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Thermal Properties and Crystal Structures of Rhenium(I) Carbonyl Complexes with Tridentate Ligands: Preparation of Rhenium-Containing Ionic Liquids

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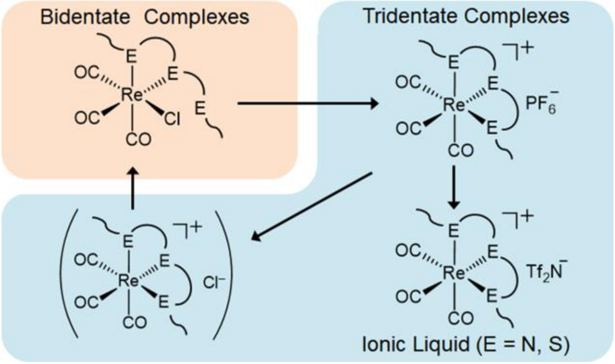
ABSTRACT: Although the coordination chemistry of rhenium complexes is a rapidly expanding research field, little is known about their thermal properties. In this study, we synthesized several rhenium tricarbonyl complexes with tridentate ligands (**L**) having S or N as donor atoms, *fac*-[Re(CO)$_3$**L**]X (X = Tf$_2$N [= bis(trifluoromethanesulfonyl)amide)], PF$_6$) and *fac*-[Re(CO)$_3$**L**Cl], and investigated their thermal properties and crystal structures. The Tf$_2$N salts were room temperature ionic liquids. The *S*-coordinated complexes, having longer coordination bonds, were less thermally stable than the *N*-coordinated complexes. Even though *fac*-[Re(CO)$_3$**L**Cl] are bidentate coordination complexes, they were thermally more stable than the isomeric tridentate complexes *fac*-[Re(CO)$_3$**L**]Cl.



INTRODUCTION

Recently, there has been increased research interest in ionic liquids, which are salts with melting points below 100 °C, in view of their potential applications as solvents and electrolytes.[1] Although many of these liquids contain an organic cation, recent years have seen the development of various functional ionic liquids with a metal ion in the cation.[2,3] There are also many ionic liquids with a metal-containing anion.[4–7] Our laboratory has synthesized many ionic liquids containing cationic metal complexes,[8–12] which exhibit various functions derived from metal complexes such as magnetism and chemical reactivity. However, there are no examples of ionic liquids containing cationic rhenium (Re) complexes.

Interest has recently increased in Re(I) tricarbonyl complexes[13] with regard to their application as radiopharmaceuticals,[14,15] photocatalysts,[16,17] CO delivery agents,[18] optical materials,[19,20] supramolecular systems,[21] etc. In particular, a number of cationic complexes *fac*-$[\mathrm{Re(CO)_3}\mathbf{L}]^+$ with various tridentate chelating ligands (**L**) have been synthesized.[22–26] There are many neutral bidentate complexes with an anionic ligand.[27–31] However, little is known about their thermal properties. In addition, the examples of Re-containing ionic liquids are limited to onium salts with ReO_4 anions.[32] For this reason, in this study, we aimed to develop ionic liquids containing rhenium complexes and evaluate the thermal properties of these and related complexes.

In this study, we used tridentate chelating ligands (**L**) to synthesize the salts of cationic Re tricarbonyl complexes *fac*-$[\mathrm{Re(CO)_3}\mathbf{L}]\mathrm{X}$ (X = Tf_2N [= bis(trifluoromethanesulfonyl)amide], PF_6) and neutral complexes *fac*-$[\mathrm{Re(CO)_3}\mathbf{L}\mathrm{Cl}]$ (Figure 1). A thioether ligand ($\mathbf{L^S}$) and triamine ligand ($\mathbf{L^N}$) were used as tridentate chelating ligands, and a thioether ligand ($\mathbf{L^{S'}}$) with terminal methyl groups was also used for the synthesis of neutral complexes. Tf_2N is often used as the counteranion in ionic liquids because it tends to give salts with low melting points.[1] We investigated the thermal properties and crystal structures of these complexes and the reason for the formation of bidentate complexes *fac*-[Re(CO)$_3$**L**Cl] despite the use of tridentate ligands. The Tf$_2$N salts were found to be ionic liquids.

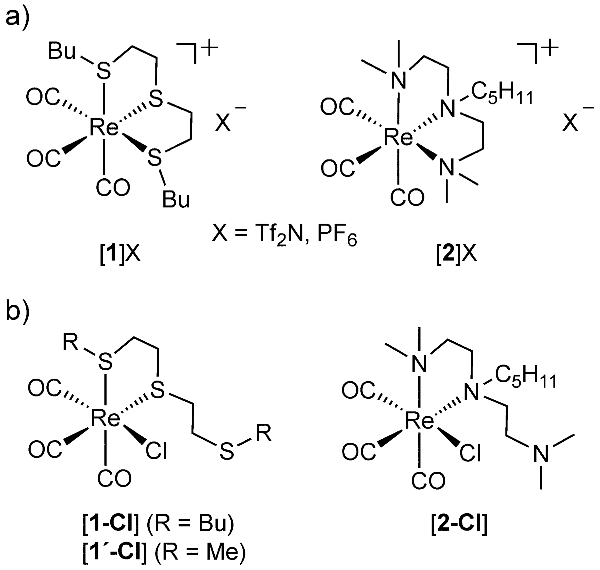


Figure 1. Structural formulas of the complexes synthesized in this study.

RESULTS AND DISCUSSION

Synthesis and Properties. The schemes for synthesis of the complexes with the thioether ligand are shown in Figure 2. Through the reaction of [Re(CO)$_5$Cl] with the ligand, we obtained [**1-Cl**] and [**1'-Cl**] as a colorless liquid and solid, respectively (yield: ~60%). These are neutral complexes with the Cl ligand, in which the chelating ligand exhibits bidentate coordination. [**1**]PF$_6$ was obtained as a colorless solid by the reaction of [**1-Cl**] and AgPF$_6$ (yield: 35%). Through the anion exchange of this salt, [**1**]Tf$_2$N was obtained as a colorless liquid (yield: 82%).

The complexes with the triamine ligand were synthesized in a similar manner. In contrast to the thioether ligands, the triamine ligand, having only one alkyl chain, afforded only solid products. The reaction of [Re(CO)$_5$Cl] with **L$^{\mathbf{N}}$** produced [**2-Cl**] as a colorless solid (yield: 28%). Performing this reaction in the presence of AgPF$_6$ produced a colorless solid [**2**]PF$_6$ (yield: 37%).

The crystals of [**2**]Tf_2N were obtained in very low yield through the anion exchange of [**2**]PF_6 followed by recrystallization.

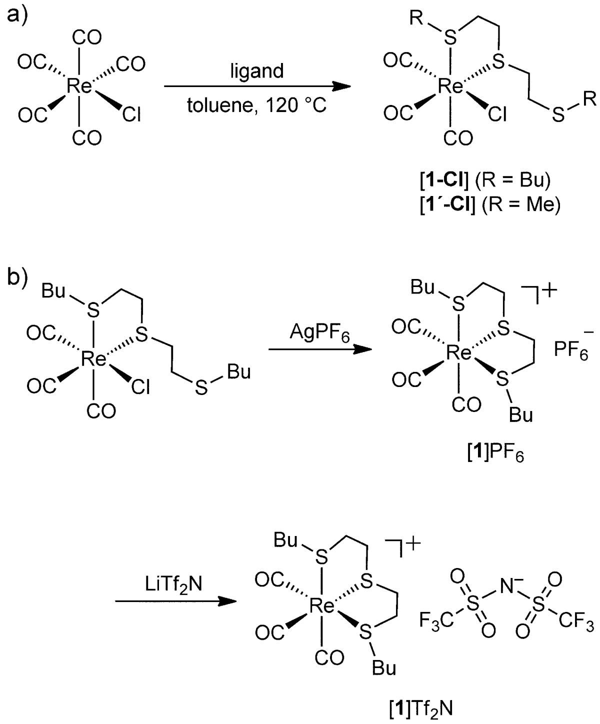


Figure 2. Schemes for synthesis of complexes with thioether ligands.

Thermal Properties. We performed differential scanning calorimetry (DSC) measurements of the complexes. Table 1 shows their melting points and melting entropies, and Figure S1 (ESI) shows their DSC curves. The melting point of [**2**]Tf_2N was determined using an automated melting point apparatus owing to the scarcity of the sample.

[**1**]Tf_2N and [**2**]Tf_2N were room-temperature ionic liquids with melting points below 100 °C. [**1**]Tf_2N was a liquid and exhibited a glass transition at –35 °C. [**2**]Tf_2N was a crystalline solid that melted at 86.9 °C. This salt remained liquid at ambient temperature when cooled from the melt and underwent a glass transition at around –30 °C. [**1**]PF_6 was a solid, which exhibited a solid-phase transition and melting successively at 143 °C (ΔS = 61.4 J mol^{-1} K^{-1}), exhibiting

crystallization upon cooling from the melt. [**2**]PF_6 melted at 149.9 °C (ΔS = 24.3 J mol^{-1} K^{-1}) and exhibited a glass transition (T_g = 31 °C) upon cooling from the melt. The Tf_2N salts exhibited much lower melting points than the PF_6 salts owing to the larger size and unsymmetrical structure of the anion.

[**1-Cl**] was a liquid exhibiting a glass transition at –32 °C, whereas this complex formed crystals at −50 °C in organic solvent. [**2-Cl**] was a solid that showed a solid-phase transition at 85.7 °C (ΔS = 53.9 J mol^{-1} K^{-1}) and melted at 99.2 °C (ΔS = 61.4 J mol^{-1} K^{-1}). Cooling the liquid led to a glass transition at T_g = –8 °C. Their melting points and glass transition temperatures were comparable to those of the Tf_2N salts, much lower than those of the PF_6 salts because the chloride complexes are neutral complexes.

The ratios of melting point to glass transition temperature (T_g/T_m) for [**1**]PF_6 and [**2-Cl**] were 0.72, which is consistent with the empirical value for molecular liquids (T_g/T_m = 0.67).[33]

Table 1. Glass transition temperatures (T_g), melting points (T_m), melting entropies (ΔS), and decomposition temperatures (T_{dec}) of the complexes

Compound	T_g / °C	T_m / °C	ΔS / J mol^{-1} K^{-1}	$T_{dec}{}^{a}$ / °C
[**1**]Tf_2N	–35			
[**2**]Tf_2N	~ –30[b]	86.9		
[**1**]PF_6		143.3	61.4[c]	242
[**2**]PF_6	31	149.9	24.3	303
[**1-Cl**]	–32			232
[**2-Cl**]	–8	99.2	21.1	218

[a]Decomposition temperatures (−5 wt%) determined by TG analysis. [b]Observed under microscope. [c]The data include the contribution of a solid-phase transition.

Thermal Stability. We performed thermogravimetric (TG) measurements of the complexes to investigate their thermal stability. Figure 3 shows the TG curves measured under nitrogen gas flow and a sweep rate of 10 K min^{-1}. The decomposition temperatures (–5 wt%) are listed in Table 1.

The decomposition temperatures of [**1**]PF_6 and [**2**]PF_6 (–5 wt%) were 242 and 303 °C, respectively, where the latter was around 60 °C higher and exhibited weight loss at higher temperatures. The decomposition temperatures of [**1-Cl**] and [**2-Cl**] were similar at 232 and 218 °C, respectively. However, the latter salt exhibited a gradual weight loss over a higher temperature range. These results suggest that *N*-coordinated complexes are more stable than *S*-coordinated complexes and are less susceptible to thermal ligand loss. This is consistent with the coordination preference of the N atom over the S atom reported for some Re tricarbonyl complexes.[34,35] Each complex showed a weight loss of around –60 wt% in one step, which corresponds to the loss of a tridentate ligand and three CO molecules (calculated values: 49–61 wt%).

A comparison of decomposition temperatures between [**1**]PF_6 and [**1-Cl**] and between [**2**]PF_6 and [**2-Cl**] showed that, in each case, the decomposition temperature of the tridentate complexes is higher than that of the chloride-coordinated bidentate complexes. This result likely suggests that ligand coordination is stronger in the tridentate complexes than in the bidentate complexes.

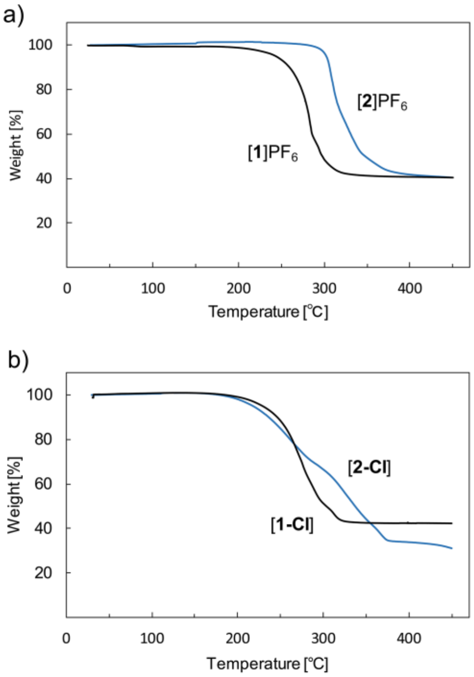
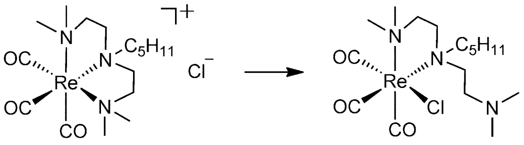


Figure 3. TG curves of (a) [**1**]PF_6 and [**2**]PF_6 and (b) [**1-Cl**] and [**2-Cl**].

Conversion from [2]Cl to [2-Cl]. As seen in the previous section, the reaction of $[Re(CO)_5Cl]$ with the ligands produced the bidentate complexes [**1-Cl**] and [**2-Cl**], despite using the tridentate ligands. A similar phenomenon has also been reported with Re complexes having a tridentate ligand consisting of quinolines and aryl thioethers.[23] To investigate the origin of these phenomena, we synthesized the isomeric tridentate salt [**2**]Cl and compared its stability to that of [**2-Cl**]. [**2**]Cl was synthesized from [**2**]PF_6 by anion exchange using an ion exchange resin, but this salt was found to gradually convert to [**2-Cl**], even at −40 °C in a solid state (Figure 4). As shown in Figure 5, examination by ^{1}H NMR showed that [**2**]Cl undergoes complete conversion to [**2-Cl**] in 1 week in a $CDCl_3$ solution at 40 °C.

This result indicates that the chloride-coordinated complex is thermally more stable than the chloride salt, which accounts for the formation of the chloride-coordinated bidentate complex. It is thus necessary to use a weakly coordinating anion to obtain a salt. As a related phenomenon, a coordination equilibrium between an iodide-coordinated neutral complex and the salt of a tridentate complex has been reported in a Pt^{IV} complex with a tridentate ligand.[36] Such a mechanism would be useful to control the structures of coordination compounds.



[**2**]Cl [**2-Cl**]

Figure 4. Structural conversion from [**2**]Cl to [**2-Cl**].

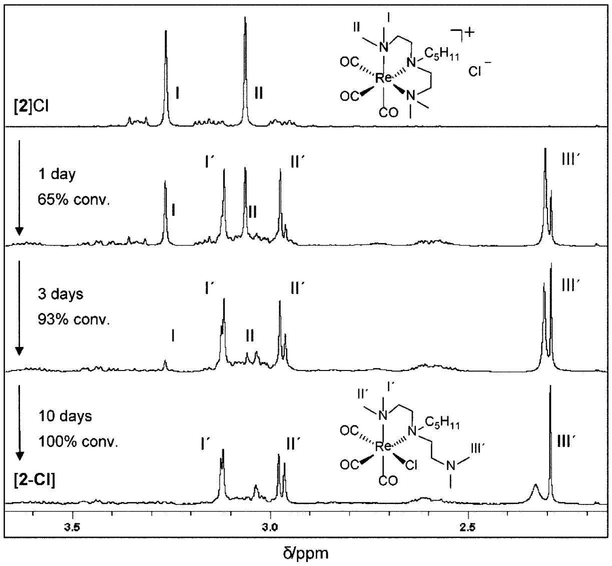


Figure 5. Change over time in the ^1H NMR spectra when [**2**]Cl in $CDCl_3$ is maintained at 40 °C (measuring temperature: 25 °C).

Crystal Structures of $[Re(CO)_3L]X$. Crystal structures of [**1**]PF_6, [**2**]PF_6, and [**2**]Tf_2N were determined at low temperature. The space groups of [**1**]PF_6 and [**2**]PF_6 are P–1 (Z = 4) and Cc (Z = 8), respectively, and both have two crystallographically independent molecules. The cations have an octahedral six-coordinate structure in which the ligand coordinates to the rhenium atom in a tridentate fashion. Figure 6 shows the molecular structures of these cations. In [**2**]PF_6, the cation containing Re2 exhibits disorder. The pentyl group, ethylene moiety, and terminal methyl groups exhibit 2-fold disorder with an occupancy ratio of approximately 1:1. In addition, the four F atoms of the anion exhibit 2-fold disorder at an approximately 1:1 ratio.

The Re–CO bond lengths in [**1**]PF_6 (1.921(5)–1.935(5) Å) are longer than those in [**2**]PF_6 (1.896(8)–1.922(8) Å), which is likely due to the difference in the *trans* effect of S and N atoms. The Re–S and Re–N bond lengths in [**1**]PF_6 and [**2**]PF_6 are 2.441(1)–2.475(1) Å and 2.237(6)–2.315(6) Å, respectively. In [**1**]PF_6, there is an intermolecular S···S contact (3.39 Å) between cation II (between S5), which is 0.2 Å shorter than the vdW distance. The coordination structure of [**1**]PF_6 is almost the same as that of similar *S*-coordinated complexes.[22] A number of N_3C_3 coordination complexes similar to [**2**]PF_6 have also been reported.[24] In each case, the coordination bonds are longer in the *S*-coordinated complexes than in the *N*-coordinated complexes, which is consistent with the lower thermal stability of the *S*-coordinated complexes.

The space group of [**2**]Tf_2N is P–1 (Z = 4), and it has two crystallographically independent molecules. Figure 7 shows the molecular structures of the cation containing Re1 (cation I) and the anions. The structures of cation I and II are similar. The coordination structure of the cations are almost identical to that in [**2**]PF_6. The Re–CO and Re–N bond lengths are 1.897(5)–1.940(5) Å and 2.235(3)–2.304(3) Å, respectively. Anion I has a *transoid* structure, whereas anion II exhibits disorder, in which the *transoid* and *cisoid* structures exist with an occupancy ratio of 0.43:0.57.

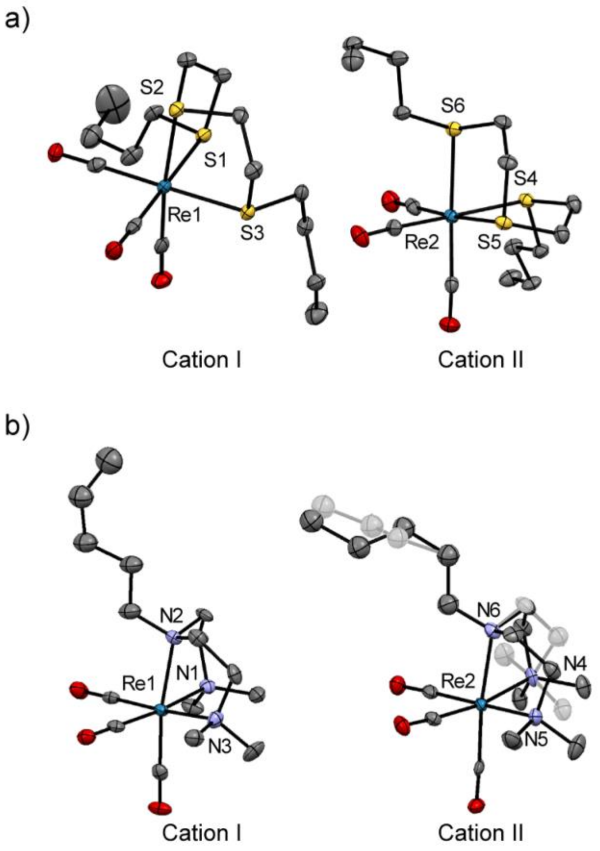


Figure 6. Molecular structures of the cations in (a) [**1**]PF_6 and (b) [**2**]PF_6. The hydrogen atoms have been omitted. The lower occupancy moiety in the disordered part is shown as partially transparent.

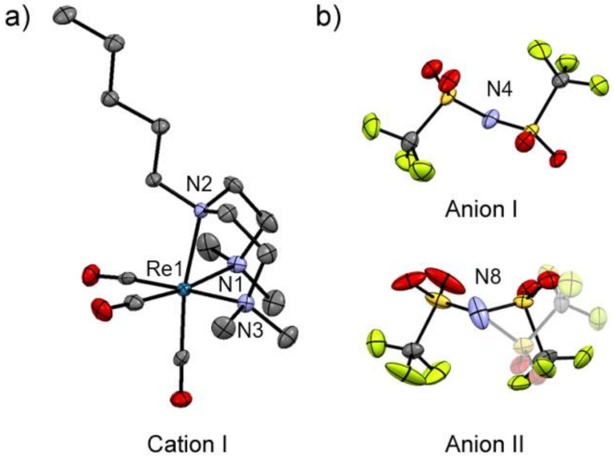


Figure 7. Molecular structures of the (a) cation and (b) anions in [**2**]Tf_2N. The hydrogen atoms have been omitted. The lower occupancy moiety in the disordered part in anion II is shown as

partially transparent.

Crystal Structures of [Re(CO)$_3$LCl]. Crystal structures of [**1'-Cl**] and [**2-Cl**] were determined at low temperature. Their space groups are $P2_1/n$ (Z = 4) and *R*3c (Z = 18), respectively, and each has one crystallographically independent molecule. Figure 8 shows the molecular structures of the complexes. Although both complexes have an octahedral coordination structure, the tridentate ligand exhibits bidentate coordination, and one of its donor atoms is free. [**2-Cl**] exhibits severe disorder where the uncoordinated terminal amino group and pentyl group are exchanged (Figure 6b), and their occupancy ratios are 0.58 and 0.42, respectively.

The Re–CO bond ([**1'-Cl**]: 1.954(3) Å, [**2-Cl**]: 1.927(12) Å) that is *trans* to the Re–Cl bond is slightly longer than the other Re–CO bonds ([**1'-Cl**]: 1.924(3) Å, 1.933(3) Å, [**2-Cl**]: 1.893(13) Å, 1.903(14) Å). Similar to [**1**]PF_6 and [**2**]PF_6, the Re–CO bonds in [**1'-Cl**] are longer than the corresponding bonds in [**2-Cl**]. The Re–Cl bond lengths are 2.4851(8) and 2.494(3) Å, respectively. The Re–S bond lengths in [**1'-Cl**] are 2.4847(8) and 2.5006(8) Å, while the Re–N bond lengths in [**2-Cl**] are 2.230(8) and 2.304(9) Å. The coordination geometries of [**1-Cl**] and [**2-Cl**] are similar to those of similar *S*-coordinated[27] and *N*-coordinated complexes,[28] respectively.

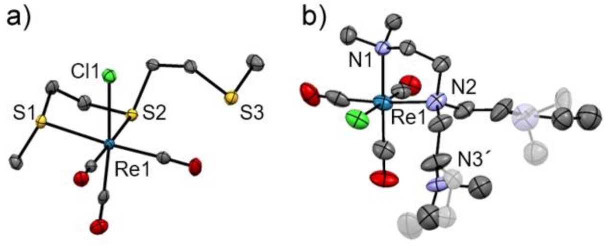


Figure 8. Molecular structures of (a) [**1'-Cl**] and (b) [**2-Cl**]. The hydrogen atoms have been omitted. The lower occupancy moiety in the disordered part is shown as partially transparent.

CONCLUSION

In this study, we synthesized the salts of rhenium carbonyl complexes *fac*-[Re(CO)$_3$**L**]X (X = Tf$_2$N, PF$_6$) with tridentate chelating ligands having S or N donor atoms and investigated their thermal properties. Of the compounds synthesized, the Tf$_2$N salts were ionic liquids, which are the first examples of ionic liquids containing cationic rhenium complexes. Thermal analysis revealed that the *S*-coordinated complexes are thermally less stable than the *N*-coordinated complexes. Furthermore, to understand the formation of bidentate complexes *fac*-[Re(CO)$_3$**L**Cl] from the tridentate ligands, we synthesized the isomeric salt *fac*-[Re(CO)$_3$**L**]Cl and found that this complex thermally transformed to the bidentate complex.

The chemistry of Re complexes has recently become a vastly expanding field. This study provides useful knowledge on the thermal properties of Re complexes and shows that Re complexes can be used to produce ionic liquids. The use of Re complexes would lead to the creation of various functional ionic liquids in the future, considering their diverse functionalities. We are currently developing Re-containing ionic liquids with photochemical functions.

EXPERIMENTAL SECTION

General. The compounds, 1-[(2-{[2-(butylthio)ethyl]thio}ethyl)thio]butane (**L**$^{\mathbf{S}}$) and 1,1´-thiobis[2-(methylthio)]ethane (**L**$^{\mathbf{S'}}$), were prepared according to the methods described in the literature,[37] and 1,1,7,7-tetramethyl-4-pentyldiethylenetriamine (**L**$^{\mathbf{N}}$) was prepared using a method described in the literature.[38,39] ^{1}H NMR spectra were recorded on a JEOL JNM-ECL-400 spectrometer. FT-IR spectra were recorded using a Thermo Scientific Nicolet iS5. DSC measurements were performed using a TA Q100 differential scanning calorimeter at a scan rate of 10 °C min^{-1}. The melting point of [**2**]Tf$_2$N was determined using an SRS MPA100 OptiMelt automated melting point system at a heating rate of 1 °C min. Thermogravimetric analyses were performed under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} on a Rigaku TG8120 thermogravimetric analyzer. ESI-MS spectra were recorded using a Thermo Fisher Scientific LTQ-Orbitrap Discovery.

Synthesis of Thioether Complexes. ***[Re(CO)$_3$L^{S}Cl] ([1-Cl]).*** A toluene solution (0.1 mL) of $\mathbf{L^1}$ (22 mg, 0.083 mmol) was added to [Re(CO)$_5$Cl] (30 mg, 0.083 mmol), and the mixture was refluxed at 120 °C for 1 h. The solution was evaporated under reduced pressure and dried under vacuum. The product was purified and isolated as solids at –50 °C by adding hexane to a dichloromethane solution, followed by the removal of the mother liquid. This procedure was repeated three times to obtain [**1-Cl**], which was a pale yellow liquid at ambient temperature (yield: 27 mg, 58%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.92 (t, 3H, C*H*$_3$, *J* = 7.20 Hz), 0.97 (t, 3H, C*H*$_3$, *J* = 7.30 Hz), 1.42 (sext, 2H, C*H*$_2$, *J* = 7.30 Hz), 1.51 (sext, 2H, C*H*$_2$, *J* = 7.30 Hz), 1.57 (quin, 2H, C*H*$_2$, *J* = 12.0 Hz), 1.72 (br, 2H, C*H*$_2$), 2.60 (t, 4H, C*H*$_2$, *J* = 8.0 Hz), 2.69–3.17 (br, 8H, C*H*$_2$). Anal. Calcd. for $C_{15}H_{26}O_3S_3ReCl$: C, 31.48; H, 4.58; N, 0.00. Found: C, 31.01, H, 4.00; N, 0.05. ESI-MS (*m*/*z*) Calcd. for [Re(CO)$_3$$\mathbf{L^1}$]$^+$: 537.0602 (100%), 535.0574 (59.7%), 538.0635 (16.2%). Found: 537.0605, 535.0584, 538.0634. FT-IR (ATR, cm^{-1}): 532, 626, 732, 835, 1199, 1262, 1416, 1887, 1999 (CO), 2028 (CO), 2870, 2926, 2956.

[Re(CO)$_3$L^S]PF$_6$ ([1]PF$_6$). A mixture of AgPF$_6$ (18 mg, 0.075 mmol) and [**1-Cl**] (43 mg, 0.075 mmol) in acetone (0.2 mL) was stirred at 50 °C for 2 days in the dark under a nitrogen atmosphere. The precipitated AgCl was removed using a syringe filter, and the filtrate was evaporated under reduced pressure. The crude product was recrystallized by diffusing diethyl ether vapor into a dichloromethane solution for 3 days at –4 °C. The product was obtained as colorless crystals (yield: 18.8 mg, 35%).^{1}H NMR (400 MHz, CDCl$_3$): δ 1.00 (t, 6H, C*H*$_3$, *J* = 7.30

Hz), 1.56 (sext, 4H, C*H*$_2$, *J* = 7.50 Hz), 1.74 (quin, 4H, C*H*$_2$), 2.80–3.08 (br, 8H, C*H*$_2$). ^{19}F NMR (400 MHz, CDCl$_3$): δ –72.23 (d, *J* = 713.18 Hz). Anal. Calcd. for $C_{15}H_{26}O_3S_3RePF_6$: C, 26.43; H, 3.84; N, 0.00. Found: C, 26.12, H, 3.79; N, 0.00. FT-IR (ATR, cm^{-1}): 536, 556, 571, 597, 619, 741, 824 (PF_6^-), 1296, 1420, 1937 (CO), 2038 (CO), 2960.

[Re(CO)$_3$L^S]Tf$_2$N ([1]Tf$_2$N). An aqueous solution (0.2 mL) of LiTf$_2$N (27 mg, 0.095 mmol) was added to an acetone solution (0.2 mL) of [**1**]PF$_6$ (22 mg, 0.032 mmol), and the mixture was stirred at room temperature for 2 h. The acetone was evaporated under reduced pressure and the resulting suspension was extracted four times with dichloromethane. The organic layer was washed three times with water and dried over anhydrous sodium sulfate. The procedure was repeated 2 times, at which point the complete disappearance of PF$_6$ was confirmed by ^{19}F NMR spectroscopy (CDCl$_3$). The obtained liquid was dried under a vacuum at room temperature for 3 h. The product was dissolved in a small amount of dichloromethane and passed through a short plug of alumina (eluent: acetonitrile). The solution was evaporated and dried under a vacuum at 60 °C for 12 h to afford a colorless liquid (yield: 22 mg, 82%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.99 (t, 6H, C*H*$_3$, *J* = 7.30 Hz), 1.50 (sext, 4H, C*H*$_2$, *J* = 7.50 Hz), 1.74 (quin, 4H, C*H*$_2$), 2.80–3.08 (br, 8H, C*H*$_2$). ^{19}F NMR (400 MHz, CDCl$_3$): δ –78.66 (s). Anal. Calcd. for $C_9H_{14}O_3S_3ReCl$: C, 24.99; H, 3.21; N, 1.71. Found: C, 25.60; H, 2.87; N, 2.08. FT-IR (ATR, cm^{-1}): 528 (CF$_3$), 652 (SNS), 739, 761 (SNS), 835, 921, 946, 1133 (SO), 1225 (CF$_3$), 1347 (SO), 1418, 1712, 1935 (CO), 2042, 2876, 2963.

[Re(CO)$_3$L^{S}'Cl] ([1'-Cl]). [**1'-Cl**] was synthesized by the same procedure as for [**1-Cl**], using [Re(CO)$_5$Cl] (30 g, 0.08 mmol) and **L$^{S'}$** (20 mg, 0.11 mmol). The crude product was recrystallized by the diffusion of hexane into a dichloromethane solution over 3 days at –4 ℃. The product was obtained as colorless crystals (yield: 22.3 mg, 57%). ^{1}H NMR (400 MHz,

$CDCl_3$): δ 2.14 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.70–2.83 (m, 4H, CH_2), 2.83–3.00 (m, 4H, CH_2). Anal. Calcd. for $C_9H_{14}O_3S_3ReCl$: C, 22.15; H, 2.89; N, 0.00. Found: C, 21.80; H, 2.10; N, 0.06. FT-IR (ATR, cm^{-1}): 570, 636, 743, 831, 970, 1021, 1108, 1180, 1271, 1379, 1416, 1715, 1882 (CO), 2023 (CO), 2360, 2920.

Synthesis of Triamine Complexes. ***[Re(CO)$_3$L^{N}Cl] ([2-Cl]).*** [**2-Cl**] was synthesized using the same procedure as for [**1-Cl**], using $[Re(CO)_5Cl]$ (30 g, 0.08 mmol) and **L$^{\mathbf{N}}$** (30 mg, 0.14 mmol). The residue was dissolved in dichloromethane and treated with activated carbon. Subsequently, the crude product was dissolved in dichloromethane/hexane, and the solution was cooled slowly from room temperature to –40 °C. The product was obtained as colorless crystals (yield: 11.9 mg, 28%).^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85–0.97 (m, 3H), 1.19–1.63 (m, 6H), 1.74–1.93 (m, 1H), 2.28 (d, 6H, CH_3), 2.50–2.72 (m, 3H), 2.97 (d, 3H, CH_3), 3.00–3.11 (m, 3.5H), 3.14–3.32 (m, 0.5H), 3.39–3.52 (m, 1H) , 3.53–3.65 (m, 1H). FT-IR (ATR, cm^{-1}): 532, 550, 638, 657, 740, 789, 810, 946, 1032, 1098, 1158, 1262, 1291, 1456, 1879 (CO), 2015, 2768, 2820, 2933. Anal. Calcd. for $C_{16}H_{31}O_3N_3Re$ Cl: C, 35.91; H, 5.84; N, 4.85. Found: C, 36.04, H, 5.97; N, 7.79.

[Re(CO)$_3$L^N]PF$_6$ ([2]PF$_6$). A mixture of $[Re(CO)_5Cl]$ (48.4 mg, 0.13 mmol), $AgPF_6$ (68.7 mg, 0.27 mmol), and **L$^{\mathbf{N}}$** (37.8 mg, 0.17 mmol) in toluene (0.2 mL) was stirred at 120 °C for 2.5 h in the dark under nitrogen atmosphere. The precipitated AgCl was removed using a syringe filter, and the filtrate was evaporated under reduced pressure. The residue was dissolved in dichloromethane, and the precipitated unreacted $AgPF_6$ was removed using a syringe filter. The filtrate was washed three times with water, and the organic layer was dried over anhydrous sodium sulfate. The obtained oil was dissolved in a small amount of dichloromethane and passed through a short plug of alumina (eluent: acetonitrile), and the solvent was removed by evaporation. The slow cooling of a dichloromethane-ether solution of the product to –40 °C afforded the desired product as colorless platelet crystals (yield: 14.8 mg, 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, 3H, CH_3, *J* = 7.34 Hz), 1.27–1.43 (m, 4H, CH_2CH_2), 1.75 (quin, 2H, CH_2, *J* = 7.30 Hz), 2.93 (s, 6H, CH_3), 2.94–3.02 (m, 2H, CH_2), 3.15–3.24 (m, 4H, CH_2), 3.27 (s, 6H, CH_3), 3.31–3.39 (m, 4H, CH_2). ^{19}F NMR (400 MHz, $CDCl_3$): δ –72.33 (d, *J* = 712.68 Hz). FT-IR (ATR, cm^{-1}): 541, 632, 659, 749, 782, 827 (PF_6), 932, 965, 1003, 1040, 1464, 1913 (CO), 2029, 2951. Anal. Calcd. for $C_{16}H_{31}O_3N_3RePF_6$: C, 29.81; H, 4.85; N, 6.52. Found: C, 29.90, H, 4.86; N, 6.63. ESI-MS (m/z) Calcd. for $[Re(CO)_3\mathbf{L}^\mathbf{N}]^+$: 500.1923 (100%), 498.1895 (59.7%), 501.1957 (17.3%). Found: 500.1928, 498.1904, 501.1961. $[PF_6]^-$: 144.9642 (100%). Found: 144.9653. Furthermore, this complex could be synthesized by the reaction of [**2-Cl**] with an equimolar amount of $AgPF_6$ in acetone; however, the yield was low (10% yield).

$[Re(CO)_3L^N]Tf_2N$ ([2]Tf_2N). [**2**]Tf_2N was synthesized by the same procedure as [**1**]Tf_2N, using [**2**]PF_6 (24.2 g, 0.038 mmol) and $LiTf_2N$ (34.2 mg, 0.12 mmol). The crude product was dissolved in a small amount of dichloromethane and purified by a short plug of alumina (eluent: acetonitrile). The solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane and treated with activated carbon. After the disappearance of PF_6 was confirmed by ^{19}F NMR spectroscopy ($CDCl_3$), the solution was evaporated and dried under a vacuum to afford a pale yellow liquid (yield: 14 mg, 47%). Recrystallization of the product from dichloromethane–hexane afforded a small amount of platelet single crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, 3H, CH_3, *J* = 7.34 Hz), 1.27–1.43 (m, 4H, CH_2CH_2), 1.70–1.81 (m, 2H, CH_2), 2.94 (s, 6H, CH_3), 2.90–3.00 (m, 2H, CH_2), 3.15–3.26 (m, 4H, CH_2), 3.28 (s, 6H, CH_3), 3.32–3.46 (m, 4H, CH_2). ^{19}F NMR (400 MHz, $CDCl_3$): δ –78.59 (s). ESI-MS (*m*/*z*) Calcd. for $[Re(CO)_3\mathbf{L}^\mathbf{N}]^+$: 500.1923 (100%), 498.1895 (59.7%), 501.1957 (17.3%). Found: 500.1918, 498.1885, 501.1944. $[Tf_2N]^-$: 279.9173 (100%), 281.9131 (8.9%), 280.9207 (2.2%). Found: 279.9185, 281.9141, 280.9228. FT-IR (ATR, cm^{-1}): 532 (CF_3), 544, 555, 566, 609 (SNS), 1051, 1175 (SO), 1351 (SO), 1904 (CO), 2027 (CO).

$[Re(CO)_3L^N]Cl$ ([2]Cl). A solution of [**2**]PF_6 (32.8 mg, 0.05 mmol) in a mixture of methanol (20 mL) and dichloromethane (2 mL) was charged on an anion exchange column (Dowex 1X8-100, chloride form, eluent: methanol). The product was eluted by methanol, and the eluent was concentrated at room temperature. The product was eluted through an ion-exchange column once more. After the disappearance of PF_6 was confirmed by ^{19}F NMR spectroscopy ($CDCl_3$), the solvent was evaporated under reduced pressure at room temperature, and the product was dried under a vacuum. The product obtained as a white powder (yield: 24 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, 3H, CH_3, J = 7.20 Hz), 1.27–1.43 (m, 4H, CH_2CH_2), 1.76 (quin, 2H, CH_2, J = 7.70 Hz), 2.93–3.01 (m, 2H, CH_2), 3.07 (s, 6H, CH_3), 3.11–3.20 (m, 2H, CH_2), 3.26 (s, 6H, CH_3), 3.31–3.38 (m, 2H, CH_2), 3.73–3.95 (m, 4H, CH_2). This salt gradually converted to [**2-Cl**] even in the solid-state. The analytical data after the conversion were consistent with those of [**2-Cl**].

Single Crystal X-ray Diffraction Studies. Single crystals of [**1′-Cl**] for use in X-ray crystallography were obtained by the diffusion of hexane into a dichloromethane solution at −4 °C for 3 days. The single crystals of [**1**]PF_6 were obtained by diffusing diethyl ether vapor into a dichloromethane solution. The single crystals of [**2-Cl**] and [**2**]PF_6 were obtained by slow cooling of a solution in dichloromethane/hexane and dichloromethane/diethyl ether, respectively, from room temperature to −40 °C. XRD data were collected using a Bruker APEX II Ultra CCD diffractometer with MoKα radiation at 100 K or 90 K. The structures were determined by direct methods using SHELXL.[40] The crystallographic parameters are shown in Tables S1 and S2 (ESI).

ASSOCIATED CONTENT

Supporting Information

DSC traces, packing diagrams, and crystallographic tables.

Accession Codes

CCDC-1921415 ([**1**]PF_6), 1936030 ([**2**]PF_6), 1958535 ([**2**]Tf_2N), 1921414 ([**1'-Cl**]), and 1921416 ([**2-Cl**]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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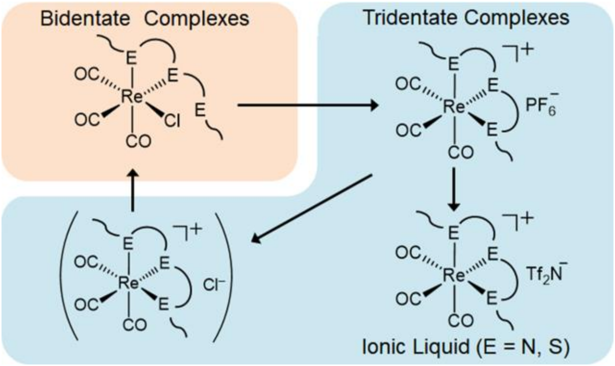
For Table of Contents Only

We synthesized ionic liquids *fac*-[Re(CO)$_3$**L**]Tf$_2$N (**L**: tridentate ligand), solid salts *fac*-[Re(CO)$_3$**L**]PF$_6$, and neutral complexes *fac*-[Re(CO)$_3$**L**Cl] and elucidated their thermal properties and crystal structures.



Supporting Information

Thermal Properties and Crystal Structures of Rhenium(I) Carbonyl Complexes with Tridentate Ligands: Preparation of Rhenium-Containing Ionic Liquids

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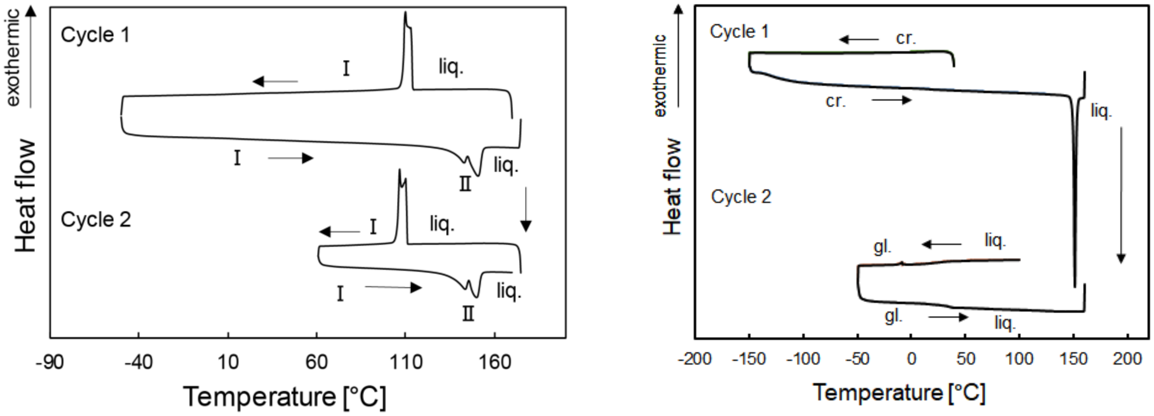
a) [**1**]PF_6 b) [**2**]PF_6



c) [**2-Cl**]

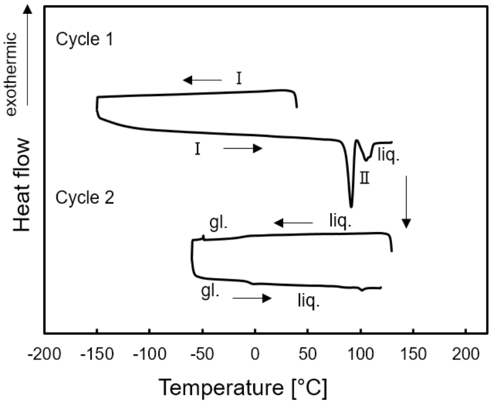
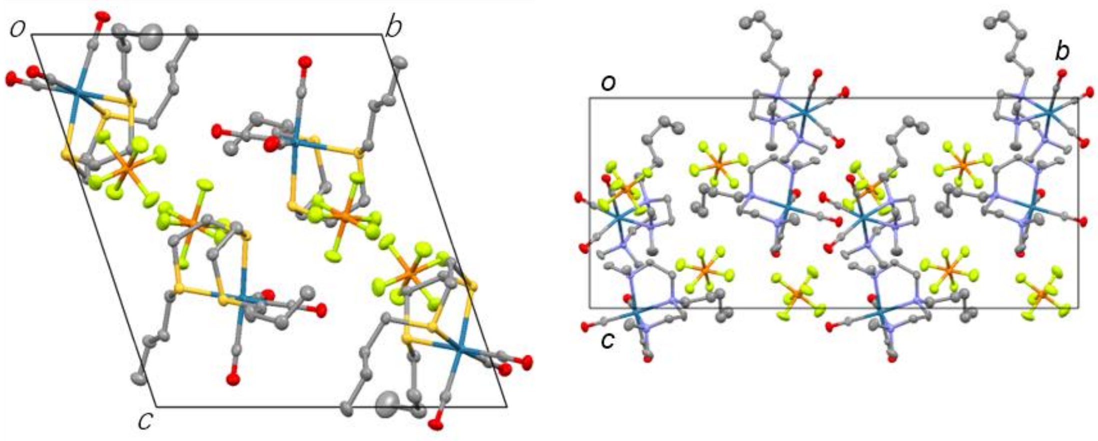
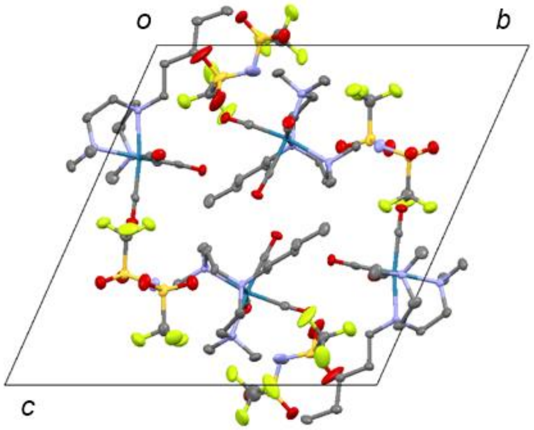


Figure S1. DSC traces.

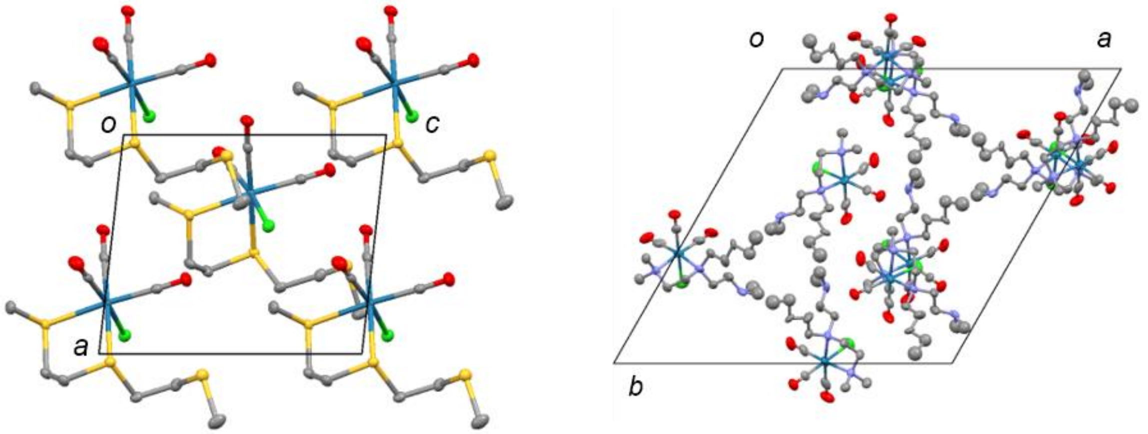


a) [**1**]PF_6

b) [**2**]PF_6



c) [**2**]Tf_2N



d) [**1'-Cl**]

e) [**2-Cl**]

Figure S2. Packing diagrams. In the disordered part, the lower occupancy moieties have been omitted.

Table S1. Crystallographic parameters

	[**1**]PF$_6$	[**2**]PF$_6$	[**2**]Tf$_2$N
Empirical formula	$C_{15}H_{26}S_3O_3ReF_6P$	$C_{16}H_{31}N_3O_3RePF_6$	$C_{18}H_{31}F_6N_4O_7ReS_2$
Formula weight	681.71	644.61	779.79
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*–1	*C*c	*P*–1
a [Å]	12.101(3)	13.490(11)	9.7417(10)
b [Å]	13.378(3)	28.17(2)	17.7109(18)
c [Å]	15.687(4)	12.581(11)	18.1194(19)
α [°]	70.089(3)	90	111.7300(10)
β [°]	71.784(3)	105.98(2)	103.9650(10)
γ [°]	82.403(3)	90	96.0330(10)
V [Å^3]	2267.1(10)	4596.0(7)	2751.9(5)
Z	4	8	4
ρ_{calcd} [g cm^{-3}]	1.997	1.863	1.882
$F(000)$	1328.0	2528	1536
μ (mm^{-1})	5.77	5.426	4.652
Temperature [K]	100	90	90
Reflns collected	9938	12551	12907
R (int)	0.0204	0.0118	0.0246
$R_1{}^a$, $R_w{}^b$ ($I > 2\sigma$)	0.0252, 0.0600	0.0220, 0.0584	0.0256, 0.0639
$R_1{}^a$, $R_w{}^b$ (all data)	0.0314, 0.0663	0.0228, 0.0587	0.0290, 0.0651
Goodness of fit	1.138	1.041	1.063

$^aR_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^bR_w = [\Sigma w (F_o^2 - F_c^2)^2/\Sigma w (F_o^2)^2]^{1/2}$.

Table S2. Crystallographic parameters

	[**1'-Cl**]	[**2-Cl**]
Empirical formula	$C_9H_{14}S_3O_3ReCl$	$C_{16}H_{31}N_3O_3ReCl$
Formula weight	488.03	535.09
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/n$	$R3c$
a [Å]	7.9569(15)	22.703(4)
b [Å]	19.283(4)	22.703(4)
c [Å]	9.5161(18)	20.758(3)
α [°]	90	90
β [°]	96.405(2)	90
γ [°]	90	120
V [Å^3]	1451.0(5)	9266(3)
Z	4	18
ρ_{calcd} [g cm^{-3}]	2.234	1.726
F (000)	928	4752
μ (mm^{-1})	8.982	6.049
Temperature [K]	100	90
Reflns collected	7536	17133
R (int)	0.0201	0.0234
$R_1{}^a$, $R_w{}^b$ ($I > 2\sigma$)	0.0166, 0.0429	0.0298, 0.0674
$R_1{}^a$, $R_w{}^b$ (all data)	0.0169, 0.0430	0.0367, 0.0712
Goodness of fit	1.133	1.054

$^aR_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^bR_w = [\Sigma w (F_o{}^2 - F_c{}^2)^2/\Sigma w (F_o{}^2)^2]^{1/2}$.