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Imido-transfer reactions to carbonyl moiety induced by the reactions of imido-bridged cobaltadithiolene complexes with trivalent phosphorus halides

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Abstract

The reactions of the imido-bridged cobaltadithiolene complexes [CpCo{$S_2C_2(COOMe)_2$}(NR)] (R = Ts, Ms) with PCl_3 led to the imido-transfer reactions to the carbonyl moiety, and these reactions gave the novel imine complexes [CpCo{S_2C_2(COOMe)(C=NROMe)}]. In the case of PI_3, another imido-transfer reaction to carbonyl moiety occurred and the novel amide complexes [CpCo{S_2C_2(COOMe)(CONHR)}] were formed. PBr_3 showed an intermediate reactivity value in between that of PCl_3 and that of PI_3. Both novel imido-transfer reactions were caused by intermolecular reactions, these reaction processes were determined by crossover experiments.

Keywords: Cobaltadithiolene; Imido-transfer; Imine; Amide; Phosphorus trihalide

1. Introduction

Metalladithiolene complexes are unique and interesting compounds because of their ability to exhibit both the unsaturated and the aromatic character [1]. The substitution [2] and the addition reactions [3–7] of cyclopentadienyl metalladithiolene complexes have been reported. These reactions can be explained as due to the dual characters of metalladithiolene complexes. A typical addition reaction often occurs between the metal and the sulfur (M–S) bond of metalladithiolene ring. As in the case of the reactions of cyclopentadienyl metalladithiolene complexes [CpM($S_2C_2Z_2$)] (M = Co, Rh; Z = COOMe, Ph, and so on) with diazo compounds ($R^1R^2CN_2$), these reactions yield the alkylidene-bridged metalladithiolene complexes [CpM($S_2C_2Z_2$)(CR^1R^2)] (R^1, R^2 = H, H; H, COOEt; COOMe, COOMe) [3]. The corresponding alkene [4]- or norbornene [5]-bridged metalladithiolene complexes are also obtained by the reactions with alkyne or quadricyclane, respectively. Recently, it has been reported that cyclopentadienyl *o*-carboranedithiolato cobalt complexes [CpCo{S_2C_2-($B_{10}H_{10}$)}] also undergo similar addition reactions [6]. Likewise, the reaction of cobaltadithiolene complex [CpCo{$S_2C_2(COOMe)_2$}] with (*N*-tosylimino)phenyliodinane (PhI=NTs) or tosyl azide give the corresponding tosylimido-bridged cobaltadithiolene complex [CpCo{$S_2C_2(COOMe)_2$}(NTs)] (**1a**) [7].

Imido metal complexes (M=NTs) often lead to imido-transfer reactions, which are important as analogous oxo-transfer reactions [8]. According to a recent report, the reactions of bis(tosylimido)ruthenium porphyrin complexes [Ru^{VI}(Por)$(NTs)_2$] (Por = porphyrinato ligand) with alkenes or hydrocarbons give aziridination and amidation products (Scheme 1) [9]. Mechanistic and kinetic studies are also discussed in this report. The most useful imido-transfer reaction is the reaction of PhI=NTs [10] with alkenes and hydrocar-

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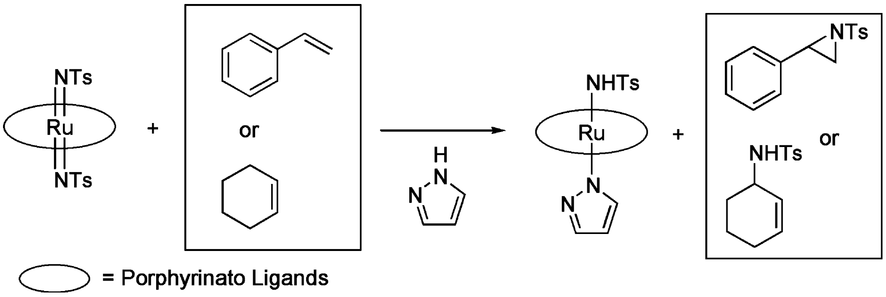


Scheme 1.

bons in the presence of a catalyst. A large number of examples of catalytic aziridinations [11] and amidations [12] have been reported using PhI=NTs. Proposed intermediates of these catalytic reactions are also imido metal complexes (M=NTs). Similarly, the trifluoroacetylimido manganese complexes formed by the corresponding nitrido manganese complexes are also imido-transfer reagents, and these complexes react with alkenes to give aziridines and amides [13]. In addition, the reactions of tosylimido molybdenum complexes $[Mo(NTs)_2(Et_2dtc)_2]$ ($Et_2dtc = N,N$-diethydithiocarbamate) with phosphines give iminophosphoranes by the imido-transfer reactions from molybdenum to phosphines [14]. Therefore, imido metal complexes are very important complexes as imido sources.

We have focused on the tosylimido-bridged cobaltadithiolene complex **1a** as a source of a novel imido-transfer reaction, because such a reaction in an organometallic complex has never been reported. Complex **1a** has the three-membered ring consisting of cobalt, sulfur and nitrogen (cobaltathiaziridine), and it is a distorted and a reactive ring like a typical aziridine. A previous report explained that complex **1a** undergoes an aziridine-like reaction, namely, the ring opening of the three-membered ring by a protic acid [7]. However, we have also discovered that the reaction of complex **1a** with phosphine or phosphite leads to the intramolecular imido-migration reaction to the Cp ring [15]. Complex **1a** reacts with phosphine or phosphite at room temperature to give the sulfilimine ($S^+{-}N^-$) intermediate due to the ring opening of the cobaltathiaziridine. Upon heating, this sulfilimine intermediate further undergoes the migration reaction of the imido group to the Cp ring; here the novel amide-substituted Cp complex $[(C_5H_4{-}NHTs)Co\{S_2C_2(COOMe)_2\}]$ is formed (Scheme 2). Since the migration reaction is induced by trivalent phosphorus compounds, we focused our attention on the reactions of trivalent phosphorus halides with complex **1a** and the corresponding mesylimido-bridged complex $[CpCo\{S_2C_2(COOMe)_2\}(NMs)]$ (**1b**).

Here we report the novel imido-transfer reactions to carbonyl moiety induced by the reactions of imido-bridged cobaltadithiolene complexes having carbonyl groups with trivalent phosphorus halides.

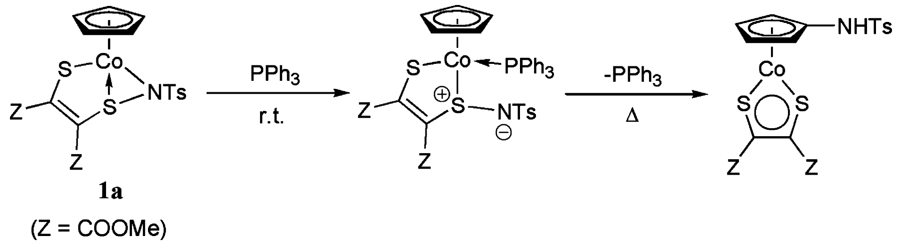
2. Results and discussion

2.1. Reactions of imido-bridged cobaltadithiolene complexes with trivalent phosphorus halide, PCl_3

Each imido-bridged cobaltadithiolene complex **1a** or **1b** was prepared from $[CpCo\{S_2C_2(COOMe)_2\}]$ (**4**) with TsN_3 or MsN_3 using the procedure developed in our laboratory [7]. Complex **1a** reacted with two equivalents of PCl_3 in refluxing benzene to give complex **4** and the novel tosylimine complex $[CpCo\{S_2C_2(COOMe)(C{=}NTsOMe)\}]$ (**2a**) in yields of 39 and 4% (Scheme 3 and Table 1). The analogue complex **1b** led to same reaction, and this reaction gave the corresponding mesylimine complex $[CpCo\{S_2C_2(COOMe)(C{=}NMsOMe)\}]$ (**2b**) (5% yield) and complex **4** (39% yield), respectively. These reactions were complicated, and other products were not determined. The structures of complexes **2a** and **2b** were determined by X-ray structure analyses. The ORTEP drawings of complexes **2a** and **2b** are shown in Fig. 1a and b, respectively. In Fig. 1a, the bond lengths of cobaltadithiolene are similar to those of a typical cyclopentadienyl cobaltadithiolene complex **4** [3e]. The bond length of N1–C4 is 1.271 Å, which is slightly longer than that of a typical C=N bond (1.24 Å) [16]. The tosyl group is oriented at the syn form to the plane of the cobaltadithiolene ring. The IR spectrum of complex **2a** showed two strong bands at 1699 and 1600 cm^{-1} corresponding to C=O and C=N stretching vibrations, respectively. These results support the tosylimine structure of complex **2a**. Similarly, the X-ray data and the spectroscopic data of complex **2b** also support its mesylimine structure. Therefore, the reaction of complexes **1a** and **1b** with PCl_3 lead to the imido-transfer reaction to the carbonyl moiety of cobaltadithiolene substituent, and the novel imine complexes are formed.

2.2. Reactions of imido-bridged cobaltadithiolene complexes with trivalent phosphorus halides, PBr_3 and PI_3

The reactions of complexes **1a** and **1b** with other trivalent phosphorus halides, PBr_3 and PI_3, were also

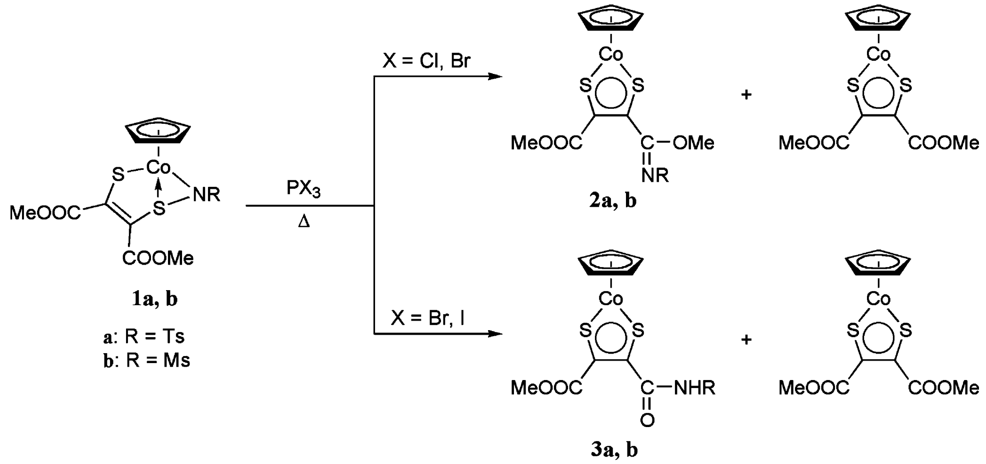


Scheme 2.

investigated. The reaction of complex **1a** with two equivalents of PBr_3 in refluxing benzene gave complex **4** (61% yield), tosylimine complex **2a** (trace amount), and the novel tosylamide complex $[CpCo\{S_2C_2(COOMe)(CONHTs)\}]$ (**3a**) (10% yield). In the case of PI_3, complex **2a** was not formed. The only products were complex **4** (77% yield) and complex **3a** (14% yield, Scheme 3 and Table 1). The analogue complex **1b** was allowed to experience the same reaction by PI_3, and this reaction gave the corresponding mesylamide complex $[CpCo\{S_2C_2(COOMe)(C{=}NMsOMe)\}]$ (**3b**) (9% yield) and complex **4** (78% yield). The structure of complex **3a** was determined by X-ray structure analyses. The ORTEP drawing of complex **3a** is shown in Fig. 2. The bond lengths of cobaltadithiolene are similar to those of complex **2a** and to those of a typical cyclopentadienyl cobaltadithiolene complex $[CpCo\{S_2C_2(COOMe)_2\}]$ [3e]. The IR spectrum of complex **3a** showed two strong bands at 1713 and 1680 cm^{-1} corresponding to two different C=O stretching vibrations. In addition, the broad bands of 3113 cm^{-1} in IR and 9.7 ppm in ^{1}H-NMR spectra were attributed to the NH group of amide. These results support the tosylamide structure of complex **3a**. The structure of complex **3b** was also determined by spectroscopic data. Therefore, the reaction of complexes **1a** and **1b** with PI_3 lead to the imido-transfer reaction to the carbonyl moiety of cobaltadithiolene substituent, and the novel amide complexes are formed. On the other hand, PBr_3 caused the imination and the amidation reactions to carbonyl moiety. We assume that PBr_3 has an intermediate reactivity value in between that of PCl_3 and that of PI_3 in the reaction with imido-bridged cobaltadithiolene complex.

2.3. Reactions of imido-bridged cobaltadithiolene complex with pentavalent phosphorus halides and Lewis acids

The reactions of pentavalent phosphorus chloride were also investigated. Complex **1a** was made to react with PCl_5 or $O{=}PCl_3$ as a pentavalent phosphorus chloride instead of PCl_3. In the case of PCl_5, although a trace amount of complex **4** was formed under same reaction conditions shown in Table 1, most complexes were decomposed and then various unknown products were formed. Likewise, in the case of $O{=}PCl_3$, although complex **4** was obtained in 26% yield and complex **1a** was recovered in 47% yield, respectively, target product **2a** was not obtained. A pentavalent phosphorus halide often behaves as a Lewis acid. The reactions of complex **1a** with $AlCl_3$ and $TiCl_4$ as a Lewis acid were also performed. Similarly, complex **1a** decomposed and target product **2a** was not obtained. Therefore, the reaction of complex **1a** with Lewis acid was a complicated decomposition reaction. We conclude that a trivalent phosphorus halide is needed in the imination and the amidation reactions.



Scheme 3.

Table 1
Reactions of imido-bridged cobaltadithiolene complexes [CpCo{$S_2C_2(COOMe)_2$}(NR)] with trivalent phorphorus halides PX_3 (two equivalents)

X	R	Scavenger	Solvent	Yield of **2a** (%)	Yield of **3a** (%)	Yield of **4** (%)
Cl	Ts	None	Benzene	4	0	39
Cl	Ms	None	Benzene	5	0	39
Br	Ts	None	Benzene	Trace	10	61
I	Ts	None	Benzene	0	14	77
I	Ms	None	Benzene	0	9	78
Cl	Ts	Cyclohexene	Benzene	5	0	43
Cl	Ts	Complex **4**	Benzene	13	0	96
Cl	Ts	PhCOMe	Benzene	3	0	43
Cl	Ts	None	PhCOMe	0	0	36

All reaction times are 1 h, and all yields are isolated pure ones.

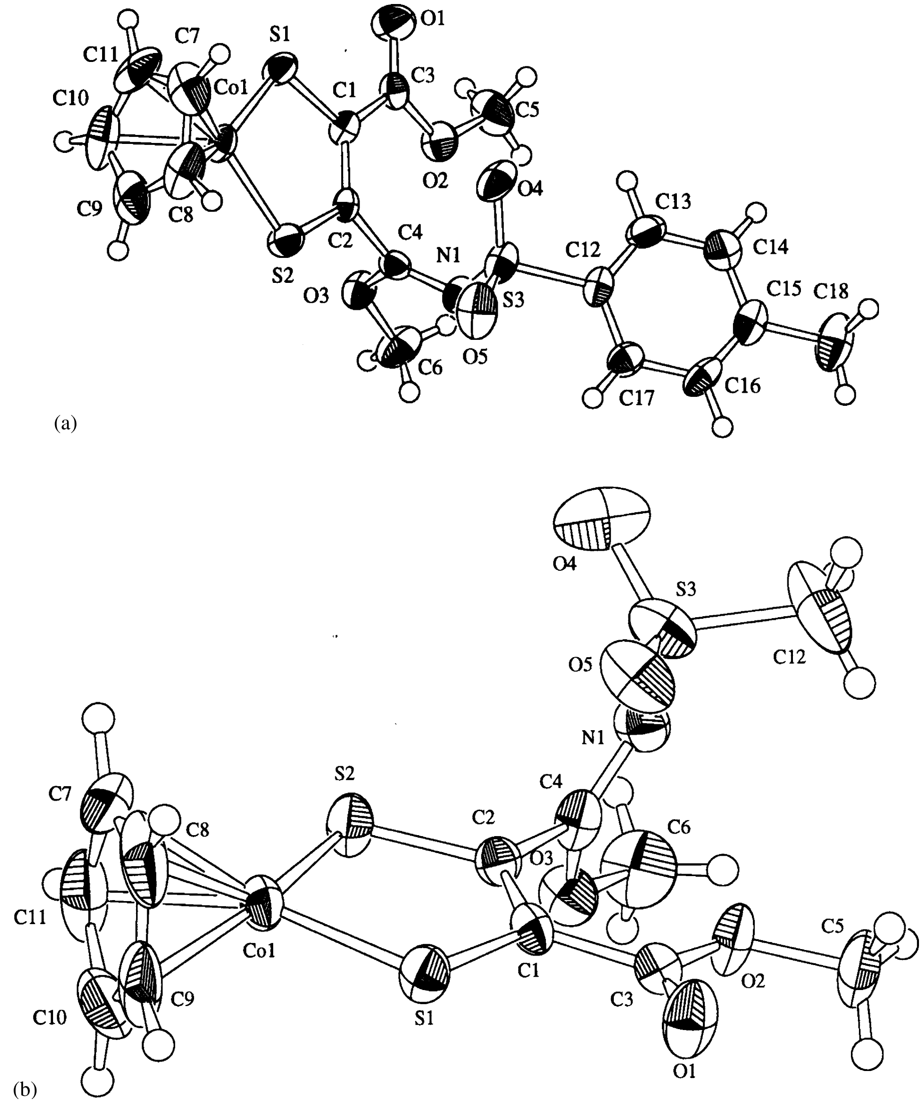


Fig. 1. (a) ORTEP drawing of complex **2a**. Selected bond lengths (Å): Co1–S1 2.103(2), Co1–S2 2.105(2), S1–C1 1.731(6), S2–C2 1.715(6), C1–C2 1.357(8), N1–C4 1.271(7). Selected bond angles (°): S1–Co1–S2 92.29(7), Co1–S1–C1 104.9(2), Co1–S2–C2 104.5(2), S1–C1–C2 118.2(5), S2–C2–C1 120.1(4), N1–C4–C2 128.9(8), S3–N1–C4 121.0(4). (b) ORTEP drawing of complex **2b**. Selected bond lengths (Å): Co1–S1 2.106(2), Co1–S2 2.109(2), S1–C1 1.719(7), S2–C2 1.711(7), C1–C2 1.364(10), N1–C4 1.282(9). Selected bond angles (°): S1–Co1–S2 92.35(9), Co1–S1–C1 104.6(3), Co1–S2–C2 104.5(3), S1–C1–C2 119.1(6), S2–C2–C1 119.5(5), N1–C4–C2 129.8(8), S3–N1–C4 123.4(6).

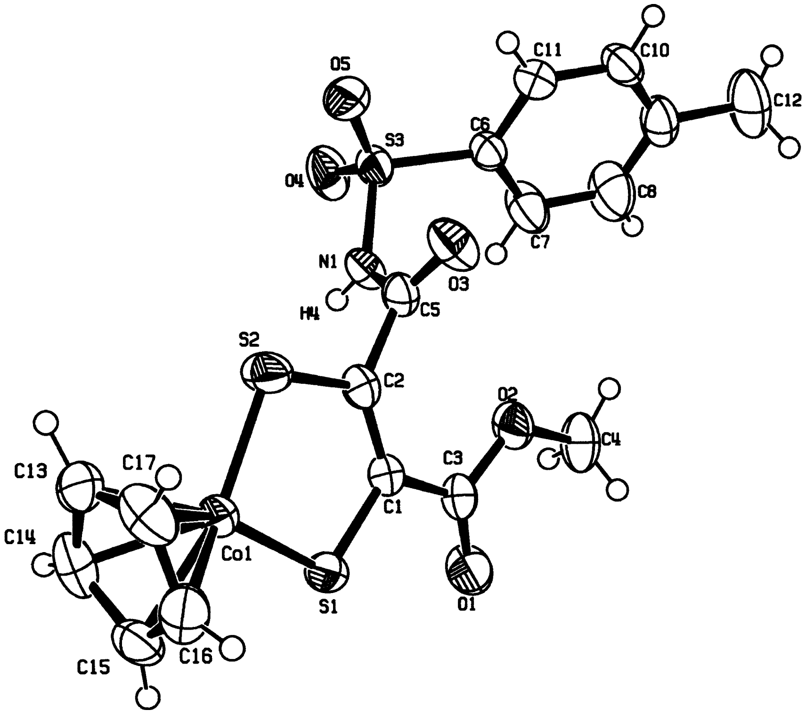


Fig. 2. ORTEP drawing of complex **3a**. Selected bond lengths (Å): Co1–S1 2.1070(10), Co1–S2 2.1050(10), S1–C1 1.728(2), S2–C2 1.718(2), C1–C2 1.360(3). Selected bond angles (°): S1–Co1–S2 91.70(3), Co1–S1–C1 105.22(9), Co1–S2–C2 105.42(9), S1–C1–C2 118.6(2), S2–C2–C1 119.0(2).

2.4. Investigation of reaction mechanism

In the imination reaction, the ^{1}H-NMR and GC-Mass spectra of the reaction mixture also showed the presence of *p*-toluenesulfonylamide ($TsNH_2$) [17]. A trace amount of $TsNH_2$ was detected. The possible role of $TsNH_2$ in the formation of the tosylimine complex **2a** was also investigated. A typical imine compound is prepared by the reactions of amines with aldehydes or ketones involving dehydration [16], so the possibility of $TsNH_2$ as an imine source can be not ignored. An attempt to synthesize complex **2a** by the reaction of complex **4** with $TsNH_2$ in the presence of PCl_3 did not occur reaction, and complex **4** was quantitatively recovered. Such a result suggests that $TsNH_2$ does not concern in the formation of complex **2a**. In amidation by the reaction of complex **1a** with PI_3, $TsNH_2$ was also detected. Occasionally, the reactions of carboxylic ester with amines give amides [18]. Likewise, though we tried to synthesize complex **3a** using $TsNH_2$ as an amide source, complex **3a** was not formed and the effect of $TsNH_2$ was also not confirmed.

The reaction of complex **1a** with PCl_3 in the presence of water was performed under same condition shown in Table 1. The yield of expected imination product **2a** decreased, and a trace amount of complex **2a** was obtained. Therefore, the water containing in the reaction prevents this imido-transfer reaction. We assume that complex **1a** reacted with the HCl formed by the hydrolysis of PCl_3, and this reaction led to the imido elimination and the formation of $TsNH_2$ [7]. On the other hand, the reaction of complex **1** with PCl_3 in the presence of deuterated water was attempted, and the deuterated *p*-toluenesulfonylamide ($TsND_2$) was detected. Therefore, the hydrogen source of *p*-toluene sulfonyl amide is the water slightly containing in the solution or the HCl formed by the hydrolysis of PCl_3.

Imine compounds can be also synthesized by the reaction of carbonyl compounds with iminophosphoranes ($R_3P^+{-}N^-Ts$) through the Wittig-type reaction. Namely, it is conceivable that tosylimine complex **2a** was formed by the reaction of the iminophosphorane ($Cl_3P^+{-}N^-Ts$). This type of iminophosphorane occasionally leads to conversion from an isocyanate (–N=C=O) to a carbodiimide (–N=C=NR) [19]. Probable precursors of $Cl_3P^+{-}N^-Ts$ in this reaction are tosyl nitrene (:NTs) and tosylsulfilimine ($R_2S^+{-}N^-Ts$). Complex **1a** was made to react with PCl_3 under a large excess of cyclohexene as a nitrene scavenger (Table 1). It is known that nitrenes react with alkenes to give the corresponding allylamines or aziridines. However, the presence of amine or aziridine in the reaction mixture was not detected even at GC-Mass sensitivity level. Therefore, the detected $TsNH_2$ [17] is not formed by the hydrogen abstraction of tosyl nitrene. On the other hand, we have reported the isolation and the characterization of a stable sulfilimine complex by the reactions of complex **1a** with PPh_3 or $P(OPh)_3$ as a nucleophile [7,15]. Similarly, the mechanism for the reaction of complex **1a** with PCl_3 seems to involve the formation of an analogous but unstable sulfilimine intermediate. This intermediate was probably formed through the nucleophilic attack of PCl_3 on the cobalt atom of complex **1a**. However, the isolation and the characterization of sulfilimine intermediate and iminophosphorane have not succeeded.

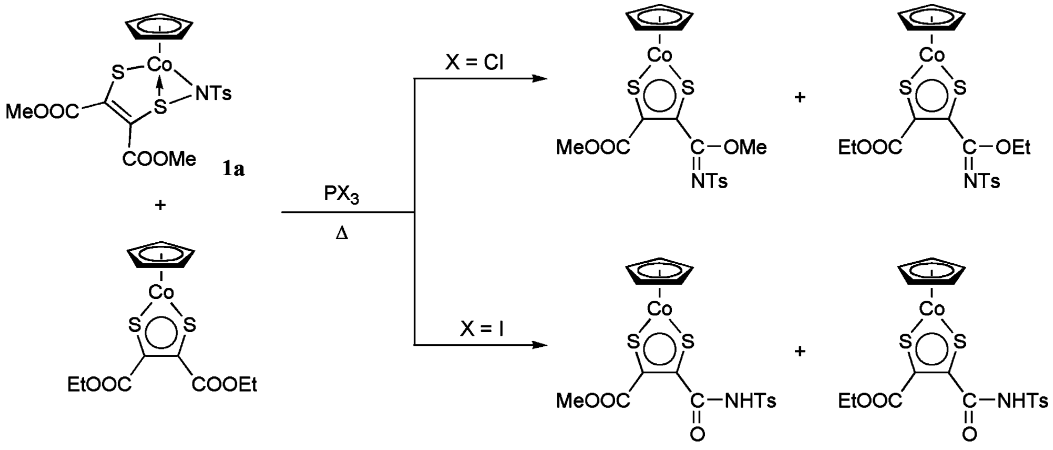
2.5. Crossover experiments

The crossover experiment as shown in Scheme 4 was performed. A mixture of complex **1a** and 10 equivalents of [CpCo{$S_2C_2(COOEt)_2$}] was heated in the presence of PCl_3. Results revealed that not only complex **2a** but also [CpCo{S_2C_2(COOEt)(C=NTsOEt)}] (**2a′**) were formed. If this imine formation is caused by an intramolecular reaction, only complex **2a** should be formed. The formation of complex **2a′** suggests that this reaction is caused by an intermolecular imido-transfer reaction. The formation ratio of complexes **2a** to **2a′** was about 2:3, according to ^{1}H-NMR spectra. In addition, when ten equivalents of complex **4** were used as scavenger, the yield of complex **2a** increased on the basis of the amount of **1a** (Table 1). A similar crossover experiment was also performed using PI_3. Two different amide complexes **3a** and [CpCo{S_2C_2(COOEt)(CONHTs)}] (**3a′**) were formed. So we conclude that the amide formation in this case is also caused by an intermolecular imido-transfer reaction.

Furthermore, in another series of crossover experiments, the reactions of complex **1a** with PCl_3 in the presence of various carbonyl compounds were performed. Benzaldehyde, acetophenone, benzophenone, 3-pentanone, methyl benzoate and acetylferrocene were used as typical carbonyl compounds. When 10 equivalents of the carbonyl compound were used, the reaction yielded complex **2a** and the corresponding imination products of the carbonyl compounds. When these carbonyl compounds were used as the solvents of the reaction, complex **2a** was not formed at all (Table 1). These products were detected by GC-Mass spectra. Therefore, this imination reaction can be applied to a typical carbonyl compound. Especially, tosylimines are very important imines because they are one of the few types of electron-deficient imines that are stable enough to be isolated but reactive enough to undergo addition reactions [20]. However, the synthetic methods of tosylimines have been limited to aldehydes and ketones as a starting material. In this method, the tosylimination is also applied to esters. However, a weak point in this reaction condition is the low efficiency of the reaction. In the future, the reaction condition should be improved and re-investigated.

2.6. Conclusion

Imido metal complexes (M=NTs) often lead to the aziridination of alkenes and the amidation of hydrocarbons. On the other hand, the imido-bridged cobaltadithiolene complex [CpCo{$S_2C_2(COOMe)_2$}(NR)] (R = Ts (**1a**), R = Ms (**1b**)) led to the novel imination and amidation reactions to carbonyl moiety through an intermolecular imido-transfer reaction by the reactions with trivalent phosphorus halides. Although the yields of products were not good, the novel imine complexes [CpCo{S_2C_2(COOMe)(C=NROMe)}] (R = Ts (**2a**), R = Ms (**2b**)) and the novel amide complexes [CpCo{S_2C_2(COOMe)(CONHR)}] (R = Ts (**3a**), R = Ms (**3b**)) were isolated and characterized. An amide group and an imine group are useful for conversions to other nitrogen groups. Therefore, we will be able to obtain the novel cobaltadithiolene complexes with various nitrogen groups. The formations of complexes **2a**–**b** and **3a**–**b** reveal that cobaltathiaziridine as an aziridine analogue showed not only the reactivity of aziridines [7] but also the reactivity of imido metal complexes. It is interesting that the imido-transfer reactions of complexes **1a** and **1b** are different from



Scheme 4.

the intramolecular imido-migration by the reaction with PPh_3 or $P(OPh)_3$.

3. Experimental

3.1. Gneneral remarks

All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. Solvents were purified by ketyl distillation before use. The cobaltadithiolene complexes $[CpCo(S_2C_2Z_2)]$ (Z = COOMe (**4**), COOEt) were prepared by the literature methods [21]. The phosphorus trihalides, PCl_3, PBr_3 and PI_3, were used without further treatment. Silica gel, Wakogel C-300 was obtained from Wako Pure Chemical Industries, Ltd. Mass and IR spectra were recorded on a JEOL JMS-D300 and a Shimadzu model FTIR 8600PC, respectively. GC-Mass spectra were measured with a Shimadzu model GCMS-QP5000. NMR spectra were measured with a JEOL LA500 spectrometer. UV–vis were recorded on a Hitachi model UV-2500PC. Elemental analyses were determined by using a Shimadzu PE2400-II instrument. Melting points were measured by a Yanaco Micro melting point apparatus.

3.2. Reactions of imido-bridged cobaltadithiolene complexes with trivalent phosphorus halides, PX_3

3.2.1. Reactions of imido-bridged cobaltadithiolene complexes with trivalent phosphorus chloride, PCl_3

A solution of complex **1a** (50 mg, 0.1 mmol) and PCl_3 (17.5 μl, 0.2 mmol) in benzene (10 ml) was refluxed for 1 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wako-gel C300, eluent dichloromethane). Products **2a** and **4** were obtained in 4 (2.0 mg, 0.004 mmol) and 39% (13 mg, 0.039 mmol) yields, respectively. Purple solid (**2a**); m.p. 254–255 °C (dec.), Mass (EI^+, 1.3 kV) *m*/*z* (rel. intensity) 483 (M^+, 68.7), 328 (M^+-Ts, 77.1), 188 ($CpCoS_2^+$, 100), 155 (Ts^+, 10.8), 124 ($CpCo^+$, 51.8), 91 ($C_6H_4Me^+$, 53.0), 59 (Co^+, 30.1). ^1H-NMR (500 MHz, $CDCl_3$, vs. Me_4Si) δ 7.56 (d, $J = 8.08$ Hz, 2H, Ar), 7.16 (d, $J = 8.08$ Hz, 2H, Ar), 5.50 (5H, Cp), 3.93 (s, 3H, OMe), 3.76 (s, 3H, OMe), 2.39 (s, 3H, Me). ^{13}C-NMR (125 MHz, $CDCl_3$, vs. Me_4Si) δ 170.0, 165.4, 161.7, 155.7, 142.9, 138.2, 129.0, 127.1, 80.8, 56.7, 52.7, 21.5. UV–vis (CH_2Cl_2) λ_{max} (ε) 554 (6900), 363 (4200), 292 (32 000). IR (KBr) 1699, 1601, 1433, 1319, 1259, 1157 cm^{-1}. Anal. Calc. for $C_{18}H_{18}CoNO_5S_3$: C, 44.72; H, 3.75; N, 2.90; S, 19.90. Found: C, 44.73; H, 3.72; N, 2.95; S, 19.68%

A solution of complex **1a** (250 mg, 0.5 mmol) and PCl_3 (87.5 μl, 1.0 mmol) in the presence of water (9.0 μl, 0.5 mmol) was reacted under refluxing benzene (50 ml) for 1 h. The reaction mixture was separated by column chromatography (Wako-gel C300, eluent dichloromethane). Products **2a** and **4** were obtained in trace amount and 36% (59 mg, 0.179 mmol) yields, respectively.

A solution of complex **1b** (42 mg, 0.1 mmol) and PCl_3 (17.5 μl, 0.2 mmol) in benzene (10 ml) was refluxed for 1 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wako-gel C300, eluent dichloromethane). Products **2b** and **4** were obtained in 5 (2.0 mg, 0.005 mmol) and 39% (13 mg, 0.039 mmol) yields, respectively. Purple solid (**2b**); m.p. 194–195 °C, Mass (EI^+, 1.3 kV) *m*/*z* (rel. intensity) 407 (M^+, 34.9), 328 (M^+-Ms, 32.5), 188 ($CpCoS_2^+$, 100), 124 ($CpCo^+$, 37.3), 79 (Ms^+, 4.8), 59 (Co^+, 22.9). ^1H-NMR (500 MHz, $CDCl_3$, vs. Me_4Si) δ 5.50 (5H, Cp), 3.98 (s, 3H, OMe), 3.87 (s, 3H, OMe), 2.96 (s, 3H, Me). ^{13}C-NMR (125 MHz, $CDCl_3$, vs. Me_4Si) δ 170.4, 165.4, 161.9, 155.5, 80.8, 56.6, 52.8, 42.2. UV–Vis (CH_2Cl_2) λ_{max} (ε) 552 (6900), 361 (4100), 291 (32 000). IR (KBr) 1701, 1612, 1434, 1317, 1259, 1146 cm^{-1}. Anal. Calc for $C_{12}H_{14}CoNO_5S_3$: C, 35.38; H, 3.46; N, 3.44. Found: C, 35.49; H, 3.54; N, 3.44%.

3.2.2. Reactions of imido-bridged cobaltadithiolene complexes with trivalent phosphorus iodide, PI_3

A solution of complex **1a** (50 mg, 0.1 mmol) and PI_3 (82 mg, 0.2 mmol) in benzene (10 ml) was refluxed for 1 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wako-gel C300). In eluent dichloromethane, product **4** was separated. In eluent dichloromethane–ethyl acetate = 10:1, product **3a** was separated. Products **3a** and **4** were obtained in 14 (6.6 mg, 0.014 mmol) and 77% (25.5 mg, 0.077 mmol) yields, respectively. Purple solid (**3a**); m.p. 222–223 °C (dec.), Mass (EI^+, 1.3 kV) *m*/*z* (rel. intensity) 469 (M^+, 12.8), 314 (M^+-Ts, 7.7), 299 (M^+-NHTs, 15.4), 188 ($CpCoS_2^+$, 73.1), 124 ($CpCo^+$, 84.6), 91 ($C_6H_4Me^+$, 100), 59 (Co^+, 55.1). ^1H-NMR (500 MHz, $CDCl_3$, vs. Me_4Si) δ 9.67 (broad, 1H, NH), 8.01 (d, $J = 8.00$ Hz, 2H, Ar), 7.32 (d, $J = 8.00$ Hz, 2H, Ar), 5.49 (5H, Cp), 3.79 (s, 3H, OMe), 2.43 (s, 3H, Me). ^{13}C-NMR (125 MHz, $CDCl_3$, vs. Me_4Si) δ 165.0, 162.7, 160.9, 160.7, 144.9, 135.6, 129.5, 128.7, 81.2, 53.4, 21.7. UV–vis (CH_2Cl_2) λ_{max} (ε) 554 (6800), 363 (4500), 292 (34 000). IR (KBr) 3113, 1713, 1680, 1429, 1339, 1273, 1155 cm^{-1}. Anal. Calc. for $C_{17}H_{16}CoNO_5S_3$: C, 43.49; H, 3.44; N, 2.98; S, 20.49. Found: C, 43.43; H, 3.29; N, 3.03; S, 20.33%.

A solution of complex **1b** (42 mg, 0.1 mmol) and PI_3 (82 mg, 0.2 mmol) in benzene (10 ml) was refluxed for 1 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wako-gel C300). In eluent dichloromethane, product **4** was separated. In eluent dichloromethane–ethyl acetate = 10:1, product **3b** was separated. Products

3b and **4** were obtained in 9 (3.5 mg, 0.009 mmol) and 78% (25.7 mg, 0.078 mmol) yields. Purple solid (**3b**); m.p. 221–222 °C (dec.), Mass (EI$^+$, 1.3 kV) *m*/*z* (rel. intensity) 393 (M$^+$, 9.7), 314 (M$^+$ − Ms, 4.2), 188 ($CpCoS_2^+$, 34.7), 124 (CpCo$^+$, 93.1), 79 (Ms$^+$, 37.5), 59 (Co$^+$, 100). ^{1}H-NMR (500 MHz, $CDCl_3$, vs. Me_4Si) δ 9.2 (broad, 1H, NH), 5.53 (5H, Cp), 3.92 (s, 3H, OMe), 3.40 (s, 3H, Me). ^{13}C-NMR (125 MHz, $CDCl_3$, vs. Me_4Si) δ 164.7, 163.0, 162.6, 160.6, 81.2, 53.5, 41.3. UV–vis (CH_2Cl_2) λ_{max} (ε) 553 (6400), 366 (4200), 292 (31 000). IR (KBr) 3105, 1715, 1697, 1423, 1332, 1258, 1150 cm^{-1}. Anal. Calc. for $C_{11}H_{12}NO_5S_3Co \cdot 1/2(CH_2Cl_2)$: C, 31.69; H, 3.01; N, 3.21. Found: C, 31.82; H, 2.89; N, 3.26%.

3.2.3. Reaction of imido-bridged cobaltadithiolene complex with trivalent phosphorus bromide, PBr_3

A solution of complex **1a** (50 mg, 0.1 mmol) and PBr_3 (19 μl, 0.2 mmol) in benzene (10 ml) was refluxed for 1 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wako-gel C300). In eluent dichloromethane, products **2a** and **4** were separated. In eluent dichloromethane–ethyl acetate = 10:1, product **3a** was separated. Products **2a**, **3a** and **4** were obtained in trace amount, 10 (4.7 mg, 0.01 mmol) and 61% (20 mg, 0.061 mmol) yields, respectively.

3.3. Reactions of imido-bridged cobaltadithiolene complex with pentavalent phosphorus chlorides and Lewis acids

A solution of complex **1a** (50 mg, 0.1 mmol) and PCl_5 (42 mg, 0.2 mmol) in benzene (10 ml) was refluxed for 1 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wako-gel C300, eluent dichloromethane). Product **4** was obtained in a trace amount.

In the cases of O=PCl_3, $AlCl_3$ and $TiCl_4$ instead of PCl_5, the reactions were performed by under the same conditions. The product **4** was obtained in 26 (8.6 mg, 0.026 mmol, O=PCl_3), 38% (12.5 mg, 0.038 mmol, $AlCl_3$) and a trace amount ($TiCl_4$), respectively.

3.4. Crossover experiment

3.4.1. Reactions of imido-bridged cobaltadithiolene complex with trivalent phosphorus halides in the presence of [CpCo{$S_2C_2(COOEt)_2$}]

A mixture of complex **1a** (50 mg, 0.1 mmol) and 10 equivalents of [CpCo{$S_2C_2(COOEt)_2$}] (358 mg, 1.0 mmol) was made to react with PCl_3 (17.5 μl, 0.2 mmol) in refluxing benzene (10 ml) for 1 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wako-gel C300, eluent dichloromethane). The mixture of products **2a** and **2a′** (6.1 mg), the mixture of products **4** and [CpCo{$S_2C_2(COOEt)_2$}] (355 mg) were obtained. The formation ratio of complexes **2a** to **2a′** was about 2:3, and the formation ratio of complexes **4** to [CpCo{$S_2C_2(COOEt)_2$}] was about 1:25, according to ^{1}H-NMR spectra. Purple solid (**2a′**); Mass (EI$^+$, 1.3 kV) *m*/*z* (rel. intensity) 511 (M$^+$, 42.7), 356 (M$^+$ − Ts, 32.9), 188 ($CpCoS_2^+$, 100), 155 (Ts$^+$, 12.2), 124 (CpCo$^+$, 56.1), 91 ($C_6H_4Me^+$, 70.7), 59 (Co$^+$, 26.8). ^{1}H-NMR (500 MHz, $CDCl_3$, vs. Me_4Si) δ 7.55 (d, *J* = 8.20 Hz, 2H, Ar), 7.15 (d, *J* = 8.20 Hz, 2H, Ar), 5.49 (5H, Cp), 4.37 (q, *J* = 7.24 Hz, 2H, OCH_2), 4.20 (q, *J* = 7.24 Hz, 2H, OCH_2), 2.38 (s, 3H, Me), 1.30 (t, *J* = 7.24 Hz, 3H, Me), 1.29 (t, *J* = 7.24 Hz, 3H, Me). HR-Mass (EI$^+$, 70 eV) Calcd for $C_{20}H_{22}CoNO_5S_3$: 510.9992, Found: 510.9992.

A mixture of complex **1a** (50 mg, 0.1 mmol) and 10 equivalents of [CpCo{$S_2C_2(COOEt)_2$}] (358 mg, 1.0 mmol) was made to react with PI_3 (82 mg, 0.2 mmol) in refluxing benzene (10 ml) for 1 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wako-gel C300). In eluent dichloromethane, products **4** and [CpCo{$S_2C_2(COOEt)_2$}]) were separated. In eluent dichloromethane–ethyl acetate = 10:1, products **3a** and **3a′** were separated. The mixture of products **3a** and **3a′** (8.8 mg), the mixture of products **4** and [CpCo{$S_2C_2(COOEt)_2$}] (362 mg) were obtained. The formation ratio of complexes **3a** to **3a′** was about 1:2, and the formation ratio of complexes **4** to [CpCo{$S_2C_2(COOEt)_2$}] was about 2:25, according to ^{1}H-NMR spectra. Purple solid (**3a′**); Mass (EI$^+$, 1.3 kV) *m*/*z* (rel. intensity) 483 (M$^+$, 9.0), 328 (M$^+$ − Ts, 6.4), 188 ($CpCoS_2^+$, 62.8), 124 (CpCo$^+$, 60.3), 91 ($C_6H_4Me^+$, 100), 59 (Co$^+$, 50.0). ^{1}H-NMR (500 MHz, $CDCl_3$, vs. Me_4Si) δ 9.8 (broad, 1H, NH), 7.81 (d, *J* = 7.91 Hz, 2H, Ar), 7.31 (d, *J* = 7.91 Hz, 2H, Ar), 5.48 (5H, Cp), 4.29 (q, *J* = 7.20 Hz, 2H, OCH_2), 2.42 (s, 3H, Me), 1.27 (t, *J* = 7.20 Hz, 3H, Me). HR-Mass (EI$^+$, 70 eV) Calc. for $C_{18}H_{18}CoNO_5S_3$: 482.9679, Found: 482.9669.

3.4.2. Reactions of imido-bridged cobaltadithiolene complex with trivalent phosphorus chloride in the presence of carbonyl compounds

A mixture of complex **1a** (50 mg, 0.1 mmol) and 10 equivalents of carbonyl compounds (benzaldehyde, acetophenone, benzophenone, 3-pentanone, methyl benzoate, acetylferrocene) were reacted with PCl_3 (17.5 μl, 0.2 mmol) in refluxing benzene (10 ml) for 1 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wako-gel C300, eluent dichloromethane). Products **2a** and **4** were obtained. The yields of complexes **2a** and **4** are as follows: using benzaldehyde; **2a** (2.0 mg, 0.004 mmol, 4%) and **4** (15.5 mg, 0.047 mmol, 47%), using acetophenone; **2a** (1.5 mg, 0.003 mmol, 3%) and **4** (14.2

mg, 0.043 mmol, 43%), using benzophenone; **2a** (2.0 mg, 0.004 mmol, 4%) and **4** (13.5 mg, 0.041 mmol, 41%), using 3-pentanone; **2a** (2.4 mg, 0.005 mmol, 5%) and **4** (13.5 mg, 0.041 mmol, 41%), using methyl benzoate; **2a** (2.1 mg, 0.004 mmol, 4%) and **4** (14.5 mg, 0.044 mmol, 44%), using acetylferrocene; **2a** (1.5 mg, 0.003 mmol, 3%) and **4** (21.5 mg, 0.065 mmol, 65%).

For trace analysis of the corresponding imine products, the GC-Mass spectrum instrument was used in the reaction mixture before column separation. The GC-Mass spectral data of the corresponding imine compounds are as follows: (EI$^+$, 1.3 kV) m/z (rel. intensity); using benzaldehyde 259 (M$^+$, 9.0), 155 (Ts$^+$, 44.9), 104 (M$^+$ −Ts, 12.8), 91 ($C_6H_4Me^+$, 100), 77 (Ph$^+$, 14.1), using acetophenone 273 (M$^+$, 6.4), 155 (Ts$^+$, 43.6), 118 (M$^+$ −Ts, 14.1), 91 ($C_6H_4Me^+$, 100), 77 (Ph$^+$, 34.6), using benzophenone 335 (M$^+$, 7.7), 180 (M$^+$ −Ts, 100), 155 (Ts$^+$, 17.9), 91 ($C_6H_4Me^+$, 67.9), 77 (Ph$^+$, 84.6), using 3-pentanone 239 (M$^+$, 5.1), 155 (Ts$^+$, 65.4), 91 ($C_6H_4Me^+$, 100), using methyl benzoate 289 (M$^+$, 7.7), 155 (Ts$^+$, 11.5), 134 (M$^+$ −Ts, 6.4), 91 ($C_6H_4Me^+$, 100), 77 (Ph$^+$, 14.1), using acetylferrocene 381 (M$^+$, 59.0), 316 (M$^+$ −Cp, 5.1), 226 (M$^+$ −Ts, 14.1), 185 (Fc$^+$, 100), 155 (Ts$^+$, 10.3), 91 ($C_6H_4Me^+$, 26.9).

3.5. X-ray diffraction study

Crystal data are shown in Table 2. The measurements of complexes **2a** and **2b** were made on a Rigaku AFC 5S diffractometer with graphite-monochromated Mo–K_α radiation, and the measurement of complex **3a** was made on a Rigaku MERCURY diffractometer with graphite-monochromated Mo–K_α radiation. Each structure was solved by direct methods and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Idealized positions of complexes **2a** and **2b** were used for the teXsan, and idealized positions of complex **3a** were used for the CRYSTAL STRUCTURE crystallographic software package of Molecular Structure Corp.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 199248, 199247, 199246 for compounds **2a**, **2b**, **3a**. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 2
Crystallographic data for compounds **2a**, **2b** and **3a**

	2a	**2b**	**3a**
Empirical formula	$C_{18}H_{18}CoNO_5S_3$	$C_{12}H_{14}CoNO_5S_3$	$C_{17}H_{16}CoNO_5S_3$
Formula weight (g mol^{-1})	483.46	407.36	469.43
T (K)	296	296	296
Crystal color	Purple	Purple	Purple
Crystal habit	Prismatic	Prismatic	Platelet
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	13.877(2)	13.259(4)	9.3528(10)
b (Å)	6.982(2)	7.162(4)	7.6109(6)
c (Å)	21.389(3)	17.509(4)	27.459(3)
β (°)	102.72(1)	93.99(2)	102.732(5)
V (Å^3)	2021.5(8)	1658.7(9)	1906.6(3)
Z	4	4	4
D_{calc} (g cm^{-3})	1.588	1.631	1.635
μ (Mo–K_α) (cm^{-1})	11.89	14.31	12.58
Crystal size (mm)	0.10 × 0.13 × 0.37	0.10 × 0.20 × 0.30	0.20 × 0.03 × 0.12
$2\theta_{max}$ (°)	55.0	55.0	55.0
Unique data (R_{int})	4638 (0.022)	3911 (0.025)	4285 (0.039)
Observations	1909	1453	3164
Variables	271	213	308
R_1, wR_2 (all data)	0.043, 0.050	0.048, 0.054	0.039, 0.027
Goodness-of-fit on F^2	1.11	1.17	1.24
Largest difference peak and hole (e Å^{-3})	0.42, −0.42	0.36, −0.40	0.30, −0.38

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