Reactions of cobaltadithiolene complexes with aryl azides Formations of metal chelate rings containing nitrogen atoms by substitution reactions via nitrene

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Abstract

In the reactions of cobaltadithiolene complexes $[CpCo(S_2C_2Z_2)]$ (Z = CN, COOMe, Ph, Me) with aryl azides, two types of substitution reactions occurred. One is the replacements of the sulfur of cobaltadithiolene by arylimido groups and the other is the replacements of the S–CZ=CZ moiety of cobaltadithiolene. The product of latter reaction was also formed by the reactions of the metal cluster complex $[Cp_4Co_4S_6]$ with aryl azides. The azides with electron-donating substituents gave these products in higher yields than those with electron-withdrawing substituents. In these reactions, arylnitrenes as intermediates were predictable. The reactions of $[CpCo(dmit)]$ (dmit = C_3S_5) with phenyl azide and tosyl azide led to the replacements of the terminal sulfur (C=S) of the dmit ligand by imido groups to give novel imine complexes $[CpCo(S_2C_2S_2C=NR)]$ (R = Ph, Ts).
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1. Introduction

Organic azides (RN_3) are very important nitrogen sources [1]. It forms three nitrogens-containing five-membered heterocycles. An azide is one example of a 1,3-dipole like a diazo compound or an isocyanate. In general, 1,3-dipoles lead to [2+3] cycloadditions to an unsaturated moiety [2]. However, 1,4-(P,N) and 1,3-(P,N) dipolar cycloadditions of phosphorus azide to $MeO_2CC≡CCO_2Me$ (dimethyl acetylenedicarboxylate) were reported [3]. On the other hand, an azide can be converted to a nitrene (:NR) [4] as an unstable and reactive nitrogen species by thermolysis and photolysis. A nitrene is one of the important imido sources, because it leads to an alkene aziridination and an amination due to an addition and a C–H insertion, respectively [4].

An azide also causes unique reactions to metal complexes [5]. The reactions of azides with metal complexes are mainly classified into two categories. The first category is the reaction of azide as a 1,3-dipole: for example, [2+3] cycloadditions to Ge=C [6a], W=C [6b] and Co–C and Rh–C [7] bond by an azide. The second category is the reaction of nitrene formed by an azide: for example, the imido insertions into Pt–H [8], M–(CO) (M = Pd, Pt) [9], V–V [10], and the replacement of coordinated halogen [11] or carbonyl [12] by an imido group. In other reactions, N_2 transfer [13] was also reported. The most interesting point in the reactions of metal complexes with azides is the fixing of an unstable species. If a compound is unstable, the compound is possibly to be stabilized by fixing to a metal complex. An unstable nitrene fixing is one of such examples. The phenylnitrene formed by phenyl azide reacts with $[MoCl_4(PR_3)_2]$ [14] to give the stable imido metal complex following oxidation of the metal center. In addition, the tetraazadiene iron complex $[Fe(CO)_3(N_4Me_2)]$ was reported to be formed by the reaction of $[Fe_2(CO)_9]$ with MeN_3 [12]. In general, a

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tetraazadiene is unstable species; however, it stabilizes by fixing to a metal complex. Other tetraazadiene complexes were also reported in the reactions of [CpCo(CO)$_2$] [15a], [Ni(1,5-COD)$_2$] [15b], [Pt(PPh$_3$)$_4$] and [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] [15c] with azides.

In previous work, we focused on the fixation of an imido group to the Co–S moiety of cobaltadithiolene complexes, because an imido complex is one of the reagents for azirization and amidation [16]. Although the cobaltadithiolene ring has pseudo-aromaticity [17] because of having 6π electrons, it also has unsaturation between Co and S bond. An addition reaction can be led to the Co–S moiety of cobaltadithiolene ring. Various adduct formations of cobaltadithiolene have been reported: the alkylidene adduct [18], the alkene adduct [19] and the norbornene adduct [20], which were formed by the reactions with diazo compounds alkynes and quadricyclane, respectively. Likewise, the reactions of cobaltadithiolene complex with sulfonyl azides (RSO$_2$N$_3$) give the imido-bridged cobaltadithiolene adduct [CpCo(S$_2$C$_2$Z$_2$)(NSO$_2$R)] (Z = COOMe, R = C$_6$H$_4$Me, Me) [21] due to addition reaction. It is assumed that this imido-addition reaction is a 1,3-dipole reaction rather than a nitrene reaction, because this reaction efficiently occurs under refluxing benzene (80 °C), and this temperature is lower than the decomposition temperature of tosyl azide (155 °C) [22].

In this work, we focused on the reactions of cobaltadithiolene complexes with aryl azides, which generate nitrene species under relatively low temperature [23]. In this paper, we report the replacements of sulfur by arylimido groups and the replacements of the S–CZ= CZ moiety of cobaltadithiolene ring. (These results were partially reported in a previous communication [24].) In addition, the reactions of [CpCo(dmit)] (dmit = C$_3$S$_5$) having five sulfur atoms with tosyl azide and phenyl azide were also investigated.

2. Results and discussion

2.1. Reactions of cobaltadithiolene complexes with aryl azides

The reaction of a cobaltadithiolene complex [CpCo(S$_2$C$_2$Z$_2$)] (Z = CN; **1**) with five equivalents of phenyl azide under refluxing xylene gave three products [CpCo{(NPh)SC$_2$(CN)$_2$}] (**2a**), [CpCo-{(NPh)$_2$C$_2$(CN)$_2$}] (**3a**) and [CpCo{(NH)S(C$_6$H$_4$)}] (**4a**) [24,25]. We assume that complexes **2a** and **3a** were formed by the replacement of sulfur by phenylimido group, and complex **4a** was formed by the elimination of the S–CZ=CZ moiety of complex **1**. The reactions of complex **1** with other aryl azides, *p*-methylphenyl azide, *p*-nitrophenyl azide and 3-fluoro-4-nitrophenyl azide (FNPA) were investigated. These results are shown in

Scheme 1 and Table 1. All reactions were complicated and various products were formed. Although the yields of products **2**–**4** were low yields in all cases, the products were obtained as main ones. In this work, other products could not be identified. The azides with electron-donating substituent gave these products in higher yields than those with electron-withdrawing substituents. Although the reaction rate of complex **1** with FNPA was slow, the products of this reaction were formed by the reaction after a sufficiently long time. The reactions of *p*-nitrophenyl azide and FNPA with complex **1** gave complexes **2c**, **2d**, **3c** and **3d** by the replacement of sulfur by arylimido groups, however, these reactions did not give the corresponding complexes **4c** and **4d** by the elimination of the S–CZ=CZ moiety.

The reactions of other cobaltadithiolene complexes [CpCo(S$_2$C$_2$Z$_2$)] (Z = COOMe, Ph, Me) with FNPA were investigated. These reactions only gave complex **4d**. According to the results of Table 1, the cobaltadithiolene complexes with electron-withdrawing substituents gave complexes **2d** and **3d** in higher yields than those with electron-donating substituents, and the cobaltadithiolene complex with an electron-donating substituent gave complex **4d** in higher yield than those with electron-withdrawing substituents. In other reaction, the reaction of complex **2a** with phenyl azide gave complexes **3a** (10%) and **4a** (10%). Similarly, we assume that complex **3a** was formed by the replacement of sulfur with arylimido groups and complex **4a** was formed by the replacement of NPh–CZ=CZ moiety.

The ORTEP drawings of complexes **4a** and **4d** are shown in Figs. 1 and 2. These complexes have coordinatively unsaturated and penta-coordinated metal center. The bond lengths between Co and S of complexes **4a** (2.134 Å) and **4d** (2.150 Å) were almost identical to that of a typical cyclopentadienyl cobaltadithiolene complex (2.1 Å) [26]. On the other hand, the bond lengths between Co and N of complexes **4a** (1.80 Å) and **4d** (1.796 Å) were shorter than that of the Co–S bond. The five-membered metallacycles of these complexes remained almost planar. The cyclopentadienyl ring and the five-membered metallacycle of these complexes were perpendicular to each other.

2.2. Nitrene trapping

A nitrene trapping experiment was performed. Cyclooctene as a nitrene scavenger and a solvent was added into the mixture of complex **1** and FNPA, and then this solution was made to react under the conditions described in Scheme 1. If the corresponding nitrene species is generated, aziridine due to an addition and the secondary amine due to a C–H insertion should be formed. According to GC–MS data, the mass number of the corresponding aziridine or secondary amine, *m/*

Table 1
Reactions of cobaltadithiolene complexes [CoCo(S$_2$C$_2$Z$_2$)] with aryl azides (five equivalents)

Aryl azides	Time (h)	Z	Yield of **2** (%)	Yield of **3** (%)	Yield of **4** (%)	Recovery (%)
PhN$_3$	5	CN	12	6	3	11
p-MeC$_6$H$_4$N$_3$	5	CN	17	3	4	10
p-NO$_2$C$_6$H$_4$N$_3$	5	CN	2	1	0	10
FNPA	24	CN	9	6	0	27
FNPA	24	COOMe	0	0	5	10
FNPA	24	Ph	0	0	6	33
FNPA	24	Me	0	0	7	49

$z = 264$, was detected. The mass numbers of the azobenzene analogue due to a nitrene dimerization and the primary amine due to a hydrogen abstraction were also detected at $m/z = 308$ and 156, respectively. Therefore, the formations of complexes **2**–**4** can be explained by a nitrene reaction. In the reactions of cobaltadithiolene complexes with aryl azides, the reactions were complicated and the low yields of products were obtained. The reason can be assumed by the strong reactivity of a nitrene. When the reaction was performed under refluxing benzene (80 °C), which was a milder condition than refluxing xylene (140 °C), complexes **2**–**4** were not obtained at all. The reason is that aryl azides do not thermally decompose in refluxing benzene.

In the thiophene compound, a similar replacement reaction of sulfur and imido group has been observed in the reactions of thiophene or 2,6-dimethylthiophene with ethyl azidoformate (N$_3$COOEt); such reactions form *N*-carbetoxypyrroles [27]. This reaction reveals that nitrene undergoes 1,4-addition to the thiophene ring (Scheme 2). The formations of complexes **2** and **3** can also be explained by the similar case of thiophene. Nitrene leads to addition reactions to the Co and the C of cobaltadithiolene ring, and then the sulfur atom of cobaltadithiolene is eliminated. These are the thiophene-like reactions of cobaltadithiolene ring as an aromatic heterocycle. Proposed mechanisms for the formation of complexes **2** and **4** are shown in Scheme 3. On the other hand, we consider that nitrene formed from aryl azide
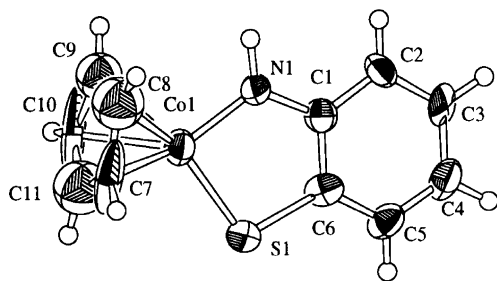

Fig. 1. ORTEP drawing of **4a**. Selected bond lengths (Å): Co1–S1, 2.134(8); Co1–N1, 1.80(1); S1–C6, 1.76(2); N1–C1, 1.37(2); C1–C6, 1.41(2). Selected bond angles (°): S1–Co1–N1, 87.8(5); Co1–S1–C6, 99.5(6); Co1–N1–C1, 122(1); N1–C1–C6, 116(1); S1–C6–C1, 113(1).
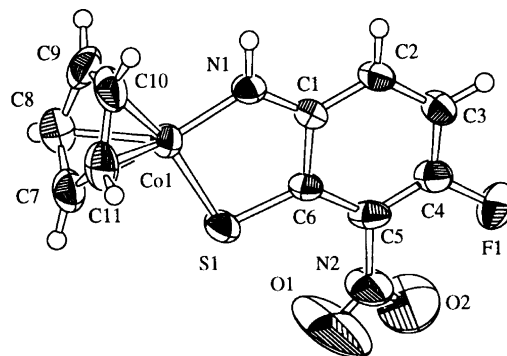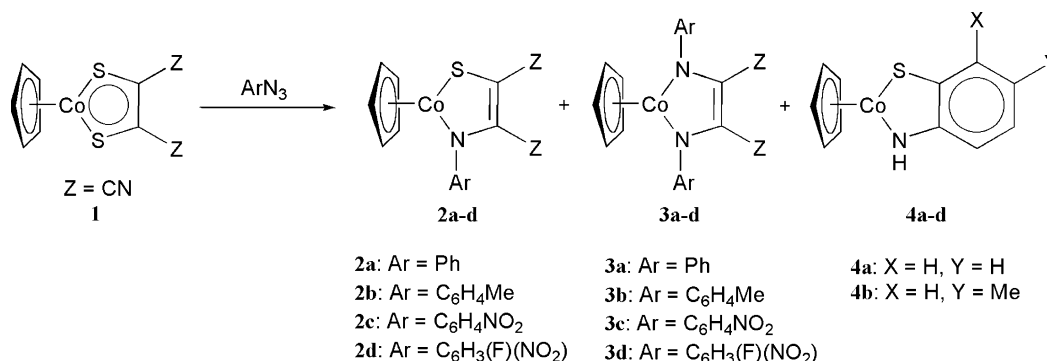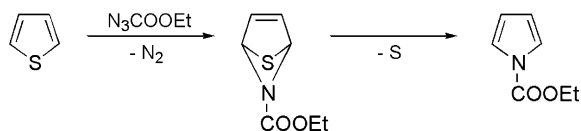

Fig. 2. ORTEP drawing of **4d**. Selected bond lengths (Å): Co1–S1, 2.150(3); Co1–N1, 1.796(8); S1–C6, 1.708(10); N1–C1, 1.35(1); C1–C6, 1.44(1). Selected bond angles (°): S1–Co1–N1, 87.4(3); Co1–S1–C6, 99.5(3); Co1–N1–C1, 123.6(7); N1–C1–C6, 114.8(9); S1–C6–C1, 114.6(7).

2a: Ar = Ph
2b: Ar = C$_6$H$_4$Me
2c: Ar = C$_6$H$_4$NO$_2$
2d: Ar = C$_6$H$_3$(F)(NO$_2$)

3a: Ar = Ph
3b: Ar = C$_6$H$_4$Me
3c: Ar = C$_6$H$_4$NO$_2$
3d: Ar = C$_6$H$_3$(F)(NO$_2$)

4a: X = H, Y = H
4b: X = H, Y = Me

Scheme 1.

Scheme 2.

leads to the addition reaction to the Co–S bond of cobaltadithiolene, because the Co–S bond has unsaturation [18–21]. However, the expected adduct was not formed at all. We have reported that cobaltadithiolene complex reacts with sulfonyl azides as 1,3-dipoles to give the imido-bridged cobaltadithiolene adducts [21]. These results suggest that aryl azides as 1,3-dipoles do not react with cobaltadithiolene complexes, if anything, the arylnitrenes formed by the thermolysis of aryl azides react with cobaltadithiolene complexes.

In another case, the replacements of CpCo moiety by imido group have been reported in the reactions of cyclopentadienyl cobaltacyclopentadiene complexes with azides. This is one of the synthetic methods of highly substituted pyrroles [28]. However, in the reactions of cyclopentadienyl cobaltadithiolene complexes with azides, the expected replacements of CpCo moiety by imido group were not confirmed.

### 2.3. Reactions of metal cluster complex with aryl azides

When the metal cluster complex [Cp$_4$Co$_4$S$_6$] [29] was made to react with aryl azides under refluxing xylene, complexes **4a**–**4c** were formed (Scheme 4). In these reactions, the azide with an electron-donating substituent gave higher yield of complexes **4a**–**4c** than that with an electron-withdrawing substituent. This substituent effect is similar to that in the reactions of cobaltadithiolene complexes with aryl azides. However, the reaction of [Cp$_4$Co$_4$S$_6$] with FNPA did not give the desired product **4d**. This result may be because of the very low reactivity of 3-fluoro-4-nitrophenylnitrene formed from

FNPA. The formations of complexes **4a**–**4c** involve the elimination of the alkene moiety of cobaltadithiolene. Therefore, we conclude that only the units of Cp, Co and S are necessary in the formations of complexes **4a**–**4c**. This cobalt cluster is known as a precursor of cobaltadithiolene complexes and this cluster reacts with alkynes to give cobaltadithiolene complexes [30]. In this work, we found new synthetic methods of complexes **4a**–**4c** by the reaction of [Cp$_4$Co$_4$S$_6$] with aryl azides.

2.4. Reactions of CpCo(dmit) with azides

The reactions of [CpCo(dmit)] (**5**) with phenyl azide and tosyl azide led to the replacement of terminal sulfur by imido groups and these reactions gave the novel imine complexes [CpCo(S$_2$C$_2$S$_2$C=NR)] (R = Ph (**6a**) and R = Ts (**6b**), Scheme 5). In the IR spectra of complexes **6a** and **6b**, the signals of C=N stretching vibrations appeared at 1576 and 1472 cm^{-1}, respectively. These results reveal that complexes **6a** and **6b** have the phenylimine and the tosylimine moieties, respectively. Complex **6b** was formed in refluxing benzene, and this temperature is lower than the decomposition temperature of tosyl azide. Therefore, complex **6b** can be formed without generating any nitrene species. The analogous products [CpCo(dmiCN)] [31] and [CpCo{S$_2$C$_2$S$_2$C=C(COOMe)$_2$}] [32] have already been obtained in the reactions of complex **5** with tetracyanoethylene oxide (TCNEO) and diazomalonate, respectively. These complexes have a more elongated π system (complex **6a**: 688 nm; complex **6b**: 648 nm; [CpCo(dmiCN)]: 669 nm [31], [CpCo{S$_2$C$_2$S$_2$C=C(COOMe)$_2$}]: 686 nm [32]) than a typical dithiolene complex (e.g. [CpCo{S$_2$C$_2$(CN)$_2$}]: 572 nm [26]).

In the reactions of TCNEO with cobaltadithiolene complexes, two other types of reactions have already been observed [33]. One is the reaction of cobaltadithiolene complexes bearing phenyl or ester groups

Scheme 3.

4a: Y = H,   8%
4b: Y = Me,   10%
4c: Y = NO$_2$, 5%
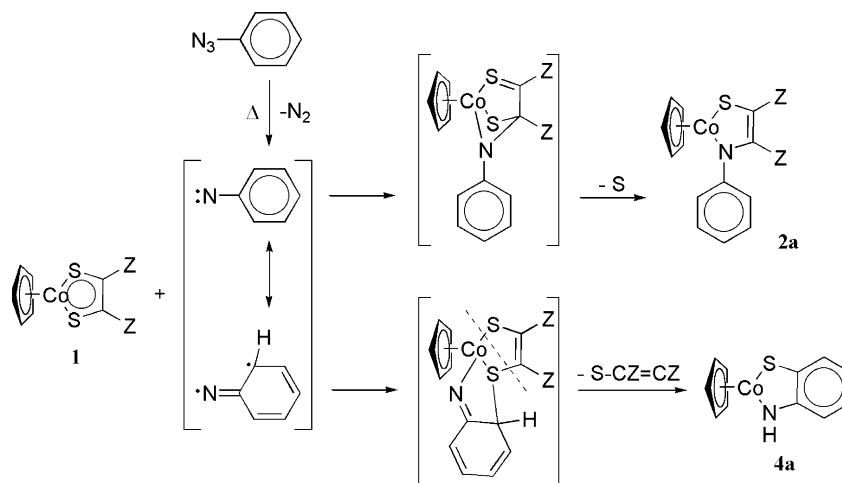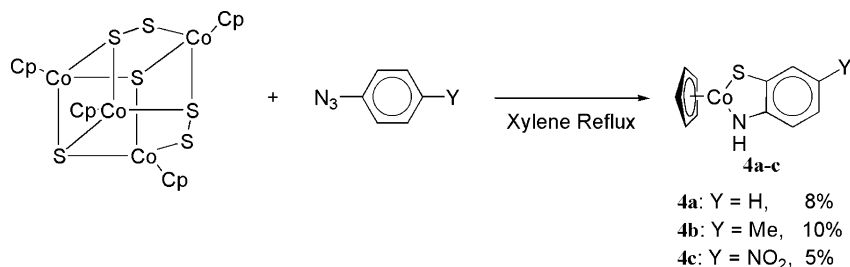
Scheme 4.

[CpCo(S$_2$C$_2$Z$_2$)] (Z = Ph or COOMe). These reactions give the dicyanomethylene-bridged cobaltadithiolene complexes due to the unsaturation of the Co–S bond. The other is the reaction of cobaltadithiolene complex bearing 4-pyridyl groups [CpCo{S$_2$C$_2$(4-py)$_2$}]; this reaction gives the cobaltadithiolene complexes having pyridinium dicyanomethylide groups. These three types of reactions can be explained by the electrophilicity of TCNEO [34].

On the other hand, an azide is one example of a nucleophile [1]. We assume that these azides lead to the nucleophilic attack to the carbon of thiocarbonyl group, and then the thiatriazoline moiety is formed via 1,3-dipolar cycloaddition. In addition, complexes **6a** and **6b** are formed by a desulfurization and molecular nitrogen elimination. A plausible mechanism is shown in Scheme 5. A similar reaction has been reported in an organic sulfur compound. The reaction of phenyl azide with thioketone bearing hinder groups gives the corresponding phenyl imine via an intermediate thiatriazoline [35].

2.5. Conclusion

Cobaltadithiolene complex [CpCo(S$_2$C$_2$Z$_2$)] (Z = COOMe) reacts with tosyl azide as a 1,3-dipole to give the imido-bridged cobaltadithiolene complex due to the unsaturation of the cobaltadithiolene ring [21]. In this work, we found three other types of reactions in the reactions of [CpCo(S$_2$C$_2$Z$_2$)] (Z = CN, COOMe, Ph, Me) and [CpCo(dmit)] with azides. The first was the replacement reaction of sulfur of [CpCo(S$_2$C$_2$Z$_2$)] by

arylimido groups, which is a thiophene-like reaction via an arylnitrene [27]. This is one of the reactions due to the aromaticity of the cobaltadithiolene ring. In other cases, the electrophilic substitution and radical substitution due to the aromaticity of cobaltadithiolene ring have been reported [17]. We can synthesize the five-membered metal chelate ring containing a nitrogen group by the reactions of cobaltadithiolene complexes with arylnitrenes. The second type of reaction to afford complexes **4a**–**4d** we found was the elimination of the S–CZ=CZ moiety of [CpCo(S$_2$C$_2$Z$_2$)] via an arylnitrene. Complexes **4a**–**4d** could also be formed by the reactions of the metal cluster complex [Cp$_4$Co$_4$S$_6$] with aryl azides. This metal cluster complex consisted of only Cp, Co and S units. Therefore, in this reaction we conclude that only the units of Cp, Co and S are necessary. The third type of reaction we found was the replacement reaction of the terminal sulfur (C=S) of [CpCo(dmit)] by imido groups. In this case, azides as 1,3-dipoles reacted with [CpCo(dmit)]. In this work, we found novel desulfurization reactions by the reactions of sulfur-containing cobalt complexes with azides.

3. Experimental

3.1. General remarks

All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. The cobaltadithiolene complexes [CpCo(S$_2$C$_2$Z$_2$)] (Z = CN,

6a: R = Ph, 7%
6b: R = Ts, 37%
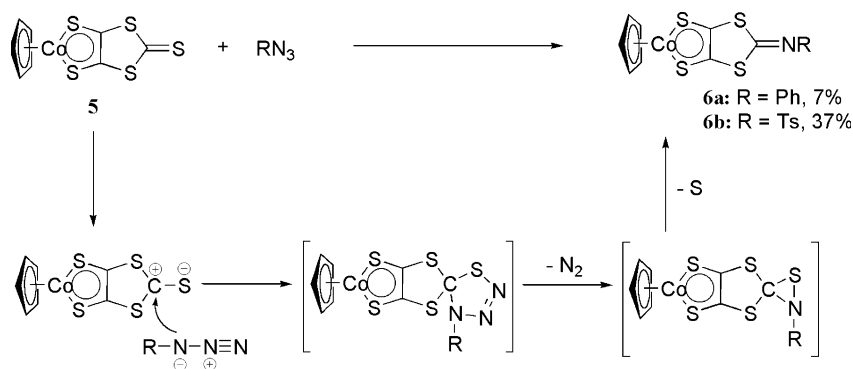
Scheme 5.

COOMe, Ph, Me) [36] and [CpCo(dmit)] [37] were prepared by the literature methods. The solvents of reactions were purified by ketyl distillation before use. The aryl azides were synthesized by known procedures; the reactions of arylhydrazine hydrochloride with sodium nitrite. FNPA, silica gel and Wakogel C-300 were obtained from Wako Pure Chemical Industries, Ltd. Thin-layer chromatography plate filled silica gel 60 (20 cm × 20 cm, 0.25 mm in thick) was obtained from Merck Japan Ltd. HPLC was performed using model LC-908 produced by Japan Analytical Industry Co. Mass and IR spectra were recorded on a JEOL JMS-D300 and a Shimadzu model FTIR 8600PC, respectively. GC–MS were measured with a Shimadzu model GCMS-QP5000. NMR spectra were measured with a JEOL LA500 spectrometer. UV–Vis spectra were recorded on Hitachi model UV-2500PC. Elemental analyses were determined by using a Shimadzu PE2400-II instrument. Melting points were measured by Yanaco model Micro melting point apparatus.

3.2. Reactions of cobaltadithiolene complex with aryl azides

3.2.1. Reaction of cobaltadithiolene complex 1 with phenyl azide

A solution of complex 1 (80 mg, 0.3 mmol) and phenyl azide (1.5 mmol) in xylene (20 ml) was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300) and then the product was further separated by HPLC. Products 2a, 3a and 4a were obtained in 12% (11.6 mg, 0.036 mmol), 6% (6.9 mg, 0.018 mmol) and 3% (2.2 mg, 0.0089 mmol) yields, respectively. Purple solid (2a): m.p. 167 °C. Mass (EI$^+$, 70 eV) m/z (rel. intensity) 323 ([M$^+$], 100), 253 ([M$^+$ – SCCN], 28), 232 ([M$^+$ –NPh], 36), 124 ([CpCo$^+$], 16). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 7.68 (m, 3H, Ar), 7.57 (m, 2H, Ar), 5.08 (s, 5H, Cp) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 158.8, 139.8, 129.1, 128.0, 124.0, 120.7, 118.2, 112.1, 80.1 ppm. UV–Vis (CH$_2$Cl$_2$) λ_{max} (ε) 568 (5800), 376 (5100), 290 (21 000), 236 (11 800). IR (KBr disk) 3105, 2360, 2198, 1635, 1523, 1508, 1489, 1053, 729 cm^{-1}. Anal. Calcd. for C$_{15}$H$_{10}$N$_3$SCo: C, 55.73; H, 3.12; N, 13.00. Found: C, 55.80; H, 3.16; N, 13.21%. Purple solid (3a): Mass (EI$^+$, 70 eV) m/z (rel. intensity) 382 ([M$^+$], 100), 129 ([NPhCCN$^+$], 89), 124 ([CpCo$^+$], 6). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 7.75 (m, 4H, Ar), 7.53 (m, 6H, Ar), 4.59 (s, 5H, Cp) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 156.8, 129.0, 127.4, 123.5, 121.9, 113.3, 78.6 ppm. UV–Vis (CH$_2$Cl$_2$) λ_{max} (ε) 530 (13 000), 355 (19 000), 304 (16 300), 265 (17 000), 234 (17 400). IR (KBr disk) 3062, 2206, 1635, 1589, 1508, 1485, 1419, 741 cm^{-1}. Anal. Calcd. for C$_{21}$H$_{15}$N$_4$Co: C, 65.98; H, 3.95; N, 14.65. Found: C, 66.05; H, 4.03; N, 14.84%. Purple

solid (4a): m.p. 164 °C. Mass (EI$^+$, 70 eV) m/z (rel. intensity) 247 ([M$^+$], 100), 182 ([M$^+$–Cp], 34), 124 ([CpCo$^+$], 9), 123 ([M$^+$ –CpCo], 7) ppm. ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 11.3 (broad, 1H, NH), 7.66 (d, J = 8.42 Hz, 1H, Ar), 7.39 (m, 2H, Ar), 6.97 (m, 1H, Ar), 5.28 (s, 5H, Cp) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 163.6, 148.7, 130.2, 124.7, 118.8, 118.7, 77.4 ppm. UV–Vis (CH$_2$Cl$_2$) λ_{max} (ε) 793 (1000), 571 (14 600), 274 (19 300), 241 (15 000). IR (KBr disk) 3305, 3050, 1651, 1558, 1539, 1508, 1454, 756, 729 cm^{-1}. Anal. Calcd. for C$_{11}$H$_{10}$NSCo: C, 53.45; H, 4.08; N, 5.67. Found: C, 53.64; H, 4.03; N, 5.70%.

3.2.2. Reaction of cobaltadithiolene complex 1 with p-methylphenyl azide

A solution of complex 1 (80 mg, 0.3 mmol) and p-methylphenyl azide (1.5 mmol) in xylene (20 ml) was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300) and then the product was further separated by HPLC. Products 2b, 3b and 4b were obtained in 17% (17.2 mg, 0.051 mmol), 3% (3.7 mg, 0.0090 mmol) and 4% (3.1 mg, 0.012 mmol) yields, respectively. Purple solid (2b): Mass (EI$^+$, 70 eV) m/z (rel. intensity) 337 ([M$^+$], 100), 267 ([M$^+$ –SCCN], 17), 246 ([M$^+$ –C$_6$H$_4$Me], 22). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 7.57 (d, J = 7.94 Hz, 2H, Ar), 7.36 (d, J = 7.94 Hz, 2H, Ar), 5.08 (s, 5H, Cp), 2.50 (s, 3H, Me) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 156.6, 139.9, 137.9, 129.6, 123.7, 120.5, 118.3, 111.2, 80.1, 21.3 ppm. UV–Vis (CH$_2$Cl$_2$) λ_{max} (ε) 570 (10 400), 305 (18 200), 259 (16 400), 237 (19 400). IR (KBr disk) 3112, 3037, 2920, 2362, 2193, 1654, 1540, 1507, 1446, 1345, 1229, 1142, 1053, 838, 526, 518 cm^{-1}. HR-Mass (EI$^+$, 70 eV) Calcd. for C$_{16}$H$_{12}$N$_3$S$_1$Co: 337.0084, Found: 337.0090. Purple solid (3b): m.p. > 300 °C. Mass (EI$^+$, 70 eV) m/z (rel. intensity) 410 ([M$^+$], 100), 91 ([C$_6$H$_4$Me$^+$], 46). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 7.64 (m, 4H, Ar), 7.32 (m, 6H, Ar), 4.58 (s, 5H, Cp), 2.45 (s, 6H, Me). ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 154.5, 137.2, 129.5, 123.3, 121.8, 113.4, 78.5, 21.3 ppm. UV–Vis (CH$_2$Cl$_2$) λ_{max} (ε) 529 (10 300), 358 (16 500), 308 (14 400), 268 (16 000), 235 (15 500). IR (KBr disk) 3114, 3030, 2950, 2920, 2203, 1654, 1540, 1506, 1457, 1375, 1113, 797 cm^{-1}. HR-Mass (EI$^+$, 70 eV) Calcd. for C$_{23}$H$_{19}$N$_4$Co: 410.0943, Found: 410.0945. Purple solid (4b): Mass (EI$^+$, 70 eV) m/z (rel. intensity) 261 ([M$^+$], 100), 196 ([M$^+$ –Cp], 18). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 11.3 (broad, 1H, NH), 7.43 (s, 1H, Ar), 7.27 (d, J = 7.93 Hz, 1H, Ar), 6.83 (d, J = 7.93 Hz, 1H, Ar), 5.22 (s, 5H, Cp), 1.83 (s, 3H, Me) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 162.0, 149.3, 130.5, 128.9, 126.7, 118.5, 77.2, 21.8 ppm. UV–Vis (CH$_2$Cl$_2$) λ_{max} (ε) 797 (1100), 578 (15 200), 276 (21 400), 241 (17 800). IR (KBr disk) 3307, 3094, 2917, 1654, 1636, 1617, 1577, 1559, 1540, 1457, 1350, 1193,

1108, 1004, 809 cm^{-1}. HR-Mass (EI$^+$, 70 eV) Calcd. for C$_{12}$H$_{12}$N$_1$S$_1$Co: 261.0023, Found: 261.0028.

3.2.3. Reaction of cobaltadithiolene complex 1 with p-nitrophenyl azide

A solution of complex **1** (80 mg, 0.3 mmol) and *p*-nitrophenyl azide (1.5 mmol) in xylene (20 ml) was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300) and then the product was further separated by HPLC. Products **2c** and **3c** were obtained in 2% (2.2 mg, 0.0060 mmol) and 1% (1.4 mg, 0.0030 mmol) yields, respectively. Purple solid (**2c**): Mass (EI$^+$, 70 eV) *m/z* (rel. intensity) 368 ([M$^+$], 100), 338 ([M$^+$−NO], 8.6), 124 ([CpCo$^+$], 36). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 8.50 (d, *J* = 9.16 Hz, 2H, Ar), 7.87 (d, *J* = 9.16 Hz, 2H, Ar), 5.15 (s, 5H, Cp). UV−Vis (CH$_2$Cl$_2$) λ$_{max}$ (ε) 572 (2900), 293 (7500), 235 (6000). HR-Mass (EI$^+$, 70 eV) Calcd. for C$_{15}$H$_9$N$_4$O$_2$S$_1$Co: 367.9778, Found: 367.9775. Purple solid (**3c**): Mass (EI$^+$, 70 eV) *m/z* (rel. intensity) 472 ([M$^+$], 100), 124 ([CpCo$^+$], 14). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 8.31 (d, *J* = 8.93 Hz, 4H, Ar), 7.57 (d, *J* = 8.93 Hz, 4H, Ar), 4.67 (s, 5H, Cp). HR-Mass (EI$^+$, 70 eV) Calcd. for C$_{21}$H$_{13}$N$_6$O$_4$Co: 472.0331, Found: 472.0324.

3.2.4. Reactions of cobaltadithiolene complexes with FNPA

A solution of complex **1** (29 mg, 0.11 mmol) and FNPA (101 mg, 0.55 mmol) in xylene (20 ml) was refluxed for 24 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 **2d** and **3d** were obtained in 9% (3.8 mg, 0.0098 mmol) and 6% (3.4 mg, 0.0067 mmol) yields, respectively. Purple solid (**2d**): Mass (EI$^+$, 70 eV) *m/z* (rel. intensity) 386 ([M$^+$], 87), 124 ([CpCo$^+$], 50), 59 ([Co$^+$], 100). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 8.53 (m, 1H, Ar), 7.94 (m, 1H, Ar), 7.56 (m, 1H, Ar), 5.19 (s, 5H, Cp). ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 235.0, 232.4, 227.0, 224.6, 218.3, 207.1, 131.0, 122.2, 119.6, 119.4, 80.3 ppm. UV−Vis (CH$_2$Cl$_2$) λ$_{max}$ (ε) 572 (6200), 292 (12 300). HR-Mass (EI$^+$, 70 eV) Calcd. for C$_{15}$H$_8$N$_4$O$_2$F$_1$S$_1$Co: 385.9684, Found: 385.9698. Purple solid (**3d**): Mass (EI$^+$, 70 eV) *m/z* (rel. intensity) 508 ([M$^+$], 58), 192 ([C$_6$H$_3$F(NO$_2$)NCCN$^+$], 100), 124 ([CpCo$^+$], 38), 59 ([Co$^+$], 6). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 8.58 (m, 2H, Ar), 7.98 (m, 2H, Ar), 7.53 (m, 2H, Ar), 4.73 (s, 5H, Cp). ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 175.1, 163.0, 152.7, 136.6, 135.2, 133.7, 129.5, 123.2, 77.5 ppm. UV−Vis (CH$_2$Cl$_2$) λ$_{max}$ (ε) 544 (2400), 361 (3100), 296 (3900). HR-Mass (EI$^+$, 70 eV) Calcd. for C$_{21}$H$_{11}$N$_6$O$_4$F$_2$Co: 508.0142, Found: 508.0136.

A solution of [CpCo(S$_2$C$_2$Z$_2$)] (Z = COOMe, Ph, Me) (0.11 mmol) and FNPA (101 mg, 0.55 mmol) in xylene

(20 ml) was refluxed for 24 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. Product **4d** was obtained in 5% (1.7 mg, 0.0055 mmol, Z = COOMe), 6% (2.0 mg, 0.0065 mmol, Z = Ph) and 7% (2.4 mg, 0.0077 mmol, Z = Me) yields, respectively. Purple solid (**4d**): m.p. 171–172 °C. Mass (EI$^+$, 70 eV) *m/z* (rel. intensity) 310 ([M$^+$], 100), 264 ([M$^+$−NO$_2$], 34), 124 ([CpCo$^+$], 55), 59 ([Co$^+$], 19). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 7.47 (dd, *J* = 9.77, 9.16 Hz, 1H, Ar), 6.95 (dd, *J* = 9.77, 4.58 Hz, 1H, Ar), 5.36 (s, 5H, Cp). ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 161.3, 149.6, 147.5, 140.8, 131.0, 129.0, 78.4. ^{19}F-NMR (376 MHz, CDCl$_3$ vs. CFCl$_3$) δ −132.9 (dd, *J* = 9.16 Hz, 4.58) ppm. UV−Vis (CH$_2$Cl$_2$) λ$_{max}$ (ε) 565 (11 200), 277 (15 200). IR (KBr disk) 3466, 1535, 1333, 1246 cm^{-1}. HR-Mass (EI$^+$, 70 eV) Calcd. for C$_{11}$H$_8$N$_2$O$_2$F$_1$S$_1$Co: 309.9622, Found: 309.9611.

3.2.5. Nitrene trapping

A solution of complex **1** (30 mg, 0.11 mmol) and FNPA (101 mg, 0.55 mmol) in cyclooctene (20 ml) was refluxed for 5 h. The GC−MS of the reaction mixture was measured.

3.2.6. Reactions of [Cp$_4$Co$_4$S$_6$] with aryl azides

A solution of [Cp$_4$Co$_4$S$_6$] (86 mg, 0.12 mmol) and aryl azides, PhN$_3$, *p*-Me−C$_6$H$_4$N$_3$ or *p*-NO$_2$−C$_6$H$_4$N$_3$ (2.5 mmol) in xylene (20 ml) was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300). Products **4a**, **4b** and **4c** were obtained in 8% (9.5 mg, 0.038 mmol), 10% (12.5 mg, 0.048 mmol) and 5% (7.0 mg, 0.024 mmol) yields, respectively. Purple solid (**4c**): m.p. 218 °C. Mass (EI$^+$, 70 eV) *m/z* (rel. intensity) 292 ([M$^+$], 100), 246 ([M$^+$−NO$_2$], 18), 124 ([CpCo$^+$], 20). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 11.3 (broad, 1H, NH), 8.62 (d, *J* = 2.24 Hz, 1H, Ar), 7.82 (dd, *J* = 2.24, 9.16 Hz, 1H, Ar), 7.33 (d, *J* = 9.16 Hz, 1H, Ar), 5.42 (s, 5H, Cp) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 167.0, 146.1, 138.4, 126.2, 120.2, 117.1, 78.4 ppm. UV−Vis (CH$_2$Cl$_2$) λ$_{max}$ (ε) 793 (750), 585 (11 400), 403 (5200), 284 (12 200), 236 (10 500). IR (KBr disk) 3335, 3109, 3088, 3081, 1577, 1570, 1559, 1540, 1496, 1483, 1473, 1453, 1121, 1054, 1041, 1007, 891, 843, 831, 813 cm^{-1}. Anal. Calcd. for C$_{11}$H$_9$N$_2$O$_2$SCo: C, 45.22; H, 3.10; N, 9.59. Found: C, 45.28; H, 3.28; N, 9.69%.

3.2.7. Reaction of [CpCo(dmit)] with phenyl azides

A solution of complex **5** (105 mg, 0.33 mmol) and phenyl azides (180 μl, 1.64 mmol) in xylene (20 ml) was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300) and then the product was further separated by HPLC. Product **6a** was

obtained in 7% (8.8 mg, 0.023 mmol) yield. Green solid (**6a**): Mass (EI$^+$, 70 eV) m/z (rel. intensity) 379 ([M$^+$], 100), 276 ([CpCoS$_2$C$_2$S$_2^+$], 79), 212 ([CpCoS$_2$C$_2^+$], 8), 200 ([CpCoS$_2$C$^+$], 32), 188 ([CpCoS$_2^+$], 36), 168 ([CpCoSC$^+$], 62), 65 ([Cp$^+$], 15). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 7.37 (m, 2H, Ar), 7.17 (m, 1H, Ar), 7.00 (m, 2H, Ar), 5.35 (s, 5H, Cp) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 173.2, 154.6, 154.3, 150.5, 129.8, 129.7, 129.5, 125.3, 120.0, 78.8 ppm. UV–Vis (CH$_2$Cl$_2$) λ_{max} (ε) 688 (15 700), 424 (2900). IR (KBr disk) 1576 cm^{-1}. HR-Mass (EI$^+$, 70 eV) Calcd. for C$_{14}$H$_{10}$N$_1$S$_4$Co: 378.9028, Found: 378.9026.

3.2.8. Reaction of [CpCo(dmit)] with tosyl azides

A solution of complex **5** (64 mg, 0.2 mmol) and tosyl azides (31 μl, 0.2 mmol) in benzene (20 ml) was refluxed for 2 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300) and then the product was further separated by HPLC. Product **6b** was obtained in 37% (34 mg, 0.074 mmol) yield. Green solid (**6b**): m.p. 266–267 °C. Mass (EI$^+$, 70 eV) m/z (rel. intensity) 457 ([M$^+$], 100), 276 ([CpCoS$_2$C$_2$S$^+$], 29), 212 ([CpCoS$_2$C$_2^+$], 4), 200 ([CpCoS$_2$C$^+$], 7), 188 ([CpCoS$_2^+$], 20), 155 ([Ts$^+$], 23), 124 ([CpCo$^+$], 61), 91 ([C$_6$H$_4$Me$^+$], 70), 65 ([Cp$^+$], 22), 59 ([Co$^+$], 7). ^{1}H-NMR (500 MHz, CDCl$_3$ vs. TMS) δ 7.88 (d, $J = 8.44$ Hz, 2H, Ar), 7.32 (d, $J = 8.44$ Hz, 2H, Ar), 5.48 (s, 5H, Cp), 2.44 (s, 3H, Me) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$ vs. TMS) δ 193.2, 171.1, 165.7, 144.5, 136.8, 129.8, 127.3, 79.4, 21.8 ppm. UV–Vis (CH$_2$Cl$_2$) λ_{max} (ε) 648 (11 800), 347 (10 000). IR (KBr disk) 1472, 1302, 1150, 1086 cm^{-1}. Anal. Calcd. for C$_{15}$H$_{12}$NO$_2$S$_5$Co: C, 39.38; H, 2.64; N, 3.06. Found: C, 39.33; H, 2.58; N, 3.03%.

3.2.9. X-ray diffraction study

Measurements of complexes **4a** and **4d** were made on a Rigaku AFC 5S diffractometer with graphite-mono-chromated Mo–K$_\alpha$ radiation. Cell constants and an orientation matrix for data collection were obtained by using 25 carefully centered reflections. The data were collected using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 55.0°. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. Each structure was solved by direct methods and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters (see Table 2). Complexes **4a** and **4d** of idealized positions were used for the teXsan crystallographic software package of Molecular Structure Corp.

Table 2
Crystallographic data for compounds **4a** and **4d**

	4a	4b
Formula	C$_{11}$H$_{10}$NSCo	C$_{11}$H$_8$N$_2$O$_2$FSCo
Formula weight (g mol^{-1})	247.20	310.19
Crystal color	purple	purple
Crystal habit	prismatic	prismatic
Crystal size (mm^3)	0.13 × 0.13 × 0.47	0.13 × 0.17 × 0.47
Crystal system	orthorhombic	monoclinic
Space group	$Fdd2$ (No. 43)	$P2_1/n$ (No. 14)
a (Å)	23.493(9)	7.495(2)
b (Å)	28.611(5)	18.222(1)
c (Å)	6.058(8)	8.403(1)
β (°)		92.58(1)
V (Å^3)	4072(5)	1146.4(3)
Z	16	4
D_{calc} (g cm^{-3})	1.613	1.797
μ(Mo–K$_\alpha$) (cm^{-1})	18.45	16.85
T (K)	296	296
$2\theta_{max}$ (°)	55.0	55.0
Unique data (R_{int})	1277 (0.108)	2631 (0.044)
Number of observations	591	1098
Number of variables	113	171
R_1, wR_2 (all data)	0.059, 0.067	0.060, 0.074
Goodness-of-fit on F^2	1.58	1.72
Largest difference peak and hole (e Å^{-3})	0.50, −0.47	0.56, −0.52

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 202772 (**4a**) and 202773 (**4d**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam. ac.uk).

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