α-Sulfinyl Transition Metal Bond. 1. Naked α-Sulfinyl Anions and Their Reactivity with Metal Carbonyls: Synthesis of Metal–Carbon Bonded α-Sulfinyls and α-Sulfinylcarbenes

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Deprotonation of $ArSOCH_3$ [Ar = C_6H_5, **1**; Ar = 4-MeC_6H_4, **2**] with KH in THF in the presence of 18-crown-6 and Kryptofix-2,2,2 led to the isolation of the respective ion-contact and ion-separated pairs: [$ArS(CH_2)O\cdots K$(18-crown-6)] [Ar = C_6H_5, **3**; Ar = 4-MeC_6H_4, **4**]; [$ArS(CH_2)O\cdots K$(kryptofix-2,2,2)] [Ar = C_6H_5, **5**; Ar = 4-MeC_6H_4, **6**]. The complexation of the potassium cation in both **4** and **6** causes the complete racemization of the α-sulfinyl anion. The structures of **3** and **5** have been determined with an X-ray analysis. The reaction of **3** and **4** with [$Cr(CO)_5$(THF)] led to the formation of α-sulfinyl carbonylmetalates containing a Cr–C σ bond, in $[ArS(O)CH_2Cr(CO)_5]^-$[K(18-crown-6)]$^+$[Ar = C_6H_5, **7**; Ar = 4-MeC_6H_4, **8**]. The high nucleophilicity of **3** is demonstrated in the reaction with a weakly electrophilic CO in [$Cr(CO)_6$]. The reaction gives an unprecedented metallacarbene–sulfinyl anion complex, [{$(CO)_5Cr{=}C(O){-}CH{-}S(O)Ph$}$\cdots${K(18-crown-6)}$_2$], **10**, in which the carbene sulfoxide fragments migrate to a carbon monoxide, forming an α-sulfinylcarbene metallacycle, [$(CO)_4Cr{-}${S(O)PhCH=C(O)—C(O)}$\cdots${K(18-crown-6)}$_2$], **11**. Exhaustive silylation of the peripheral oxygens of **11** led to the corresponding silylated form **12**. Crystallographic details: **3** is monoclinic, space group $P2_1$, with a = 9.025(1) Å, b = 15.799(2) Å, c = 8.579(1) Å, $\alpha = \gamma = 90°$, β = 107.76(1)°, Z = 2, and R = 0.040; **5** is triclinic, space group $P\bar{1}$, with a = 10.713(1) Å, b = 10.825(1) Å, c = 14.877(1) Å, α = 112.07(1)°, β = 112.83(1)°, γ = 80.39(1)°, Z = 2, and R = 0.067; **11** is triclinic, space group $P\bar{1}$, with a = 15.251(4) Å, b = 16.774(2) Å, c = 11.833(2) Å, α = 109.75(1)° β = 110.30(2)°, γ = 85.94(1)°, Z = 2, and R = 0.049.

Introduction

The α-sulfinyl anion has been used to develop new methods in C–C bond making[1] and to introduce a chiral group into a variety of substrates.[2] The chirality transfer by the α-sulfinyl anion is largely dependent on the chirality of the carbanion in the ion-pair precursor.[3] The only structural information on such species in the solid state was reported for [{PhCH(Me)S(O)Ph}$_2$(μ-LiTMEDA)$_2$],[4] which revealed an O–Li interaction in a dimeric structure. Although transition metals have been widely used to drive the chemistry of enolates,[5] this is not the case for the α-sulfinyl anions.

In principle, both O- and C-bonded species should be possible, with an appropriate choice of metals.[5] Because of the relevance of α-sulfinyl anions in organic synthesis, a major objective was the synthesis and the structural characterization of highly nucleophilic naked forms. We used them to make metal–carbon σ bonds with [$Cr(CO)_5$] and as nucleophilic reagents with weak electrophilic metal bonded CO for the generation of Fischer type carbenes containing the α-sulfinyl functionality. Some preliminary results were communicated.[6]

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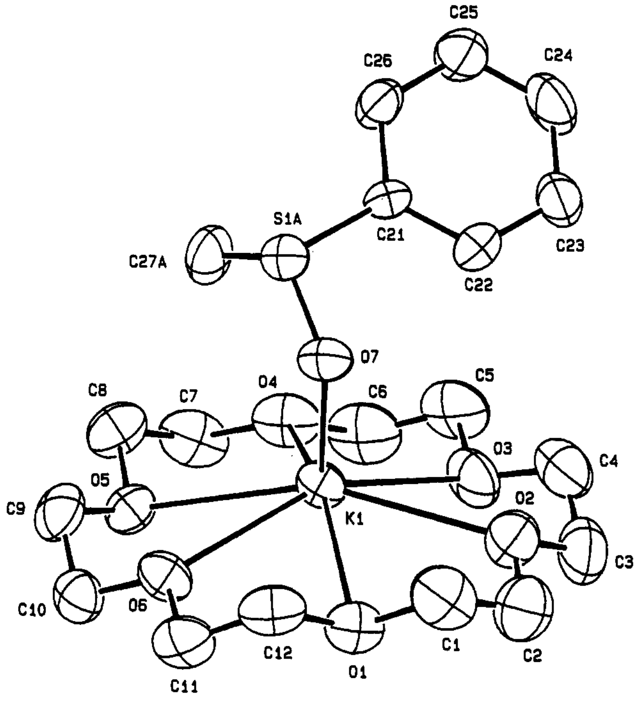
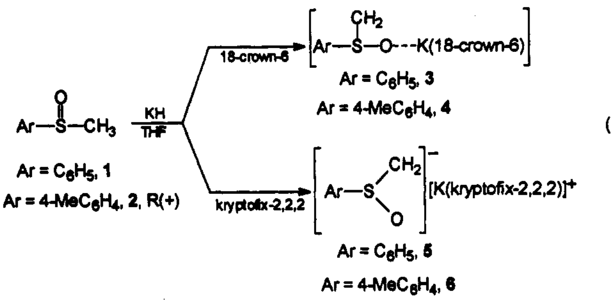


Figure 1. ORTEP drawing for complex **3** (30% probability ellipsoids). For clarity only the A position is given for the disordered S1 and C27 atoms.

Results and Discussion

The deprotonation of methyl aryl sulfoxides was carried out with KH in THF, in the presence of a potassium complexing agent like 18-crown-6 or Kryptofix-2,2,2:



(1)

The deprotonation of optically pure enantiomer **2** leads to the racemic forms **4** and **6**, while the THF solution of the α-sulfinyl anion maintains its optical purity ($\alpha_D = 101 \pm 1.3°$) before addition of the complexing agent. The loss of optical activity is due to the cleavage of the strong alkali cation/α-sulfinyl anion, ion-pair interaction. X-ray analyses were carried out on **3** and **5**, and their structures are shown in Figures 1 and 2, with selected structural parameters in Tables V and VI. In the case of **3**, we observed a self-resolution in the solid state with an ee of 83%; so Figure 1 and Table V refer to the main enantiomer.

A tight ion-pair form of **3** is supported by the short K···O7 distance [2.664(7) Å], which is significantly shorter than the bond length between K and the oxygen atoms of 18-crown-6 [from 2.770(7) to 2.986(6) Å]. Although the α-sulfinyl anion is affected by a high degree of disorder in **5**, the structural parameters are close for the anion in the free and ion-pair form. The S1A–O7 [1.521(7)Å] and S1A–C27A [1.66(2) Å] distances should be compared with those in the lithiated dimeric form [$\{PhCH(Me)S(O)Ph\}_2(\mu\text{-}LiTMEDA)_2$] [S–O, 1.58(1) Å and S–C, 1.63(1) Å].[4]

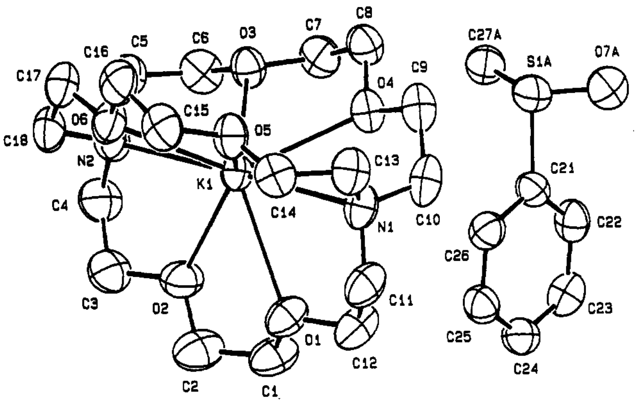


Figure 2. ORTEP view of the anion and the cation for complex **5** (30% probability ellipsoids). For clarity only the A position is given for the disordered S1, O7, and C27 atoms.

The K···O interaction, weaker than the Li···O interaction, may be responsible for the differences in S–C and S–O distances. The "$SOCH_2$" moiety is twisted by 110.4(6)° with respect to the aromatic ring in complex **3**. The sulfoxide group shows a configurational disorder, indicating that enantiomers A and B are present in 83% and 17% amounts, respectively. Since the space group is polar, the interchanged population for the enantiomers is not possible.

The ^1H NMR spectra of complexes **3**–**5** deserve comment. The two methylene protons appear as singlets at 2.50, 2.57, and 2.73 ppm, respectively, more upfield than the corresponding CH_2 protons in naked acetophenone enolates, which range from 4.00 to 4.70 ppm.[7] The same variation has been observed in the ^{13}C NMR spectra. Unlike **3**–**5**, the ^1H NMR spectrum of the α-sulfinyl anion **6** shows a complex pattern derived from the likely presence of two isomers in a 1:2 ratio. Each isomer shows a triplet at 1.13 and 1.32 ppm for the methyl groups, and a quartet at 2.54 and 2.68 ppm for the methylene groups. We do not have any reasonable explanation for such a spectroscopic behavior of **6**.

The reaction of the ion-pair form or of the naked forms of α-sulfinyl anions with cp_2MCl_2 [M = Ti, Zr] did not lead to an identifiable compound, though the reaction appears to proceed with the reduction of the metal for titanium and deoxygenation for zirconium. Such behavior would prevent the binding of the α-sulfinyl anion *via* the oxygen to an oxophilic transition metal, as is often observed for the analogous enolates.[5,8,9] Moving to more carbophilic metals, the binding of the α-sulfinyl anion to a transition metal was achieved with [$Cr(CO)_5(THF)$], which has a very labile THF ligand. The reaction was carried out by adding [$Cr(CO)_5(THF)$] (prepared *in situ*) to a THF solution of **3** or **4**.

$$[ArS(CH_2)O\cdots K(18\text{-crown-}6)] + [Cr(CO)_5(THF)] \xrightarrow{THF} [ArS(O)CH_2Cr(CO)_5]^-[K(18\text{-crown-}6)]^+ \quad (2)$$

Ar = C_6H_5, **3**
Ar = 4-MeC_6H_4, **4**

Ar = C_6H_5, **7**
Ar = 4-MeC_6H_4, **8**

Complexes **7** and **8** have been isolated in high yield as yellow crystalline solids. As with enolates,[7] there is a bond between the metal and the "CH_2" of the α-sulfinyl anion,

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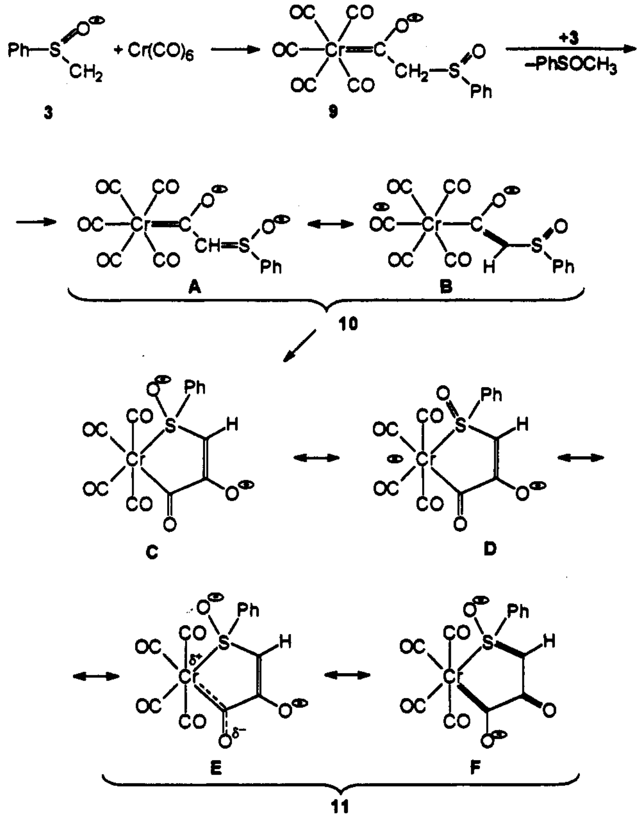
[7] Veya, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* 1991, *10*, 1652.

Scheme I



as seen in a low quality X-ray structure.[10] The proposed structure is in agreement with the spectroscopic results. The four IR bands at 2035 (w), 1948 (sh), 1906 (s), and 1867 (m) cm^{-1} are expected for a LM(CO)$_5$ complex [L = asymmetrical ligand]. The low frequency of the CO stretching is associated with the transfer of the electronic charge to the [Cr(CO)$_5$] fragment and particularly to the CO *trans* to the nucleophilic "CH$_2$".[7] In both 7 and 8, the "CH$_2$" groups appear as AB systems (see Experimental Section), as the methylene group α to an electron-rich metal has two heterotopic protons. The absence of reactivity of 7 and 8 with benzaldehyde is expected since the α-sulfinyl functionality is converted in reaction 2 to a metal–carbon σ bond, where the "CH$_2$" has lost its nucleophilic properties. A metal–carbon bonded α-sulfinyl anion has been reported to interact with a metal carbonyl fragment in [(η^5-R$_5$C$_5$)(CO)$_3$WCH$_2$SOPh] [R = H, Me], where the sulfoxide moiety is generated from the oxidation of its sulfido precursor.[11] The IR and ^{1}H NMR data for these compounds agree with those for 7 and 8.[11] The S–O vibration is found at 1048 cm^{-1} (7). The methylene group appears in the ^{1}H NMR spectrum as AB type doublets at 1.80 and 1.94 ppm [J_{AB} = 9.75 Hz] (7) and at 1.78 and 1.94 ppm [J_{AB} = 9.75 Hz] (8).

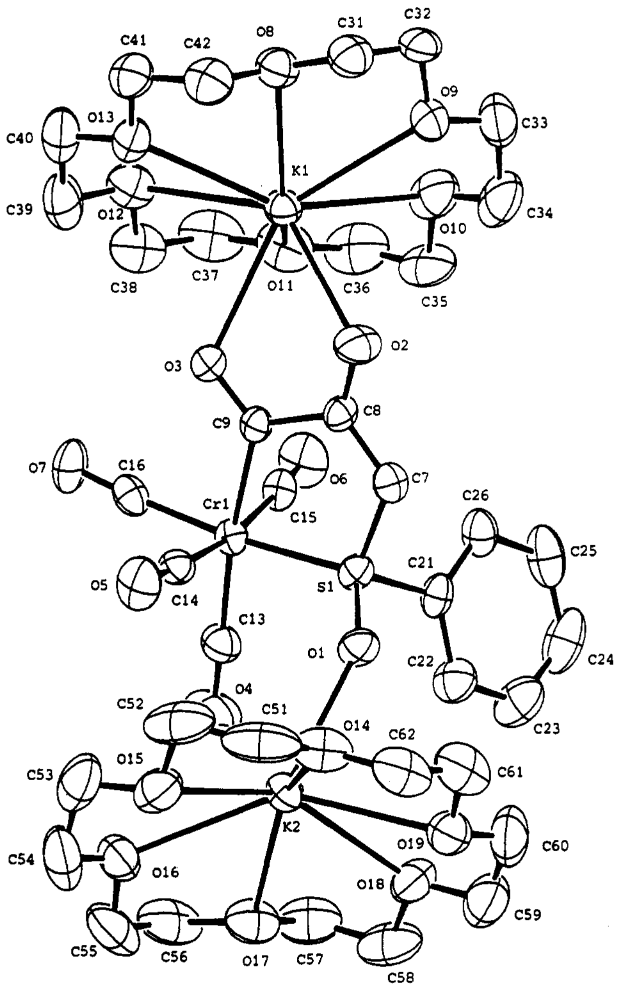


Figure 3. ORTEP view of complex 11 (30% probability ellipsoids).

The high nucleophilicity of 3 has been explored in the reaction with [Cr(CO)$_6$], which has historically been used as a source of electrophilic carbon monoxide in the Fischer carbene synthesis.[12] The reaction of 3 with [Cr(CO)$_6$] was carried out in THF at −10 °C as reported in Scheme I, where the [K(18-crown-6)]$^+$ cation has been omitted for clarity.

Complex 11 has been isolated as a yellow solid, which has been recrystallized from boiling THF to give orange crystals. The IR spectrum shows only three of the four expected CO bands at 1982, 1868, and 1822 cm^{-1}, the fourth one probably masked by a wide envelope in the range 1940–1900 cm^{-1}. Bands at 1556 and 1113 cm^{-1} support the presence of C=C and S=O bonds, respectively. The IR spectrum recorded on the yellow solid before crystallization is identical to that of the orange crystals. This rules out the possibility of thermally induced migration/insertion of CO during crystallization. Further spectroscopic support for the nature of 11 is the enolic proton seen at 5.55 ppm (CD$_2$Cl$_2$). The ^{13}C NMR spectrum shows a resonance at 302.6 ppm, which is peculiar for a metal–carbene type fragment. These facts along with the X-ray analysis give insights on the likely structure of 11, shown

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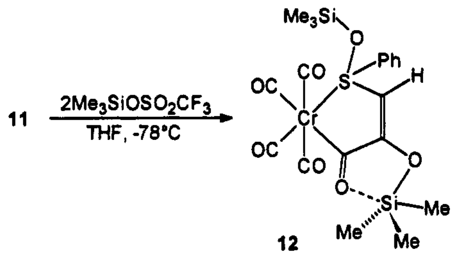
in Figure 3, with a selection of structural parameters in Table VII. The three peripheral oxygen atoms O1, O2, and O3 of the metallacycle bind the two [K(18-crown-6)]$^+$ units. The shortest and very close K···O distances are those involving O1 and O2, while the K1···O3 distance is significantly longer and in agreement with a much less negative charge on O3. The structural parameters should discriminate between the forms C, D, E, and F for the metallacycle. The Cr, C7, C8, C9, S1, O2, and O3 atoms are almost coplanar with maximum out-of-plane distances of −0.082(8) Å [C7], 0.095(8) Å [C9], −0.052(7)Å [O2], and 0.237(6) Å [O3]. The bond distances within the metallacycle are in good agreement with forms E and F, especially the C8—C7 double bond, the short C9—O2 and C9—O3 distances, and the short Cr—C9 distance. The carbene nature of C9 is additionally supported by the ^{13}C NMR data with a chemical shift of 302.3 ppm. A form like D bearing part of the negative charge on the carbon monoxide is not supported by the similar nature of the four CO, with Cr—C(CO) bond distances ranging from 1.832(9) to 1.875(8) Å and C—O from 1.140 910) to 1.176 (11) Å. The structural characteristics of the two [K(18-crown-6)] units are quite similar and analogous to those found in complex 3, with K1—O distances ranging from 2.752(7) to 3.025(7) Å and K2—O from 2.781(7) to 2.966(7) Å. The distance from the mean plane through the six oxygens of the crown ether is 0.871(2) and 0.814(2) Å for K1 and K2, respectively.

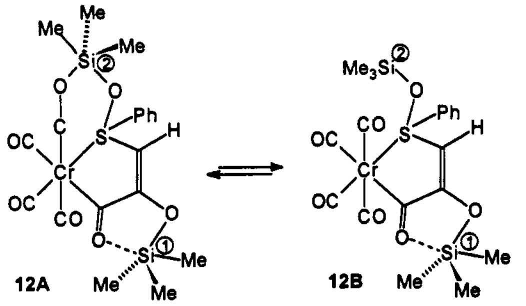
The structural determination of 11 illuminates the mechanism proposed in Scheme I. The naked α-sulfinyl anion reacts with the electrophilic CO of [Cr(CO)$_6$], forming the Fischer-type carbene 9, which is then deprotonated by the α-sulfinyl anion to give the corresponding α-sulfinylcarbene dianion 10. Both A and B could insert carbon monoxide to give the metallacycle 11. The alkylation of 11 carried out in THF at −78 °C leads to the silylation of all peripheral anionic oxygens of the metallacycle, as reported in eq 3.



(3)

Complex 12 was obtained in good yield (73%) as a red compound. Spectroscopic inspection reveals the main characteristics of 12. Four CO bands at 2071, 2029, 1941, and 1900 cm^{-1} belong to the Cr(CO)$_4$ fragment, while the CO band at 1703 cm^{-1} is due to the carbonyl α in the metallacycle. The strong band at 849 cm^{-1} reflects the S–O single bond of the sulfinyl functionality. The ^{1}H NMR spectrum, however, contains five rather than the three peaks expected for the Me groups in 12 and two enolic protons (6.69 and 6.71 ppm), rather than one. This suggested the equilibrium in eq 4.

The Si$^{(1)}$Me$_3$ group gives rise to two resonances (0.29 and 0.45 ppm) in both forms, while two resonances for the Si$^{(2)}$Me$_3$ group suggest the presence of a five-coordinated silicon in the A form (−0.06 and −0.11 ppm), and a single resonance for the tetracoordinated silicon in the B form (0.20 ppm). The spectrum suggests that the A and B forms are present in the 2:1 ratio at room temperature.



(4)

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer. ^{1}H NMR spectra were measured on a 200-AC Bruker instrument.

Synthesis of 3. Melted 1 (2.23 g, 15.9 mmol) was added with a syringe to a THF (50-mL) suspension of KH (0.67 g, 16.7 mmol), and the mixture was stirred overnight. Excess KH was filtered and the crown ether 18-crown-6 (4.21 g, 15.9 mmol) added. The solvent was evaporated, the yellow microcrystalline residue was redissolved in ether (50 mL), and the mixture was filtered. The filtrate was pulled to dryness and the solid collected and dried (6.40 g, 87%). Crystals suitable for X-ray analysis were obtained by extraction with ether. Anal. Calcd for $C_{19}H_{31}KO_7S$: C, 51.56; H, 7.06. Found: C, 51.52; H, 7.11. ^{1}H NMR (C_6D_6): δ 2.50 (s, =CH$_2$, 2 H), 3.26 (s, OCH$_2$, 24 H), 7.15–7.45 (m, Ph, 3 H), 8.67 (m, Ph, 2 H). ^{13}C NMR (C_6D_6): δ 39.9 (s, CH$_2$), 70.7 (s, OCH$_2$), 126–129 (m, Ph), 161.7 (s, Ph).

Synthesis of 4. Melted *R*(+)-2 (1.00 g, 6.48 mmol) was added with a syringe to a THF (50-mL) suspension of KH (0.31 g, 7.73 mmol), and the mixture was stirred overnight. Excess KH was filtered and the crown ether 18-crown-6 (1.65 g, 6.24 mmol) added. The solvent was evaporated, the yellow microcrystalline residue was redissolved in ether (50 mL), and the mixture was filtered. The filtrate was pulled to dryness and the solid collected and dried (2.50 g, 87%). Anal. Calcd for $C_{20}H_{33}KO_7S$: C, 52.61; H, 7.28. Found: C, 52.80; H, 7.84. ^{1}H NMR (C_6D_6): δ 2.19 (s, Me, 3 H), 2.57 (s, =CH$_2$, 2 H), 3.25 (s, OCH$_2$, 24 H), 7.18 (d, Ph, 2 H), 8.63 (d, Ph, 2 H). $[\alpha]_D = +21.7 \pm 3.2°$ (c = 0.930) in THF. Starting product: $[\alpha]_D = +159.7 \pm 1.5°$ (c = 1.315), the $[\alpha]_D$ value of the THF solution was 101.1 ± 1.3° before the addition of the 18-crown-6.

Synthesis of 5. Melted 1 (0.36 g, 2.58 mmol) was added with a syringe to a THF (50-mL) suspension of KH (0.10 g, 2.58 mmol), and the mixture was stirred overnight. Excess KH was filtered off and Kryptofix-2,2,2 (0.97 g, 2.58 mmol) added. The solvent was evaporated and the yellow oil redissolved in ether (50 mL). On standing for a few hours, a yellow crystalline product formed, which was collected by filtration and dried (1.05 g, 73%). Crystals suitable for X-ray analysis were obtained by ether extraction. Anal. Calcd for $C_{25}H_{43}KN_2O_7S$: C, 54.12; H, 7.81; N, 5.05. Found: C, 54.11; H, 8.00; N, 5.05. ^{1}H NMR (C_6D_6): δ 2.32 (t, NCH$_2$, 12 H), 2.73 (d, =CH$_2$, 2 H), 3.33 (t, OCH$_2$, 12 H), 7.05–7.50 (m, Ph, 3 H), 8.84 (m, Ph, 2 H).

Synthesis of 6. Melted *R*(+)-2 (0.40 g, 2.58 mmol) was added with a syringe to a THF (50-mL) suspension of KH (0.10 g, 2.58 mmol), and the mixture was stirred overnight. Excess KH was filtered off and Kryptofix-2,2,2 (0.97 g, 2.58 mmol) added. The solvent was evaporated and the yellow oil redissolved in ether (50 mL). On standing for a few hours, a yellow crystalline product formed, which was collected by filtration and dried (0.95 g, 65%). Anal. Calcd for $C_{26}H_{45}KN_2O_7S$: C, 54.90; H, 7.97; N, 4.92. Found: C, 54.94; H, 8.36; N, 4.75. ^{1}H NMR (C_6D_6), two isomers: δ 1.13 and 1.32 (2t, Me, $^2/_3 + ^1/_3$ 3 H), 2.34 (t, NCH$_2$, 12 H), 2.54

and 2.68 (2q, =CH$_2$, $^2/_3 + ^1/_3$ 2 H), 3.33 (t, OCH$_2$, 12 H), 3.40 (s, OCH$_2$, 12 H), 7.00–7.22 (2d, Ph, $^1/_3 + ^2/_3$ 2 H). $[\alpha]_D = 0°$ (c = 0.930) in THF.

Synthesis of 7. A [Cr(CO)$_5$·THF] solution, prepared *in situ* from Cr(CO)$_6$ (1.24 g, 5.65 mmol) and THF (250 mL), was added dropwise, at −78 °C, to a THF (50-mL) solution of **3** (2.49 g, 5.63 mmol). The orange solution was stirred over 5 h; then, the solvent was evaporated to dryness, yielding a red oil which was redissolved in ether (50 mL). A yellow crystalline solid formed slowly on standing, which was collected by filtration and dried (3.05 g, 85%). IR (THF): ν(CrC=O) 2035 (w), 1948 (sh), 1906 (s), 1867 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{31}CrKO_{12}S$: C, 45.42; H, 4.92. Found: C, 45.81; H, 5.27. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.80 and 1.94 (q, CH$_2$–Cr, 2 H, J_{AB} = 9.75 Hz), 3.60 (s, OCH$_2$, 24 H), 7.40–7.60 (m, Ph, 5 H). ^{13}C NMR (CD$_2$Cl$_2$): δ 33.1 (s, CH$_2$–Cr), 70.9 (s, OCH$_2$), 125.9, 129.1, 130.1, and 152.0 (4s, Ph), 223.2 (s, CrCO).

Synthesis of 8. A [Cr(CO)$_5$·THF] solution, prepared *in situ* from Cr(CO)$_6$ (0.77 g, 3.5 mmol) and THF (250 mL), was added dropwise, at −78 °C, to a THF (50-mL) solution of **4** (1.57 g, 3.4 mmol). The orange solution was stirred over 5 h; then, the solvent was evaporated to dryness, yielding a red oil which was redissolved in ether (50 mL). A yellow crystalline solid formed slowly on standing, which was collected by filtration and dried (1.87 g, 83%). IR (THF): ν(CrC=O) 2036 (m), 1955 (m), 1899 (s), 1853 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{33}CrKO_{12}S$: C, 46.29; H, 5.13. Found: C, 46.44; H, 5.39. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.78 and 1.94 (q, CH$_2$–Cr, 2 H, J = 9.75 Hz), 2.36 (s, Me, 3 H), 3.60 (s, OCH$_2$, 24 H), 7.22 (d, Ph, 2 H), 7.67 (d, Ph, 2 H). ^{13}C NMR (CD$_2$Cl$_2$): δ 21.8 (s, MePh), 32.8 (s, CH$_2$–Cr), 70.8 (s, OCH$_2$), 126.0, 129.7, 140.4, and 148.6 (4s, Ph), 223.2 and 226.7 (2s, CrCO). $[\alpha]_D = -14.7 \pm 1.7°$ (c = 1.575) in THF.

Synthesis of 11. To a THF (200 mL) solution of **3** (9.27 g, 20.96 mmol) at −10 °C was added Cr(CO)$_6$ (2.31 g, 10.48 mmol), and the color suddenly turned dark yellow. After 10 min a yellow solid had formed, which was collected by filtration (slow and difficult filtration), washed with ether (2 × 100 mL), and dried (6.71 g, 66%). The mother liquor contains **1**. Orange crystals were grown in hot THF. Soluble in CH$_2$Cl$_2$, the product decomposes in this solvent in 15 min. IR (CH$_2$Cl$_2$): ν(CrC=O) 1982 (w), 1868 (s), 1822 (m); ν(C=C) 1556 (w); ν(S=O) 1113 (s) cm^{-1}. IR (Nujol): ν(CrC=O) 1974 (m), 1853 (s), 1814 (s); ν(C=C) 1564 (s); ν(S=O) 1114 (s) cm^{-1}. Anal. Calcd for $C_{45}H_{70}CrK_2O_{21}S$: C, 48.72; H, 6.36. Found: C, 48.49; H, 6.45. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.81 (m, THF, 4 H), 3.65 (s, OCH$_2$ + THF, 52 H), 5.55 (s, =CH, 1 H), 7.33 (m, Ph, 3 H), 7.85 (m, Ph, 2 H). ^{1}H NMR (CD$_3$SOCD$_3$): δ 1.74 (m, THF, 4 H), 3.55 (s, OCH$_2$ + THF, 52 H), 5.18 (s, =CH, 1 H), 7.30 (m, Ph, 3 H), 7.67 (m, Ph, 2 H). ^{13}C NMR uncoupled (CD$_3$SOCD$_3$): δ 25.3 (s, THF), 67.2 (s, THF), 69.6 (s, OCH$_2$), 105.0 (s, =CH), 125.4, 127.5, and 128.1 (3s, Ph), 155.8 (s, Ph), 184.6 (s, =C–O$^-$), 224.9 and 234.7 (s, CrCO), 302.6 (s, CrCO).

Synthesis of 12. Trimethylsilyl triflate (0.40 mL, 2.20 mmol) was added dropwise to an ether (50-mL) suspension of **11** (1.15 g, 1.10 mmol) with a syringe at −78 °C. The color suddenly turned dark red. The solution was stirred for 30 min and the solvent evaporated at room temperature. The red residue was redissolved in pentane (100 mL) and the potassium salt washed with chilly pentane (30 mL). Potassium–18-crown-6 triflate is sparingly soluble in pentane. The pentane was eliminated, and a red liquid was obtained (0.41 g, 73%). IR (THF): ν(CrC=O) 2071 (vw), 2029 (w), 1941 (vs), 1900 (sh); ν(C=O) 1703 (w) cm^{-1}. IR (Nujol): ν(C=C) 1583 (w); ν(S–O) 849 (vs) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$), two isomers 38/62 and undefined impurities: (*1*) δ −0.06 and −0.11 (2s, SiMe$_3$), 0.29 and 0.45 (2s, SiMe$_3$), 6.71 (s, =CH), 6.9 (m, Ph); (*2*) δ 0.2 (s, SiMe$_3$), 0.29 and 0.45 (2s, SiMe$_3$), 6.69 (s, =CH), 6.9 (m, Ph). ^{13}C NMR uncoupled (CD$_2$Cl$_2$): δ 0.0–3.0 (m, SiMe$_3$), 123.8 (s, =CH), 128.4–138.6 (m, Ph), 146.8 (s, Ph), 165.6 (s, =COSiMe$_3$), 212.2 (s, CrCO), 215.4 and 222.9 (2s, CrCO).

Table I. Experiment Data for the X-ray Diffraction Studies on Crystalline Compounds 3, 5, and 11

	3	**5**	**11**
formula	$C_{19}H_{31}O_7KS$	$C_{25}H_{43}N_2KO_7S$	$C_{37}H_{54}CrK_2SO_{19}\cdot 1.5(C_4H_8O)$
a (Å)	9.025(1)	10.713(1)	15.251(4)
b (Å)	15.799(2)	10.825(1)	16.774(2)
c (Å)	8.579(1)	14.877(1)	11.833(2)
α (deg)	90	112.07(1)	109.75(1)
β (deg)	107.76(1)	112.83(1)	110.30(2)
γ (deg)	90	80.39(1)	85.94(1)
V (Å^3)	1165.0(3)	1473.1(3)	2668.4(1)
Z	2	2	2
fw	442.6	554.8	1073.2
space group	$P2_1$	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
t (°C)	22	22	22
λ (Å)	0.710 69	1.541 78	0.710 69
ρ_{calc} (g cm^{-3})	1.262	1.251	1.336
μ (cm^{-1})	3.43	25.9	4.70
transm coeff	0.942–1.000	0.721–1.000	0.966–1.000
R[a]	0.040 [0.041][b]	0.067	0.049
R_w	0.041 [0.042]	0.075	0.052
R_G	0.048 [0.050]		

[a] $R = \sum|\Delta F|/\sum|F_o|$. $R_w = [\sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|]$. $R_G = [\sum w|\Delta F|^2/\sum w|F_o|^2]^{1/2}$. [b] Values in square brackets refer to the "inverted" structure.

Table II. Fractional Atomic Coordinates (×10^4) for Complex 3[a]

atom	x/a	y/b	z/c
K1	4964(2)	1012(–)	1706(2)
S1A	7180(4)	−465(3)	4604(5)
S1B	7458(27)	−144(18)	4043(44)
O1	1952(6)	1019(6)	2250(8)
O2	2491(9)	16(5)	−268(10)
O3	4815(11)	630(5)	−1574(9)
O4	7327(9)	1602(6)	302(10)
O5	6780(6)	2603(4)	2761(8)
O6	4432(7)	2057(4)	4072(8)
O7	5467(7)	−241(4)	3883(8)
C1	1332(15)	182(9)	1818(23)
C2	1077(17)	55(10)	39(26)
C3	2342(20)	−23(9)	−2018(18)
C4	3970(23)	−89(10)	−2157(14)
C5	6297(21)	651(14)	−1843(16)
C6	7009(16)	1472(13)	−1378(20)
C7	8106(12)	2392(8)	845(19)
C8	8282(11)	2494(8)	2623(15)
C9	6800(13)	2753(8)	4352(14)
C10	5189(13)	2849(7)	4442(12)
C11	2977(13)	2014(9)	4351(14)
C12	2361(10)	1157(9)	3985(14)
C21	7501(7)	−1149(4)	3044(7)
C22	6240(7)	−1398(4)	1725(7)
C23	6452(7)	−1983(4)	594(7)
C24	7926(7)	−2320(4)	784(7)
C25	9187(7)	−2071(4)	2103(7)
C26	8975(7)	−1485(4)	3233(7)
C27A	8412(14)	302(10)	4505(18)
C27B	8346(74)	−581(40)	5980(85)

[a] The site occupation factors of S1 and C27 are 0.83 and 0.17 for the A and B positions, respectively.

X-ray Crystallography. The crystals of **3**, **5**, and **11** were mounted in glass capillaries and sealed under nitrogen. Crystal data and details associated with data collection are given in Table I. The reduced cells quoted were obtained using TRACER.[12] Data were collected at room temperature (295 K) on a single-crystal four circle diffractometer [Siemens AED for **3** and **5**, and Enraf-Nonius CAD4 for **11**]. For intensities and background individual reflection profiles were analyzed.[13] The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by the Wilson method.[14] The crystal quality was tested by ψ scans, showing that crystal absorption effects could not be neglected for

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Table III. Fractional Atomic Coordinates (×10^4) for Complex 5[a]

atom	x/z	y/b	z/c	atom	x/a	y/b	z/c
K1	1979.1(10)	3682.1(9)	7010.5(8)	C7	3296(6)	1752(6)	8698(5)
S1A	6306(3)	−1016(3)	8193(3)	C8	2848(6)	694(6)	7673(6)
S1B	6796(8)	−1402(8)	8062(6)	C9	2809(6)	100(5)	5971(5)
O1	3752(3)	4280(4)	6219(3)	C10	3205(6)	589(6)	5306(5)
O2	3595(4)	5935(4)	8170(3)	C11	3053(7)	2379(7)	4671(5)
O3	2391(3)	2884(3)	8687(3)	C12	4237(6)	3196(7)	5521(5)
O4	3011(3)	1138(3)	6939(3)	C13	1036(6)	1253(6)	4254(4)
O5	−300(3)	2833(3)	5140(3)	C14	−36(6)	2351(6)	4204(5)
O6	−612(3)	4913(3)	6875(3)	C15	−1450(6)	3694(6)	5079(5)
O7A	6771(16)	−2334(15)	7592(14)	C16	−1711(5)	4128(6)	6062(6)
O7B	5500(9)	−1644(9)	7116(6)	C17	−863(6)	5459(6)	7826(5)
O7C	7301(45)	−2050(40)	8662(38)	C18	249(7)	6355(5)	8636(5)
N1	2375(4)	1715(4)	5053(3)	C21	7507(4)	−5(3)	8182(3)
N2	1580(5)	5674(4)	8941(4)	C22	8910(4)	−90(3)	8659(3)
C1	4801(6)	5113(7)	7028(5)	C23	9737(4)	775(3)	8657(3)
C2	4240(7)	6302(7)	7662(5)	C24	9163(4)	1724(3)	8176(3)
C3	3040(7)	7057(6)	8793(5)	C25	7760(4)	1809(3)	7698(3)
C4	2670(7)	6633(6)	9497(5)	C26	6932(4)	944(3)	7701(3)
C5	1622(7)	4965(6)	9622(5)	C27A	6281(14)	−350(12)	9255(10)
C6	2697(6)	3882(6)	9690(4)	C27B	7236(21)	−1473(31)	9167(16)

[a] The site occupation factors are 0.7 for S1A, 0.5 for O7B, C27A, and C27B, 0.3 for S1B and O7A, and 0.2 for O7C.

Table IV. Fractional Atomic Coordinates (×10^4) for Complex 11[a]

atom	x/z	y/b	z/c	atom	x/a	y/b	z/c
Cr1	2353.5(8)	2763.2(6)	4537.4(11)	C25	2105(9)	4839(7)	1873(9)
K1	5403.5(11)	1436.2(10)	3308.4(17)	C26	2245(6)	4062(5)	2124(7)
K2	−901.7(12)	2101.0(10)	2286.1(17)	C31	6295(6)	−200(6)	1000(10)
S1	1599.1(12)	2684.7(11)	2446.8(18)	C32	6522(6)	549(7)	756(8)
O1	608(3)	2327(3)	1812(5)	C33	5985(8)	1900(9)	767(10)
O2	3659(4)	1419(4)	1757(5)	C34	5350(8)	2570(8)	1208(16)
O3	3935(4)	1643(3)	4211(5)	C35	5182(8)	3535(8)	3142(17)
O4	843(5)	3764(4)	5363(7)	C36	5667(9)	3805(7)	4561(16)
O5	1431(4)	1092(4)	4035(6)	C37	6014(8)	3331(7)	6312(14)
O6	3617(4)	4291(4)	5266(6)	C38	5799(7)	2628(8)	6653(9)
O7	3551(5)	2692(4)	7115(6)	C39	5972(8)	1205(8)	6429(9)
O8	6439(4)	5(4)	2296(6)	C40	6432(7)	460(7)	5872(12)
O9	5898(4)	1188(4)	1063(5)	C41	6547(6)	−488(6)	3972(12)
O10	5704(5)	2880(4)	2559(9)	C42	6201(7)	−687(5)	2572(11)
O11	5621(5)	3134(4)	4951(8)	C51	−1172(8)	−183(8)	376(17)
O12	6236(4)	1911(4)	6186(6)	C52	−709(8)	−116(8)	1749(19)
O13	6098(4)	218(4)	4529(6)	C53	−865(9)	514(9)	3758(18)
O14	−1111(4)	599(4)	250(8)	C54	−1434(10)	1120(12)	4426(11)
O15	−1174(4)	477(4)	2497(9)	C55	−1818(9)	2556(12)	4967(11)
O16	−1260(4)	1944(5)	4438(6)	C56	−1557(8)	3394(9)	5012(13)
O17	−1763(4)	3410(5)	3777(7)	C57	−1595(8)	4206(8)	3753(14)
O18	−1664(4)	3583(4)	1623(8)	C58	−2079(8)	4192(7)	2436(17)
O19	−1814(4)	2058(6)	−394(6)	C59	−2104(9)	3514(9)	378(18)
C7	2306(5)	2162(4)	1631(7)	C60	−1688(9)	2881(12)	−452(12)
C8	3088(5)	1833(4)	2250(7)	C61	−1379(8)	1414(11)	−1084(10)
C9	3250(5)	1997(4)	3681(7)	C62	−1572(8)	587(8)	−1037(12)
C13	1435(6)	3389(5)	5042(8)	C71	600(12)	2012(10)	7510(15)
C14	1768(5)	1751(5)	4208(7)	C72	1592(13)	2093(10)	7709(16)
C15	3123(5)	3715(4)	4939(7)	C73	1915(13)	3019(11)	8507(16)
C16	3072(6)	2720(4)	6131(9)	C74	1063(15)	3428(11)	8450(17)
C21	1511(6)	3690(4)	2199(7)	C75	336(13)	2813(12)	8197(16)
C22	665(7)	4093(5)	2103(9)	C76	4778(23)	4608(14)	−990(21)
C23	549(8)	4844(7)	1863(11)	C77	4241(23)	4617(21)	−283(40)
C24	1257(12)	5212(6)	1745(10)	C78	4247(33)	5218(29)	566(45)

[a] The site occupation factor for C78 is 0.5.

complexes **5** and **11**. The corresponding data were then corrected for absorption using ABSORB.[15] The function minimized during the full-matrix least-squares refinement was $\sum w|\Delta F|^2$. A weighting scheme $\{w = k/[\sigma^2(F_o) + g|F_o|^2]\}$ based on counting statistics was applied.[16] Anomalous scattering corrections were included in all structure factor calculations.[17b] Scattering factors for neutral atoms were taken from ref 17a for non-hydrogen atoms and from ref 18 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. All calculations were carried out on an IBM-AT personal computer equipped with an INMOS T800 transputer using SHELX-76.[16] Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map.

Complex 3. Refinement was first done isotropically and then anisotropically by full-matrix least squares for all the non-H atoms except for S1B and C27B. The SOCH$_2$ group was found to be affected by a disorder which was interpreted as due to the presence of the two possible enantiomers sharing the coordinated oxygen atom. The sulfur and carbon atoms were then split over two

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Table V. Selected Bond Distances (Å) and Angles (deg) for Complex 3

K1–O1	2.895(7)	S1A–O7	1.521(7)
K1–O2	2.832(7)	S1A–C21	1.811(8)
K1–O3	2.841(8)	S1A–C27A	1.66(2)
K1–O4	2.904(10)	S1B–O7	1.77(3)
K1–O5	2.986(6)	S1B–C21	1.81(3)
K1–O6	2.770(7)	S1B–C27B	1.75(8)
K1–O7	2.664(7)		

K1–O7–S1B	86.7(10)	O7–S1A–C21	102.1(4)
K1–O7–S1A	113.1(4)	C21–S1B–C27B	91.9(25)
C21–S1A–C27A	97.9(6)	O7–S1B–C27B	101.5(26)
O7–S1A–C27A	114.9(6)	O7–S1B–C21	93.2(13)

Table VI. Selected Bond Distances (Å) and Angles (deg) for Complex 5

K1–O1	2.852(5)	S1A–O7C	1.58(5)
K1–O2	2.802(4)	S1A–C21	1.831(6)
K1–O3	2.793(5)	S1A–C27A	1.479(15)
K1–O4	2.770(3)	S1A–C27B	1.61(3)
K1–O5	2.847(3)	S1A–O7B	1.442(8)
K1–O6	2.838(3)	S1B–O7B	1.518(10)
K1–N1	3.032(4)	S1B–C21	1.725(11)
K1–N2	3.012(5)	S1B–C27B	1.55(3)
S1A–O7A	1.494(15)		

C21–S1A–C27B	100.2(9)	O7A–S1A–C27A	136.9(9)
C21–S1A–C27A	101.8(6)	O7A–S1A–C21	96.6(8)
O7C–S1A–C27A	84.3(19)	C21–S1B–C27B	107.4(10)
O7C–S1A–C21	100.9(19)	O7B–S1B–C27B	135.7(12)
O7B–S1A–C27B	137.5(13)	O7B–S1B–C21	106.9(6)
O7B–S1A–C21	105.0(5)		

positions (A and B). The refinement of the site occupation factors gave 0.83 and 0.17 for A and B, respectively. All the hydrogen atoms, excepting those of the disordered C27 atom, were located from a difference Fourier map and introduced in the final refinement as fixed atom contributions (isotropic *U*'s fixed at 0.11 Å^2). The crystal chirality was tested by inverting all the coordinates (x, y, $z \rightarrow -x$, $-y$, $-z$) and refining to convergence once again. The resulting R values (R = 0.041, R_G = 0.051 vs R = 0.040, R_G = 0.048) indicated the original choice should be the correct one. During the refinement the phenyl ring was constrained to be a regular hexagon (C–C = 1.395 Å). The final difference map showed no unusual features with no significant peak above the general background.

Complex 5. Refinement was first done isotropically and then anisotropically by full-matrix least squares for all the non-H atoms except for S1B, O7A, and O7C. The uncoordinated $SOCH_2$ was found to be affected by the configurational disorder observed in complex 3 in addition to a rotational disorder around the C_{phenyl}–S bond. The best fit was found by splitting the sulfur (S1) and carbon atoms (C27) over two positions (A, B) and the oxygen atoms (O7) over three positions (A, B, C). The site occupation factors derived from the heights of peaks on difference maps are given in Table III. All the hydrogen atoms, excepting those of the disordered C27 atom, were located from a difference Fourier map and introduced in the final refinement as fixed atom contributions (isotropic *U*'s fixed at 0.10 Å^2). During the refinement the phenyl ring was constrained to be a regular hexagon (C–C = 1.395 Å). The final difference map showed no unusual features with no significant peak above the general background.

Table VII. Selected Bond Distances (Å) and Angles (deg) for Complex 11

Cr1–S1	2.299(2)	K2–O16	2.879(9)
Cr1–C9	2.093(8)	K2–O17	2.871(7)
Cr1–C13	1.835(9)	K2–O18	2.902(8)
Cr1–C14	1.832(9)	K2–O19	2.966(7)
Cr1–C15	1.875(8)	S1–O1	1.498(5)
Cr1–C16	1.846(10)	S1–C7	1.697(8)
K1–O2	2.652(5)	S1–C21	1.795(8)
K1–O3	2.752(7)	O2–C8	1.255(10)
K1–O8	2.920(6)	O3–C9	1.244(9)
K1–O9	2.898(7)	C7–C8	1.356(10)
K1–O10	2.958(10)	C8–C9	1.552(12)
K1–O11	2.818(6)	C21–C22	1.401(13)
K1–O12	3.025(7)	C21–C26	1.362(14)
K1–O13	2.830(8)	C22–C23	1.37(2)
K2–O1	2.631(6)	C23–C24	1.35(2)
K2–O14	2.781(7)	C24–C25	1.38(2)
K2–O15	2.889(9)	C25–C26	1.42(2)

C15–Cr1–C16	86.2(4)	Cr1–S1–O1	117.8(2)
C14–Cr1–C16	88.5(3)	C7–S1–C21	102.8(4)
C14–Cr1–C15	171.3(4)	O1–S1–C21	102.5(3)
C13–Cr1–C16	96.1(4)	O1–S1–C7	112.5(3)
C13–Cr1–C15	94.3(4)	K2–O1–S1	142.7(3)
C13–Cr1–C14	93.2(4)	K1–O2–C8	117.1(5)
C9–Cr1–C16	92.1(3)	K1–O3–C9	116.3(5)
C9–Cr1–C15	89.1(3)	S1–C7–C8	118.8(6)
C9–Cr1–C14	84.1(3)	O2–C8–C7	125.4(7)
C9–Cr1–C13	171.3(3)	C7–C8–C9	114.8(7)
S1–Cr1–C16	172.0(3)	O2–C8–C9	119.8(7)
S1–Cr1–C15	94.3(2)	O3–C9–C8	113.9(7)
S1–Cr1–C14	90.0(3)	Cr1–C9–C8	119.8(5)
S1–Cr1–C13	91.8(3)	Cr1–C9–O3	126.3(6)
S1–Cr1–C9	79.9(2)	S1–C21–C26	121.5(6)
Cr1–S1–C21	114.1(3)	S1–C21–C22	118.0(6)
Cr1–S1–C7	106.2(3)	C22–C21–C26	120.5(8)

Complex 11. Refinement was first done isotropically and then anisotropically by blocked full-matrix least squares for all the non-H atoms except for the THF solvent molecules revealed by the X-ray analysis. One of them (C76–C78) is disordered around a center of symmetry. All the atoms of THF molecules were refined as carbons, no chance to distinguish between carbon and oxygen being possible. The hydrogen atoms, excepting those of the THF molecule which were ignored, were located in a difference Fourier map and introduced in the final refinement as fixed contributors (U_{iso} = 0.10 Å^2). The final difference map showed no unusual features with no significant peak above the general background.

Final atomic coordinates are listed in Tables II–IV for non-H atoms and in Tables SI–SIV (supplementary material) for hydrogens. Thermal parameters are given in Tables SV–SVII, and selected bond distances and angles, in Tables V–VII.[19]

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (14 pages). Ordering information is given on any current masthead page.

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(19) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(20) See paragraph at the end regarding supplementary material.