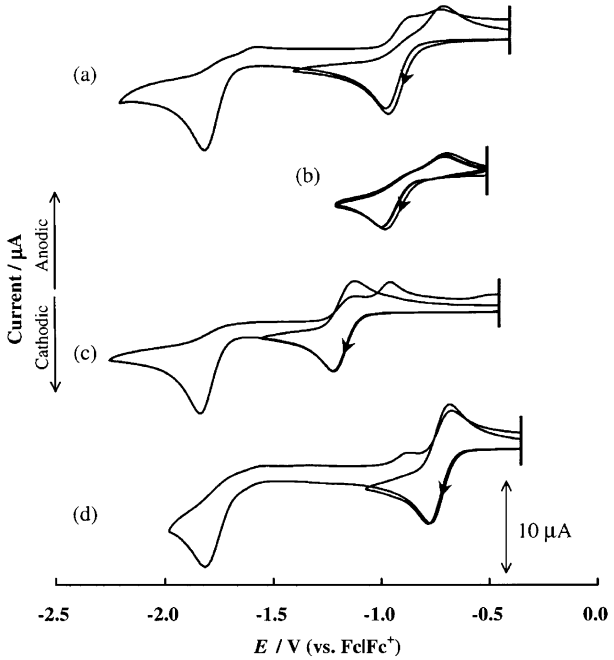


Figure 2. Cyclic voltammograms (ν = 100 mV s^{-1}, Φ = 1.6 mm Pt disk, concentration of sample 1 mM): (a) complex **2a**; (b) multiple scan of the one-electron reduction process of complex **2a**; (c) complex **2g**; (d) complex **1**.[7]

separated by column chromatography and obtained as brown solids in nearly quantitative yield (Table 1). Complexes **2a**,**b** have already been characterized.[7,12] In this work, analogous PR_3 complexes **2c**−**h** were identified by spectroscopic data. Although the purities of complexes **2c**−**h** were confirmed by ^{1}H NMR spectra, the PBu_3 complex **2g** and the $P(OMe)_3$ complex **2h** were found to exist as isomers (see the Supporting Information). We have found two types of isomers in such complexes. One is that in which the phosphite ligand and the alkylidene group are located at opposite sides of the cobaltadithiolene ring (anti form[10]), and the other is the complex of syn form.[12] Also in this case, we propose that the two isomers are syn and anti ones (Figure 1). Our elemental analyses of complexes **2c**−**h** failed because these complexes were thermally unstable or air-sensitive. The IR spectra of complexes **2a**−**h** showed two different signals around 1700 cm^{-1} attributed to the C═O stretching vibrations of the cobaltadithiolene substituents; signals around 920−930 cm^{-1} attributed to the S^+-N^- stretching vibrations also appeared (Table 1). Two different C═O signals indicate that the imido group is attached to the sulfur atom of the cobaltadithiolene ring. The latter values are similar to those for the S^+-N^- stretching vibration of a typical sulfilimine compound.[21] These results suggest that the ring opening of the cobaltathiaziridine ring was induced by the nucleophilic attack of PR_3 at the cobalt atom of complex **1**. (In the present paper, the three-membered ring consisting of Co, N, and S is described as a cobaltathiaziridine ring.) The ^{31}P NMR signals of complexes **2a**−**h** showed two trends: the δ values of the phosphine complexes **2a** and **2c**−**g** were shifted more downfield than those of the corresponding free phosphines; the δ values of the phosphite complexes **2b**[12] and **2h** were shifted more upfield than those of the corresponding free phosphites (Table 1). These tendencies have also been found in the PR_3 adducts of cobaltadithiolene complexes, $[CpCo(S_2C_2X_2)(PR_3)]$.[22]

2. Electrochemical Behavior of the Sulfilimine Complexes. In situ CV measurements of the reaction mixtures of complex **1** with PR_3 (1 equiv excess) were performed, because complexes **2a**−**h** were thermally unstable and air-sensitive. It was confirmed that complexes **2a**−**h** were quantitatively formed by in situ ^{1}H NMR spectra of the mixtures. The CVs of complexes **2a** and **2g** are shown in Figure 2a−c, and the CV of complex **1**[7] is also shown in Figure 2d for a comparison. The reduction potential data for the complexes and the reversibility of the reaction are shown in Table 2. The CV of complex **2a** showed two irreversible reduction waves at −0.93 and −1.79 V, respectively (Figure 2a). The first reduction potential of complex **2a** was more negative than that of complex **1**, and the second one was almost identical with that of complex **1** (Figure 2d). In

(21) (a) Kucsman, A.; Ruff, F.; Kapovits, I. *Tetrahedron* **1966**, *22*, 1575. (b) Tsujihara, K.; Furukawa, N.; Oae, S. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2153.

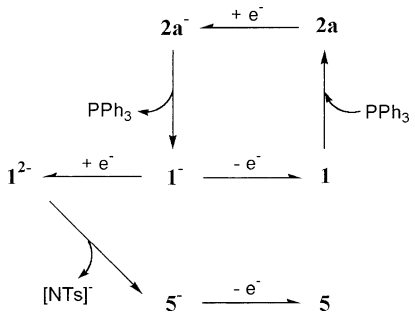
(22) Kajitani, M.; Igarashi, A.; Hatano, H.; Akiyama, T.; Sugimori, A.; Matsumoto, S.; Iguchi, Y.; Boennemann, H.; Shimizu, K.; Satô, G. P. *J. Organomet. Chem.* **1995**, *485*, 31.

Table 2. Reduction Potentials (vs $Fc|Fc^+$) of the Sulfilimine Complexes 2a−h[a]

	first redn			second redn	
complex	$E_{1/2}$/V	ΔE/mV	ΔE_p/mV	$E_{1/2}$/V	ΔE/mV
2a	−0.93[ir]	76		−1.79[ir]	70
2b	−0.83[ir]	118		−1.80[ir]	82
2c	−1.04[ir]	92		−1.83[ir]	80
2d	−0.88[ir]	72		−1.81[ir]	80
2e	−1.10[ir]	80		−1.82[ir]	70
2f	−1.04[ir]	80		−1.80[ir]	68
2g	−1.19[r]	70	98	−1.98[ir]	72
2h	−1.04[r]	74	134	−1.79[ir]	82
1[b]	−0.79[r]	68	90	−1.80[ir]	78

[a] Definitions: 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] Reference 7.

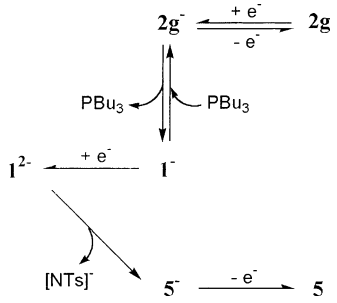
Scheme 3



addition, two reoxidation waves due to a reaction product appeared around −0.80 and −0.90 V. The former reoxidation wave appeared after the first reduction, and the latter reoxidation wave appeared after the second reduction. These reoxidation waves corresponded to the waves of **1**/**1**$^-$ and **5**/**5**$^-$ couples, respectively.

The following reduction behavior can thus be speculated: (1) The electron density of the reduction site of complex **2a** has increased more than that of complex **1**. (2) Anion **1**$^-$ was formed by the elimination of PPh_3 from the reductant **2a**$^-$. Therefore, as soon as PPh_3 is eliminated from the reductant **2a**$^-$, the cobaltathiaziridine ring is re-produced by the Co−N bond re-formation. We have also reported such a reversible Co−N bond cleavage and re-formation between complex **1** and its protic acid adduct $[CpCo\{S_2C_2(COOMe)_2\}(Cl)(NHTs)]$.[7] However, the rereduction wave of complex **1** did not appear in the multiple CV scan (Figure 2b). This result suggests that complex **2a** was re-formed by PPh_3 present at close range to the electrode as soon as the neutral complex **1** was re-formed. These electrode reactions (ECEC reactions) can be described as an electrochemical square scheme.[23] (3) When anion **1**$^-$ formed by the reduction of complex **2a** was further reduced, the imido group was eliminated to form anion **5**$^-$. This behavior has also been observed in the second reduction of complex **1**.[7] The electrochemical behavior of complex **2a** is summarized in Scheme 3. The electrochemical behavior of complexes **2b**−**f** was similar to that of complex **2a**.

Scheme 4



The CV of complex **2g** showed a reversible reduction wave at −1.19 V and an irreversible reduction wave at −1.81 V (Table 2 and Figure 2c). The first reduction potential of complex **2g** was more negative than that of complex **1**, and the second reduction potential corresponded to that of complex **1**. The first reduction and reoxidation responses of complex **2g** are different from those of complexes **2a**−**f**. This result suggests that anion **2g**$^-$ is stable on the CV time scale; therefore, the PBu_3 ligand of complex **2g** is difficult to eliminate by a one-electron reduction. However, the second reduction wave due to the **1**$^-$/**1**$^{2-}$ couple (−1.81 V) indicates the formation of anion **1**$^-$ by the elimination of PBu_3. Therefore, anions **2g**$^-$ and **1**$^-$ both coexist in an equilibrium state (Scheme 4). Likewise, after a second reduction, the reoxidation wave attributed to the wave of the **5**/**5**$^-$ couple appeared around −0.90 V. This result suggests the elimination of the imido group by a second reduction. The electrochemical behavior of complex **2g** is summarized in Scheme 4. Complex **2h** showed electrochemical behavior similar to that of complex **2g**. Therefore, $P(OMe)_3$ of complex **2h** is also difficult to eliminate.

The lifetimes of the reductants of complexes **2a**−**h** can be explained by the basicity and the cone angle[13] of the PR_3 ligand. In the case of PR_3 having stronger basicity (or nucleophilicity), the Co−P bond of the sulfilimine complex becomes stronger and the lifetime of the reductant becomes longer (e.g. the lifetimes of reductant: PPh_3 complex **2a** < PBu_3 complex **2g**; $P(OPh)_3$ complex **2b** < $P(OMe)_3$ complex **2h**). Although PCy_3 has stronger basicity than PBu_3, the lifetime of the reductant of complex **2e** is shorter than that of complex **2g**. The difference in the value of cone angle means there is some steric hindrance between the complex and PCy_3.

In situ measurements of visible absorption spectra during electrolysis were performed using an optically transparent thin-layer electrode cell (OTTLE). When complex **2a** was reduced at −1.40 V, the absorption band around 490 nm was decreased, and two isosbestic points appeared around 395 and 435 nm (Figure 3a). Spectral changes stopped after 2 min, and the final spectrum corresponded to that of anion **1**$^-$ previously reported.[7] When anion **1**$^-$ was reoxidized at −0.20 V, the absorption spectrum reverted to that of complex **2a** (Figure 3b). This result also supports the electrochemical square scheme shown in Scheme 3. In addition, when a second reduction was performed at −2.20 V (Figure 3c) and the sample was then reoxidized at −0.90 V, an absorption band appeared around 550 nm (Figure 3d). This absorp-

(23) (a) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779. (b) Bernardo, M. M.; Robant, P. V.; Schroeder, R. R.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 1224. (c) Bond, A. M.; Colton, R.; Mann, T. F. *Organometallics* **1988**, *7*, 2224. (d) Tsintavis, C.; Li, H.-L.; Chambers, J. Q. *J. Phys. Chem.* **1991**, *95*, 289. (e) Richards, T. C.; Geiger, W. E. *J. Am. Chem. Soc.* **1994**, *116*, 2028. (f) Connelly, N. G.; Geiger, W. E.; Lagunas, M. C.; Metz, B.; Rieger, A. L.; Rieger, P. H.; Shaw, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 12202.

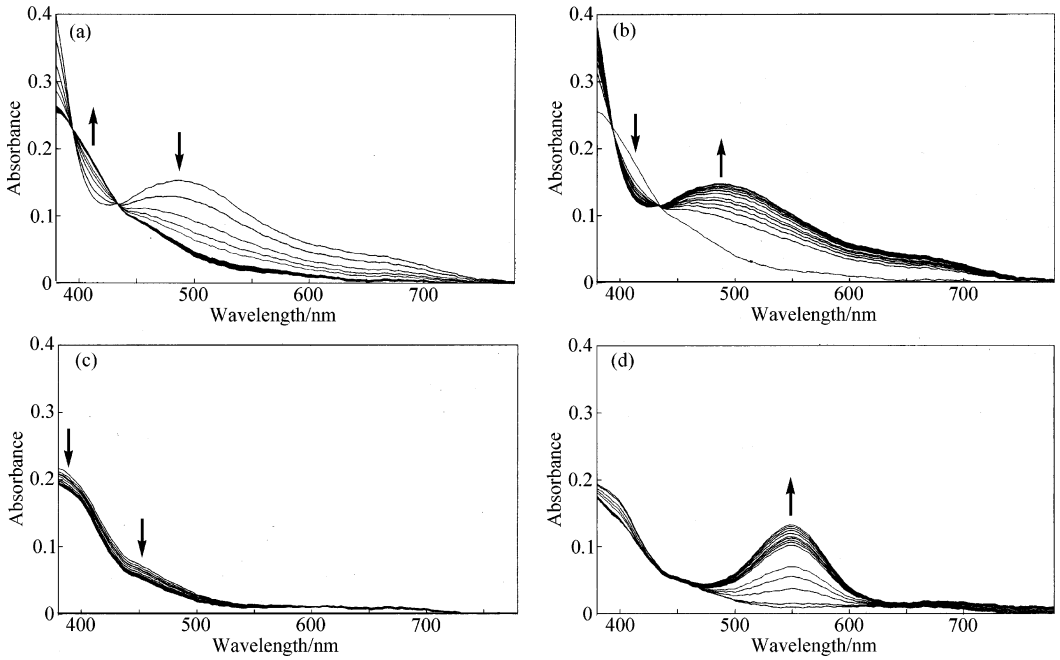


Figure 3. Visible spectral changes of complex **2a**: (a) first reduction (−1.40 V, sampling time 30 s, sampling interval 2 s); (b) reoxidation (−0.20 V, sampling time 30 s, sampling interval 2 s) after first reduction; (c) second reduction (−2.20 V, sampling time 30 s, sampling interval 2 s) after first reduction; (d) reoxidation (−0.90 V, sampling time 30 s, sampling interval 2 s) after second reduction.

Table 3. Reactions of the Imido-Bridged Cobaltadithiolene Complex 1 with 2 Equiv of PR_3 in Refluxing Benzene

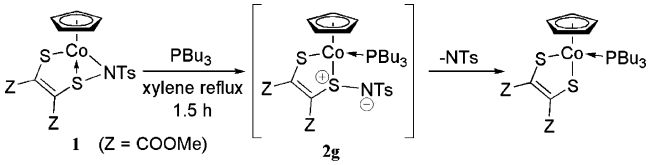
PR_3	basicity[b] (pK_a)	cone angle/ deg	time/h	yield/% 3	2a−h	5
PPh_3[a]	2.73	145	5	44	0	35
$P(p\text{-}C_6H_4Me)_3$	3.84	145	5	36	0	34
$P(p\text{-}C_6H_4Cl)_3$	1.03	145	5	35	0	48
$P(p\text{-}C_6H_4OMe)_3$	4.59	145	5	0	0	31
PBu_3	8.43	136	5	0	95	0
PCy_3	9.70	170	5	0	0	80
$P(OPh)_3$	−2.00	128	45	27	0	62
$P(OMe)_3$	2.60	107	5	0	20	55

[a] Reference 7. [b] The Brønsted basicities of the phosphorus(III) compounds (pK_a values of R_3PH^+).

tion band corresponds to that of $[CpCo\{S_2C_2(COOMe)_2\}]$ (**5**).[24] The yield of complex **5** based on the spectral changes was 50%. These spectroelectrochemical data support our speculation based on the CV data of complex **2a**.

3. Reactivities of the Sulfilimine Complexes: Migration Reactions to the Cp Ring. The reactions of complex **1** with 2 equiv of PR_3 were attempted with heating. In these reactions, the sulfilimine complexes are first formed. The products, yields, basicities, and cone angles[13] of PR_3 are shown in Table 3. The reaction of complex **1** with PPh_3 or $P(OPh)_3$ has been previously reported to give the amide-substituted Cp complex $[(C_5H_4\text{-}NHTs)Co\{S_2C_2(COOMe)_2\}]$ (**3**)[7,12] as a migration product and complex **5** (Scheme 2). In this work, complex **1** reacted with 2 equiv of $P(p\text{-}C_6H_4Me)_3$ or $P(p\text{-}C_6H_4Cl)_3$ in refluxing benzene to also give complex **3** in 36% or 35% yield, respectively (Scheme 2 and Table 3). In the reaction of complex **1** with PBu_3 in refluxing benzene, the corresponding sulfilimine complex **2g** was isolated in quantitative yield. This result, similar to the result of the reaction at room temperature (Table 1), suggests that complex **2g** is thermally stable at 80 °C. In addition, although $P(p\text{-}C_6H_4OMe)_3$ reacted with complex **1** under the same conditions, only complex **5** was formed (Table 3). $P(C_6F_5)_3$ did not react with complex **1** because of its low nucleophilicity.

Scheme 5

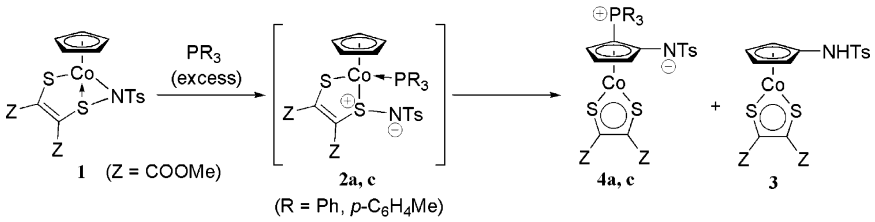


We assume that the imido migration is also influenced by the basicities of the PR_3 ligands. In the case of PR_3 having stronger basicity (or nucleophilicity), the Co−P bond also becomes thermally stable. As a result, the imido group is eliminated due to the S−N bond cleavage before the Co−P bond can cleave. We assume that the imido elimination from the sulfilimine complex **2** prevents the imido migration to the Cp ring, because this migration is intramolecular.[12] For the imido migration, the Co−P bond cleavage may conceivably occur before the S−N bond cleavage, or both bond cleavages may be simultaneous. In the reaction of complex **2g** under refluxing xylene, this reaction only gave $[CpCo\{S_2C_2(COOMe)_2\}(PBu_3)]$ due to the only S−N bond cleavage in 80% yield (Scheme 5). This reaction also supports that the Co−P bond cleaves first for the imido migration. The bond strength of the Co−P bond was also examined by the electrochemistry of complexes **2a**−**h** in this work. We conclude that the basicity (or nucleophilicity) of PR_3 is one of the important parameters for the imido migration.

Werner et al. have proposed a mechanism for the migratory insertion of a carbene ligand into the C−H

(24) Kajitani, M.; Suetsugu, T.; Wakabayashi, R.; Igarashi, A.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1985**, *293*, C15.

Scheme 6



bond of the Cp ring.[18d] Their report says that the reaction of [CpRh(=CPh_2)(P*i*Pr_3)] with PF_3 gives [(C_5H_4-$CHPh_2$)Rh(P*i*Pr_3)(PF_3)] as a migration product. Ligand displacement reactions of [$CpRhL_2$] with Lewis bases L′ are known to follow second-order kinetics.[25] A reasonable assumption is that a labile 1:1 adduct is formed from [CpRh(=CPh_2)(P*i*Pr_3)] and PF_3. A slippage of the carbene ligand to the temporarily generated η^3-C_5H_5 unit affords the migration product [(C_5H_4–$CHPh_2$)Rh(P*i*-Pr_3)(PF_3)]. We assume that the mechanism of the imido migration is similar to that of this carbene migration via a η^3-C_5H_5 intermediate.

The reaction of complex **1** with PCy_3 under refluxing benzene gave only complex **5** in good yield (Table 3). Although PCy_3 is as basic as PBu_3, the cone angle of PCy_3 ($\theta = 170°$) is larger than that of PBu_3 ($\theta = 136°$). The cone angle of a phosphorus ligand is related to the stability of the sulfilimine complex rather than to the imido migration. On the other hand, trimesitylphosphine, $P(C_6H_2Me_3)_3$, which has a larger cone angle ($\theta =$ 212°) than that of PCy_3, did not react with complex **1** due to steric hindrance.

We also attempted the reactions of complex **1** with other trivalent ligands, such as phosphite, amine, arsine, and stibine. Although the reaction of complex **1** with $P(OMe)_3$ did not form the migration product **3** under refluxing benzene, the sulfilimine complexes **2h** and **5** were obtained (Table 3). The sulfilimine complex **2h** was thermally more stable than complex **2a**, although $P(OMe)_3$ has a basicity similar to that of PPh_3. We assume that the bond pattern of a phosphite ligand with the cobalt is different from that of a phosphine ligand. This suggestion is supported by the δ value shifts of ^{31}P NMR spectra of complexes **2a**−**h** (see Table 1). The difference can be explained by the difference in back-donation from cobalt to the phosphorus ligand. On the other hand, NEt_3, NPh_3, $AsPh_3$, and $SbPh_3$ did not react with complex **1**. These results indicate that complex **1** only reacts with a trivalent phosphorus compound.

According to our previous report, the reaction of complex **1** with a large excess of PPh_3 with heating gave not only complex **3** but also the disubstituted Cp complex [{C_5H_3(NTs)(PPh_3)}Co{S_2C_2($COOMe)_2$}] (**4a**)[12] (Scheme 6). The reactions of complex **1** with various amounts of PPh_3 were examined (Table 4). Although a larger amount of PPh_3 gave a higher yield of complex **4a** than did 1 equiv of PPh_3, a lower yield of complex **3** was obtained than when 1 equiv of PPh_3 was used. The reaction of complex **1** with 1 equiv of PPh_3 gave complex **3** and did not give complex **4a**. In the reaction of complex **1** with 0.5 equiv of PPh_3, the reaction rate became slower and a lower yield of complex **3** was obtained. Therefore, 1 equiv of PPh_3 is necessary to obtain complex **3** efficiently, and a large excess of PPh_3 efficiently gives complex **4a**.

Table 4. Reactions of Imido-Bridged Cobaltadithiolene Complex 1 with Various Amounts of PR_3 in Refluxing Benzene

			yield/%			
PR_3	amt/equiv	time/h	**4**	**3**	**2a**,**c**,**d**	**5**
PPh_3[a]	2	5	trace	44	0	35
PPh_3	1	5	0	44	0	31
PPh_3	0.5	5	0	31	28	29
PPh_3	0.5	18	0	36	0	47
PPh_3	0.2	5	0	trace	20	trace
PPh_3	0.2	18	0	3	0	58
PPh_3	5	5	12	42	0	34
PPh_3	10	5	17	29	0	34
$P(p\text{-}C_6H_4Me)_3$	2	5	trace	36	0	34
$P(p\text{-}C_6H_4Me)_3$	10	5	18	34	0	15
$P(p\text{-}C_6H_4Cl)_3$	2	5	0	35	0	48
$P(p\text{-}C_6H_4Cl)_3$	10	5	0	37	0	38

[a] Reference 7.

The effects of various phosphines were examined in the formation of the disubstituted Cp complex **4**. The reactions of complex **1** with a large excess of $P(p\text{-}C_6H_4OMe)_3$ or PBu_3 did not form complexes **3** and **4**, and finally results similar to those shown in Table 3 were obtained. The reaction of complex **1** with 10 equiv of $P(p\text{-}C_6H_4Me)_3$ gave complex **3** and the corresponding disubstituted Cp complex [{C_5H_3(NTs)($P(p\text{-}C_6H_4Me)_3$)}-Co{$S_2C_2(COOMe)_2$}] (**4c**). However, a large excess of $P(p\text{-}C_6H_4Cl)_3$ only gave complex **3**, and the disubstituted Cp complex was not formed (Table 4). These results suggest that the basicity (or nucleophilicity) of phosphine is also one of the important parameters in the formation of the disubstituted Cp complex. According to a similar procedure, the NMs- and PPh_3-substituted Cp complex [{C_5H_3(NMs)(PPh_3)}Co{$S_2C_2(COOMe)_2$}] (**4a′**) was synthesized by the reaction of the imido adduct [Cp Co{$S_2C_2(COOMe)_2$}(NMs)][7] with a large excess of PPh_3. The ^{31}P NMR signals of complexes **4a′** and **4c** appeared at 23.0 and 23.3 ppm, respectively. These ^{31}P NMR signals are similar to those of a typical phosphonium salt ($PPh_4^+I^-$, 22.0 ppm) and complex **4a** (23.4 ppm) previously reported.[12] This result suggests that complexes **4a′** and **4c** also have a triarylphosphonium cyclopentadienyl ligand.[26]

Conclusions

The imido-bridged cobaltadithiolene adduct **1** reacts with PPh_3 and $P(OPh)_3$ to give the sulfilimine complexes

(25) (a) Basolo, F. *Inorg. Chim. Acta* **1985**, *100*, 33. (b) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908.

(26) (a) Tresoldi, G.; Recca, A. Finocchiaro, P.; Faraone, F. *Inorg. Chem.* **1981**, *20*, 3103. (b) Watanabe, M.; Sato, M.; Takayama, T. *Organometallics* **1999**, *18*, 5201.

$CpCo[S(NTs)SC_2(COOMe)_2](PR_3)$ (PR_3 = PPh_3 (**2a**), $P(OPh)_3$ (**2b**)) at room temperature, and these complexes undergo the imido migration to the Cp ring when heated.[7,12] In this work, the reactions of complex **1** with other PR_3 species quantitatively gave the corresponding sulfilimine complexes **2c**−**h** at room temperature. However, these sulfilimine complexes **2c**−**h** were not always intermediates in the imido migration. The imido migration was influenced by the basicities (nucleophilicities) of PR_3 ligands. Sulfilimine complexes containing strongly nucleophilic PR_3 ligands (e.g. $PR_3 = PBu_3$) were thermally stable because of the strong Co−P bond, and the nonelimination of PR_3 ligands prevents the imido migration. In the case of PR_3 having weaker basicity (e.g. $PR_3 = P(C_6F_5)_3$), the sulfilimine complex was not formed, due to its low nucleophilicity. The phosphines having $pK_a = 1.03-3.84$ (PR_3 = PPh_3, $P(p\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4Cl)_3$) were required in the imido migration. In addition, the cone angles of phosphines were only correlated with the thermal stability of the sulfilimine complex.

The elimination of PR_3 was confirmed by the investigation of the electrochemical behavior of the sulfilimine complexes **2a**−**h**. The sulfilimine complexes **2a**−**h** showed two opposite trends in a first reduction process. One is the elimination of a PR_3 ligand by the first reduction of the sulfilimine complexes (PR_3 = PPh_3, $P(OPh)_3$, $P(p\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4Cl)_3$, PCy_3, $P(p\text{-}C_6H_4OMe)_3$), and the other is the nonelimination of the PR_3 ligand; that is, the reductants of the sulfilimine complexes ($PR_3 = PBu_3$, $P(OMe)_3$) are stable. These trends revealed the different strengths of the Co−P bonds of the sulfilimine complexes. The basicities and the cone angles of PR_3 ligands also influenced the electrochemical behavior of the sulfilimine complexes.

In the formation of the disubstituted Cp complex, the amounts and the basicity values of phosphines were important parameters. A large excess of phosphine efficiently gave the disubstituted Cp complex. Only phosphines having $pK_a = 2.73-3.84$ (PR_3 = PPh_3, $P(p\text{-}C_6H_4Me)_3$) were required.

Experimental Section

All reactions were carried out under an argon atmosphere by means of standard Schlenk techniques. Solvents were purified by ketyl distillation before use. The phosphines and phosphites were used without further purification. The cobaltadithiolene complexes $[CpCo\{S_2C_2(COOMe)_2\}]$ (**5**) were prepared by literature methods.[27] Silica gel (Wakogel C-300) was obtained from Wako Pure Chemical Industries, Ltd. Thin-layer chromatography plates filled with silica gel 60 (20 × 20 cm, 0.25 mm thick) were obtained from Merck Japan Ltd. HPLC was performed on an LC-908 instrument produced by Japan Analytical Industry Co. Mass and IR spectra were recorded on JEOL JMS-D300 and Shimadzu FTIR 8600PC instruments, respectively. NMR spectra were measured with a JEOL LA500 spectrometer. UV−vis spectra were recorded on a Hitachi UV-2500PC instrument. Elemental analyses were determined by using a Shimadzu PE2400-II instrument. Melting points were measured on a Yanaco Micro melting point apparatus. All electrochemical measurements were performed under an argon atmosphere. Cyclic voltammograms were measured on a CV-50W instrument by BAS Co. Visible absorption spectra during electrolysis were measured on MCPD-7000 and MC-2530 instruments by Otsuka Electronics Co., Ltd.

Reactions of Complex 1 with PR_3 at Room Temperature. A solution of complex **1** (50 mg, 0.1 mmol) and PR_3 (0.2 mmol, PR_3 = $P(p\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4Cl)_3$, PCy_3, $P(p\text{-}C_6H_4OMe)_3$, PBu_3, $P(OMe)_3$) in dichloromethane (10 mL) was stirred at room temperature for 5 min. After the solvent was removed under reduced pressure, the residue was separated by column chromatography. Products **2c**−**h** were obtained as brown solids in quantitative yields. The yields of products are summarized in Table 1.

Reactions of Complex 1 with 2 Equiv of PR_3 with Heating. A solution of complex **1** (50 mg, 0.1 mmol) and PR_3 (0.2 mmol, PR_3 = $P(p\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4Cl)_3$, PCy_3, $P(p\text{-}C_6H_4OMe)_3$, PBu_3, $P(OMe)_3$) in benzene (10 mL) was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography. Product **3**[7,12] was obtained as a purple solid, and products **2f**−**h** were obtained as brown solids. The yields of products are summarized in Table 3.

Reactions of Complex 1 with Various Amounts of PR_3. A solution of complex **1** (50 mg, 0.1 mmol) and PR_3 (PR_3 = PPh_3, $P(p\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4Cl)_3$) in benzene (10 mL) was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was separated by thin-layer chromatography (silica gel 60) and then the product was further separated by HPLC. Products **4a** and **4c** were obtained as blue crystalline solids. In these reactions, complex **3**[7,12] was formed as a migration product and complex **5** was also formed. The yields of products are summarized in Table 4.

Complex **4a′** was synthesized by the reaction of $[CpCo\{S_2C_2(COOMe)_2\}(NMs)]$[7] with 10 equiv of PPh_3 under the same reaction conditions. The separation of complex **4a′** was also achieved by the same method, and product **4a′** was obtained as a blue crystalline solid in 25% yield. The amide-substituted Cp complex $[(C_5H_4\text{-}NHMs)Co\{S_2C_2(COOMe)_2\}]$[7] as a migration product and complex **5** were also obtained in 23% and 31% yields, respectively.

CV Measurements. CV measurements were done in 1 mmol dm^{-3} acetonitrile solutions of complexes 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.

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

$CpCo[S(NTs)SC_2(COOMe)_2][P(p\text{-}C_6H_4Me)_3]$ (2c). Mp: 134−135 °C dec. Mass (FAB^+, 70 eV): *m/z* 804 ($M^+ + 1$), 500 ($M^+ - P(p\text{-}C_6H_4Me)_3 + 1$). ^1H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.78 (d, J = 8.43 Hz, 2H, Ar), 7.56 (broad, 6H, Ar), 7.25 (broad, 6H, Ar), 7.18 (d, J = 8.43 Hz, 2H, Ar), 5.36 (s, 5H, Cp), 3.67 (s, 3H, OMe), 2.71 (s, 3H, OMe), 2.38 (s, 9H, Me), 2.37 (s, 3H, Me). ^{31}P NMR (200 MHz, $CDCl_3$, vs 85% H_3PO_4): δ 33.2 ($P(p\text{-}C_6H_4Me)_3$). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 495 (3400), 369 (11 000). IR (KBr disk; cm^{-1}): 1734, 1699, 1528, 1431, 1252, 1130, 1082, 920.

$CpCo[S(NTs)SC_2(COOMe)_2][P(p\text{-}C_6H_4Cl)_3]$ (2d). Mp: 121−122 °C dec. Mass (FAB^+, 70 eV; *m/z*): 866 ($M^+(^{37}Cl)$ +

(27) Boennemann, H.; Bogdanovic, B.; Brijoux W.; Brinkmann, R.; Kajitani, M.; Mynott, R.; Natarajan, G. S.; Samson, M. G. Y. Transition Metal-Catalyzed Synthesis of Heterocyclic Compounds. In *Catalysis in Organic Reactions*; Kosak, J. R., Ed.; Marcel Dekker: New York, 1984; pp 31−62.

1), 864 (M^+(^{35}Cl) + 1), 500 (M^+ − P(*p*-$C_6H_4Cl)_3$ + 1). ^{1}H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.73 (d, J = 8.28 Hz, 2H, Ar), 7.60 (broad, 6H, Ar), 7.46 (broad, 6H, Ar), 7.20 (d, J = 8.28 Hz, 2H, Ar), 5.41 (s, 5H, Cp), 3.68 (s, 3H, OMe), 2.79 (s, 3H, OMe), 2.38 (s, 3H, Me). ^{31}P NMR (200 MHz, $CDCl_3$, vs 85% H_3PO_4): δ 35.6 (P(*p*-$C_6H_4Cl)_3$). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 475 (2600), 369 (8300). IR (KBr disk; cm^{-1}): 1732, 1701, 1531, 1431, 1252, 1130, 1082, 922.

CpCo[S(NTs)SC$_2$(COOMe)$_2$](PCy$_3$) (2e). Mp: 114−115 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.78 (d, J = 8.07 Hz, 2H, Ar), 7.19 (d, J = 8.07 Hz, 2H, Ar), 5.64 (s, 5H, Cp), 3.83 (s, 3H, OMe), 2.95 (s, 3H, OMe), 2.36 (s, 3H, Me), 1.22−2.09 (m, 33H, Cy). ^{31}P NMR (200 MHz, $CDCl_3$, vs 85% H_3PO_4): δ 32.5 (PCy_3). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 516 (2700), 367 (11 000). IR (KBr disk; cm^{-1}): 2926, 2851, 1734, 1699, 1526, 1431, 1248, 1132, 1084, 932.

CpCo[S(NTs)SC$_2$(COOMe)$_2$][P(*p*-C$_6$H$_4$OMe)$_3$] (2f). Mp: 124−125 °C dec. Mass (FAB^+, 70 eV; *m*/*z*): 851 (M^+), 500 (M^+ − P(*p*-$C_6H_4OMe)_3$ + 1). ^{1}H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.79 (d, J = 8.28 Hz, 2H, Ar), 7.60 (broad, 6H, Ar), 7.19 (d, J = 8.28 Hz, 2H, Ar), 6.95 (broad, 6H, Ar), 5.37 (s, 5H, Cp), 3.84 (s, 9H, OMe), 3.67 (s, 3H, OMe), 2.71 (s, 3H, OMe), 2.37 (s, 3H, Me). ^{31}P NMR (200 MHz, $CDCl_3$, vs 85% H_3PO_4): δ 32.0 (P(*p*-$C_6H_4OMe)_3$). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 489 (3400), 369 (16 000). IR (KBr disk; cm^{-1}): 1732, 1697, 1593, 1431, 1259, 1126, 1022, 935.

CpCo[S(NTs)SC$_2$(COOMe)$_2$](PBu$_3$) (2g). Mp: 50−51 °C. Mass (FAB^+, 70 eV; *m*/*z*): 702 (M^+ + 1). ^{1}H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.86 (d, J = 8.14 Hz, 2H, Ar), 7.24 (d, J = 8.14 Hz, 2H, Ar), 5.35 (s, 5H, Cp), 3.75 (s, 3H, OMe), 2.95 (s, 3H, OMe), 2.39 (s, 3H, Me), 1.40−1.62 (m, 18H, Bu), 0.97 (t, J = 7.39 Hz, 9H, Bu). ^{31}P NMR (200 MHz, $CDCl_3$, vs 85% H_3PO_4): δ 49.4 (PBu_3). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 378 (12 000). IR (KBr disk; cm^{-1}): 2957, 2932, 2872, 1734, 1701, 1526, 1431, 1252, 1130, 1084, 928.

CpCo[S(NTs)SC$_2$(COOMe)$_2$][P(OMe)$_3$] (2h). Mp: 69−70 °C dec. Mass (FAB^+, 70 eV; *m*/*z*): 624 (M^+ + 1), 500 (M^+ − $P(OMe)_3$ + 1). ^{1}H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.87 (d, J = 8.39 Hz, 2H, Ar), 7.25 (d, J = 8.39 Hz, 2H, Ar), 5.44 (s, 5H, Cp), 4.02 (d, J = 10 Hz, 9H, Me), 3.76 (s, 3H, OMe), 2.99 (s, 3H, OMe), 2.40 (s, 3H, Me). ^{31}P NMR (200 MHz, $CDCl_3$, vs 85% H_3PO_4): δ 122.8 ($P(OMe)_3$). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 471 (2900), 371 (11 000). IR (KBr disk; cm^{-1}): 1734, 1699, 1433, 1254, 1132, 1020, 932.

[{C$_5$H$_3$(NMs)(PPh$_3$)}Co{S$_2$C$_2$(COOMe)$_2$}] (4a′). Mp: 219−220 °C dec. Mass (FAB^+, 70 eV, NBA; *m*/*z*): 684 (M^+ + 1). ^{1}H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.62−7.93 (m, 15H, Ph), 6.50 (1H, Cp), 5.31 (1H, Cp), 5.02 (1H, Cp), 3.80 (s, 6H, OMe), 2.55 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, vs TMS): δ 165.6, 154.1, 140.5, 140.4, 134.91, 134.88, 134.76, 134.68, 130.0, 129.9, 119.1, 118.4, 78.1, 78.0, 77.9, 68.1, 68.0, 57.5, 52.6, 36.5. ^{31}P NMR (200 MHz, $CDCl_3$, vs 85% H_3PO_4): δ 23.0 (PPh_3). IR (KBr disk; cm^{-1}): 1701, 1497, 1246, 1109. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 745 (1500), 578 (5800), 294 (22 000). Anal. Calcd for $C_{30}H_{27}NO_6PS_3Co{\cdot}CH_2Cl_2$: C, 48.44; H, 3.80. Found: C, 48.80; H, 3.82.

[{C$_5$H$_3$(NTs)(P(*p*-C$_6$H$_4$Me)$_3$)}Co{S$_2$C$_2$(COOMe)$_2$}] (4c). Mp: 140−141 °C; 228−229 °C dec. Mass (FAB^+, 70 eV, NBA; *m*/*z*): 802 (M^+ + 1). ^{1}H NMR (500 MHz $CDCl_3$, vs TMS): δ 7.75 (d, J = 5.19 Hz, 6H, Ar), 7.36 (d, J = 5.19 Hz, 6H, Ar), 7.41 (d, J = 8.24 Hz, 2H, Ar), 6.94 (d, J = 8.24 Hz, 2H, Ar), 6.20 (1H, Cp), 5.25 (1H, Cp), 4.81 (1H, Cp), 3.80 (s, 6H, OMe), 2.48 (s, 9H, Me), 2.23 (s, 3H, Me). ^{31}P NMR (200 MHz, $CDCl_3$, vs 85% H_3PO_4): δ 23.3 (P(*p*-$C_6H_4Me)_3$). IR (KBr disk; cm^{-1}): 1701, 1477, 1234, 1140. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 772 (1500), 585 (5900), 294 (23 000). Anal. Calcd for $C_{39}H_{37}NO_6PS_3Co{\cdot}CH_2Cl_2$: C, 54.18; H, 4.43. Found: C, 53.94; H, 4.80.

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Supporting Information Available: Figures giving ^{1}H NMR spectra as evidence of the purity of complexes **2c**−**h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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