

Coordinations of vinyltetrahydrothiophene to a trirhenium cluster

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Dedicated to Professor F.A. Cotton on the occasion of his 70th birthday.

Abstract

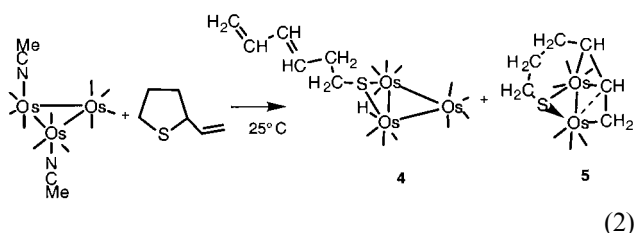
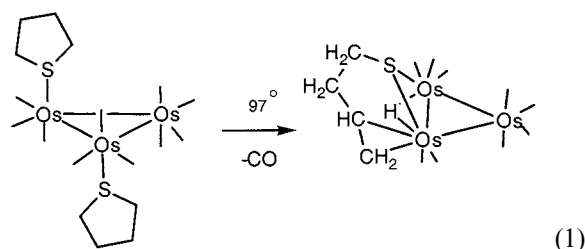
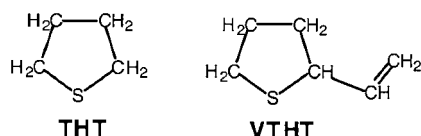
The reaction of $\text{Re}_3(\text{CO})_{10}(\text{NCMe})_2(\mu\text{-H})_3$ with 2-vinyltetrahydrothiophene (VTHT) at 25°C for 22 h yielded two products: $\text{Re}_3(\text{CO})_{10}(\mu\text{-H})_3(\mu\text{-S}(\text{CH}_2)_3\text{CHCH}=\text{CH}_2)$ (**1**; 50% yield), and $\text{Re}_3(\text{CO})_9(\mu\text{-H})_3(\mu\text{-}\eta^3\text{-S}(\text{CH}_2)_3\text{CHCH}_2)$ (**2**; 12% yield). Compound **1** exists in solution as a mixture of isomers in a dynamic equilibrium at room temperature. One of the isomers of **1** and **2** were characterized by single-crystal X-ray diffraction analyses. Compound **1** contains a triangular trirhenium cluster with ten linear terminal carbonyl ligands, three bridging hydride ligands and a bridging vinyltetrahydrothiophene ligand coordinated to two metal atoms by using both of the lone pairs of the electrons on the sulfur atom of the vinyltetrahydrothiophene molecule. Compound **2** contains a triangular cluster of three rhenium atoms and a triple-bridging vinyltetrahydrothiophene ligand that is coordinated to two of the rhenium atoms through the sulfur atom and a π -coordination of the vinyl group to the third metal atom. In both complexes there is a bridging hydride ligand across each of the three rhenium–rhenium bonds in the cluster. Facile interconversion of the two isomers of **1** was observed by 2D EXSY $^1\text{H-NMR}$ spectroscopy. Compound **2** can be obtained from **1** in 98% yield via thermal decarbonylation by refluxing a solution in methylene chloride for 18 h. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Tetrahydrothiophene; Vinyltetrahydrothiophene; Rhenium

1. Introduction

There is considerable interest in the coordination chemistry of thiophene and tetrahydrothiophene because of their importance as models to study the removal of sulfur from the organosulfur impurities that are commonly found in petroleum feedstocks [1–6].

Recently, we have shown that tetrahydrothiophene (THT) and its 2-vinylsubstituted derivative, VTHT, readily undergo ring-opening transformations in reactions with trisrhenium carbonyl complexes, Eqs. (1) and (2) [7,8].



For comparison, we have now investigated the coordination of VTHT to the $\text{Re}_3(\text{CO})_{10}(\mu\text{-H})_3$ cluster. Interestingly, we have not obtained any evidence for ring-opening reactions of the vinyltetrahydrothiophene molecule under mild conditions. These results are reported herein.

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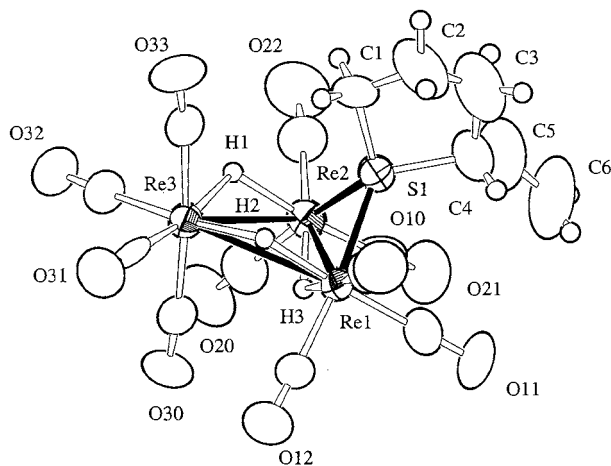


Fig. 1. An ORTEP diagram of the molecular structure $\text{Re}_3(\text{CO})_{10}(\mu\text{-H})_3(\mu\text{-S}(\text{CH}_2)_3\text{CHCH}=\text{CH}_2)$ (**1**) showing 50% probability thermal ellipsoids.

2. Results and discussion

Two products $\text{Re}_3(\text{CO})_{10}(\mu\text{-H})_3(\mu\text{-S}(\text{CH}_2)_3\text{CHCH}=\text{CH}_2)$ (**1**) (50% yield) and $\text{Re}_3(\text{CO})_9(\mu\text{-H})_3(\mu\text{-}\eta^3\text{-S}(\text{CH}_2)_3\text{CHCH}_2)$ (**2**) (12% yield) were obtained from the reaction of $\text{Re}_3(\text{CO})_{10}(\text{NCMe})_2(\mu\text{-H})_3$ with VTHT at 25°C for 22 h. Both products were characterized by a combination of IR, $^1\text{H-NMR}$ and single-crystal X-ray diffraction analyses. In the solid state the structure of compound **1** consists of a triangular trirhenium cluster with ten linear terminal carbonyl ligands, three bridging hydride ligands and a vinyltetrahydrothiophene ligand (Fig. 1). The vinyltetrahydrothiophene ligand bridges one edge of the cluster through the coordination of the sulfur atom that donates a lone pair of electrons to each of the two metal atoms. The sulfur-bridged Re–Re bond, Re(1)–Re(2) at 3.0769(9) Å, is slightly shorter than the other two Re–Re interactions, Re(1)–Re(3) = 3.2046(9) Å and Re(2)–Re(3) = 3.1947(8) Å (Tables 1 and 2). Compound **1** is structurally very similar to the compound $\text{Re}_3(\text{CO})_{10}(\mu\text{-H})_3(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2)$ (**3**) that contains a bridging 3,3-dimethylthietane ligand [9], which also shows a similar shortening in the sulfur-bridged Re–Re bond. The Re–S bond distances in **1**, Re(1)–S(1) = 2.432(4) Å and Re(2)–S(1) = 2.442(4) Å are slightly longer than those in **3**, 2.408(4) Å and 2.410(4) Å. This could be a result of steric crowding because of the presence of the vinyl substituent on one of the carbon atoms adjacent to the sulfur atom. The carbon–sulfur bond distances are typical of carbon–sulfur single bonds, S(1)–C(1) = 1.85(2) Å and S(1)–C(4) = 1.87(2) Å. The vinyl group is oriented away from the cluster in order to minimize steric interactions with the axial carbonyl ligands on the third metal atom. The three hydride ligands located and partially refined crystallographically, are inequivalent because of the

Table 1
Selected intramolecular distances for **1**^a

Distance (Å)		Distance (Å)	
Re(1)–Re(2)	3.0769(9)	O–C(av)	1.16(2)
Re(1)–Re(3)	3.2046(9)	C(1)–C(2)	1.44(3)
Re(2)–Re(3)	3.1947(8)	C(2)–C(3)	1.44(4)
Re(1)–S(1)	2.432(4)	C(3)–C(4)	1.50(3)
Re(2)–S(1)	2.442(4)	C(4)–C(5)	1.39(3)
S(1)–C(1)	1.85(2)	C(5)–C(6)	1.36(4)
S(1)–C(4)	1.87(2)	O–C(av)	1.16(2)

^a Estimated s.d. values in the least significant figure are given in parentheses.

Table 2
Intramolecular bond angles for **1**^a

Angle (°)		Angle (°)	
Re(2)–Re(1)–Re(3)	61.10(2)	C(1)–S(1)–C(4)	94.8(8)
Re(1)–Re(2)–Re(3)	61.42(2)	S(1)–C(1)–C(2)	105(2)
Re(1)–Re(3)–Re(2)	57.48(2)	C(1)–C(2)–C(3)	112(2)
Re(3)–Re(1)–S(1)	83.4(1)	C(2)–C(3)–C(4)	115(2)
Re(3)–Re(2)–S(1)	83.50(9)	S(1)–C(4)–C(3)	103(2)
Re(1)–S(1)–Re(2)	78.3(1)	S(1)–C(4)–C(5)	116(2)
Re–C–O(av)	177(1)	C(3)–C(4)–C(5)	113(2)
		C(4)–C(5)–C(6)	126(3)

^a Estimated s.d. values in the least significant figure are given in parentheses.

asymmetry of the VTHT ligand. Surprisingly, the $^1\text{H-NMR}$ spectrum of **1** shows five highly shielded singlets at $\delta = -13.26$, -13.27 , -16.19 , -16.20 , and -16.35 . The two resonances at -13.26 and -16.20 ppm are of equal intensity but are only 39% of the intensity of the two at -13.27 and -16.19 ppm. The intensity of the resonance at -16.35 ppm is equal to the sum of the strong and weak resonance from each set. The chemical-shift difference between the closely spaced resonances varies directly with the strength of the applied magnetic field which indicates that the differences between the resonances are not a result of coupling effects. In addition, the resonances for the vinyl protons also appear in two unequal sets. It was suspected that the compound exists in solution as a mixture of two isomers that accidentally have their most shielded hydride resonance at the same position. This was confirmed by a 2D EXSY $^1\text{H-NMR}$ spectrum of the vinyl proton resonances by using a mixing time of 800 ms. This spectrum, shown in Fig. 2, shows significant peaks off the diagonal between the two sets of vinyl proton resonances. This indicates not only that there are two isomers in solution, but also that they are interconverting at this temperature. It is proposed that one of these isomers has the structure that was found in the solid state **1a**. The other isomer **1b** has a similar structure with a bridging VTHT ligand, but has its vinyl group directed over the cluster. The ratio of the two isomers is

2.6:1. The mechanism of their interconversion has not been established, but a mechanism involving opening and closing of the sulfur bridge, accompanied by inversion of configuration of the terminally coordinated VTHT ligand, would be an attractive possibility (see Scheme 1).

Compound **2** crystallizes with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP dia-

gram of the molecular structure of one of these is shown in Fig. 3. Selected bond distances and angles are listed in Tables 3 and 4, respectively. Compound **2** is also composed of a trirhenium cluster with three bridging hydride ligands and a bridging VTHT ligand. In this case, however, there are only nine carbonyl ligands and the VTHT ligand is a triply bridging ligand. As in **1**, the sulfur atom is coordinated to two metal atoms, but in this molecule the vinyl group is coordinated to

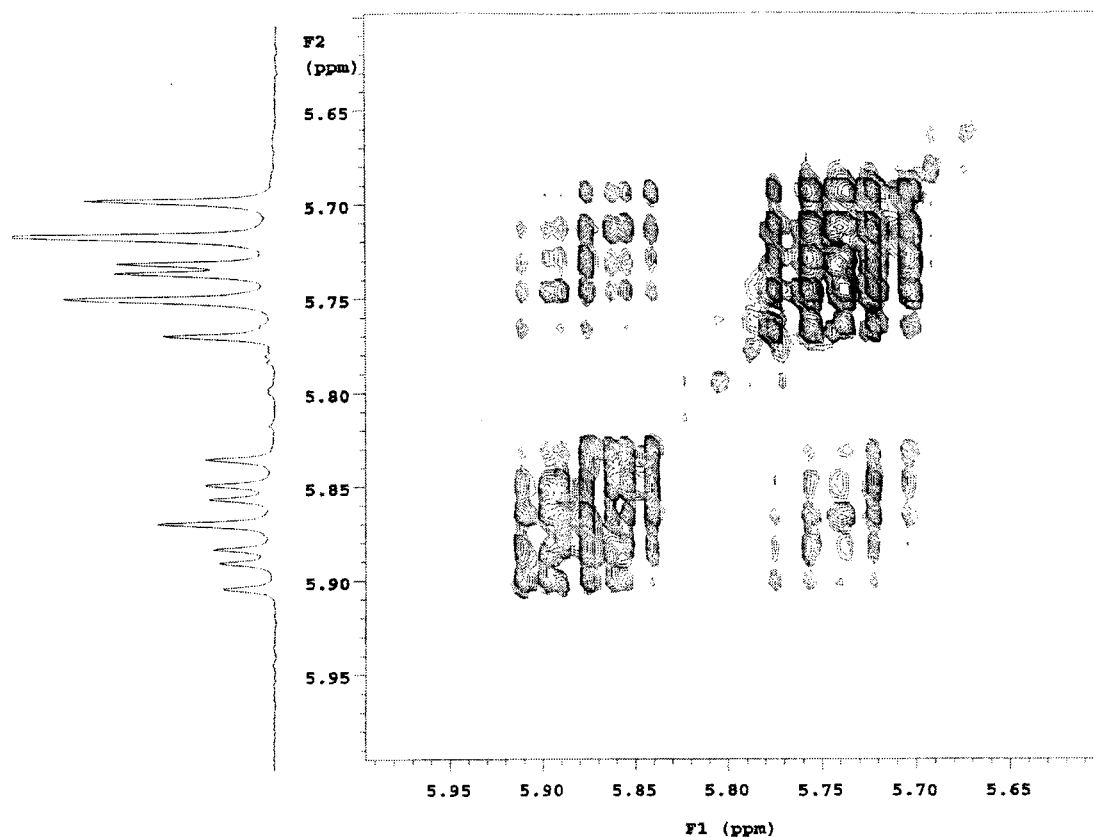
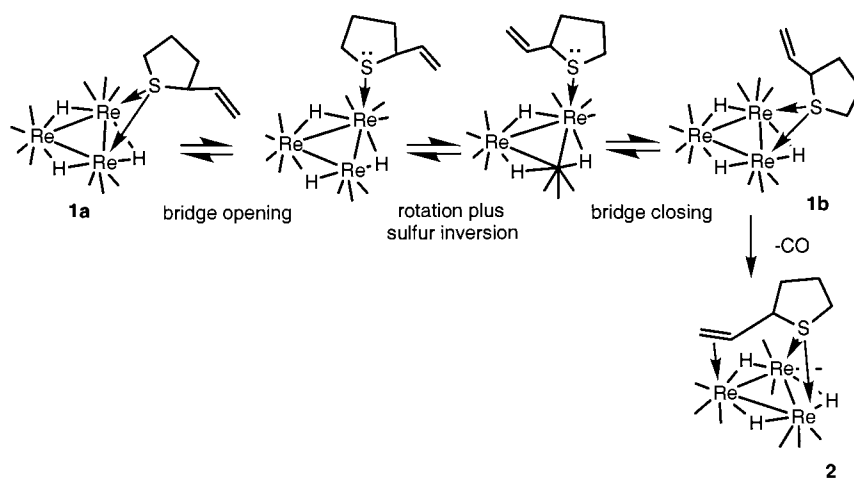


Fig. 2. A 2D EXSY spectrum of the vinyl proton resonances of **1** recorded at 25°C using a 800 ms time delay at 500 MHz.



Scheme 1.

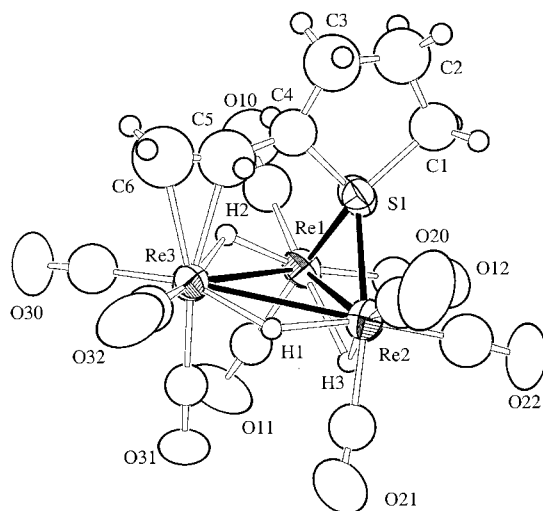


Fig. 3. An ORTEP diagram of the molecular structure of $\text{Re}_3(\text{CO})_9(\mu\text{-H})_3(\mu\text{-}\eta^3\text{-S}(\text{CH}_2)_3\text{CHCH}_2)$ (**2**) showing 50% probability thermal ellipsoids.

the third metal atom. The cluster has one short and two long Re–Re distances, which are: $\text{Re}(1)\text{--Re}(2) = 3.037(1) \text{ \AA}$ [3.046(1) \AA]; $\text{Re}(1)\text{--Re}(3) = 3.214(1) \text{ \AA}$ [3.214(1) \AA]; $\text{Re}(2)\text{--Re}(3) = 3.208(1) \text{ \AA}$ [3.230(1) \AA]. The values in brackets correspond to the second independent molecule in the crystal. The short Re–Re bond in **2** is slightly shorter than the short one found in **1** while the long values in **2** are slightly longer than the long values found in **1**. The Re–S distances: $\text{Re}(1)\text{--S}(1) = 2.396(6) \text{ \AA}$ [2.402(6) \AA]; $\text{Re}(2)\text{--S}(1) = 2.401(6) \text{ \AA}$ [2.403(6) \AA] are slightly shorter than those found in **1**. It appears that the C–S distance to the vinyl substituted carbon atom, $\text{S}(1)\text{--}(4) = 1.78(3) \text{ \AA}$ [1.83(3) \AA], is slightly shorter than that to the unsubstituted carbon atom, $\text{S}(1)\text{--C}(1) = 1.86(3) \text{ \AA}$ [1.86(3) \AA], but this difference is not significant by the 3σ criterion. The vinyl group is coordinated to the third rhenium atom: $\text{Re}(3)\text{--C}(5) = 2.36(4) \text{ \AA}$ [2.41(3) \AA] and $\text{Re}(3)\text{--C}(6) = 2.41(4) \text{ \AA}$ [2.36(4) \AA]. As expected, the $^1\text{H-NMR}$ spectrum of **2** shows only three highly shielded singlets at $\delta = -13.95$, -14.66 , and -16.04 ppm for each of the three inequivalent hydride ligands.

Compound **2** can be obtained in high yield by thermal decarbonylation of **1**. It is unlikely that **2** is obtained directly from **1a** since the vinyl group in **1a** is oriented away from the rhenium atom to which it must become coordinated. Instead, it seems to be most likely that **2** is obtained by decarbonylation of **1b**, the proposed isomer of **1a**, in which the vinyl group is oriented toward to the third rhenium atom. Isomer **1a** then spontaneously isomerizes to **1b** as the concentration of **1b** is depleted and conversion to **2**

Table 3
Intramolecular distances for **2**^a

Distance (\AA)		Distance (\AA)	
Re(1)–Re(2)	3.037(1)	Re(4)–Re(5)	3.046(1)
Re(1)–Re(3)	3.214(1)	Re(4)–Re(6)	3.214(1)
Re(2)–Re(3)	3.208(1)	Re(5)–Re(6)	3.230(1)
Re(1)–S(1)	2.396(6)	Re(4)–S(2)	2.402(6)
Re(2)–S(1)	2.401(6)	Re(5)–S(2)	2.403(6)
Re(3)–C(5)	2.36(4)	Re(6)–C(75)	2.41(3)
Re(3)–C(6)	2.41(4)	Re(6)–C(76)	2.36(4)
S(1)–C(1)	1.86(3)	S(2)–C(71)	1.86(3)
S(1)–C(4)	1.78(3)	S(2)–C(74)	1.83(3)
C(1)–C(2)	1.45(4)	C(71)–C(72)	1.52(4)
C(2)–C(3)	1.45(4)	C(72)–C(73)	1.50(5)
C(3)–C(4)	1.46(4)	C(73)–C(74)	1.47(5)
C(4)–C(5)	1.36(4)	C(74)–C(75)	1.36(4)
C(5)–C(6)	1.18(4)	C(75)–C(76)	1.21(4)

^a Estimated s.d. values in the least significant figure are given in parentheses.

Table 4
Selected intramolecular bond angles for **2**^a

Angle ($^\circ$)		Angle ($^\circ$)	
Re(2)–Re(1)–Re(3)	61.67(3)	Re(5)–Re(4)–Re(6)	62.04(3)
Re(1)–Re(2)–Re(3)	61.89(3)	Re(4)–Re(5)–Re(6)	61.54(3)
Re(1)–Re(3)–Re(2)	56.44(3)	Re(4)–Re(6)–Re(5)	56.42(3)
Re(1)–S(1)–Re(2)	78.5(2)	Re(4)–S(2)–Re(5)	78.7(2)
C(1)–S(1)–C(4)	95(1)	C(71)–S(2)–C(74)	96(1)

^a Estimated s.d. values in the least significant figure are given in parentheses.

continues in this process until all of the mixture of **1a** and **1b** is converted to **2**.

The reaction of VTHT with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ yielded two products **4** and **5** both of which involved opening of the VTHT ring (Eq. (2)) [8]. No products containing VTHT ligands were isolated from these osmium reactions.

By contrast in the reactions of the trirhenium cluster $\text{Re}_3(\text{CO})_{10}(\text{NCMe})_2(\mu\text{-H})_3$ with VTHT reported here, no products were obtained that involved opening of the VTHT ring. Both of the products **1** and **2** contained bridging VTHT ligands. We believe that the ring-opening reactions observed in the osmium reactions are dependent on metal–metal bond cleavage processes, which in turn facilitate cleavage of a carbon–sulfur bond of the VTHT ligand. The presence of the hydride ligands in the rhenium cluster inhibits these metal–metal bond cleavage reactions and thus the carbon–sulfur bond cleavage reactions do not occur. Additional evidence for this conclusion will be presented in a forthcoming report [10].

3. Experimental

3.1. General data

Reagent grade solvents were dried by using sodium-benzophenone followed by distillation and were either used immediately or stored over 4 Å molecular sieves. 2-Vinyltetrahydrothiophene (VTHT) [11] and $\text{Re}_3(\text{CO})_{10}(\text{NCMe})_2(\mu\text{-H})_3$ [9,12] were prepared by previously reported procedures. All reactions were performed under a nitrogen atmosphere unless specified otherwise. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. $^1\text{H-NMR}$ spectra were run on either a Brüker AM-300 or a Varian Inova 500 spectrometer operating at 300 and 500 MHz, respectively. Chromatographic separations were performed in air on silica gel by using Analtech (0.25 mm) F_{254} uniplates. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

3.2. Reaction of $\text{Re}_3(\text{CO})_{10}(\text{NCMe})_2(\mu\text{-H})_3$ with 2-vinyltetrahydrothiophene

A 50 mg amount of $\text{Re}_3(\text{CO})_{10}(\text{NCMe})_2(\mu\text{-H})_3$ (0.054 mmol) was dissolved in 20 ml of CH_2Cl_2 in a 50 ml round-bottomed flask. A total of 12.3 μl (0.108 mmol) of 2-vinyltetrahydrothiophene was added, and the resulting solution was stirred for 22 h at 25°C. The solvent was removed under reduced pressure and the residue was separated by TLC using a 2:1 hexane– CH_2Cl_2 solvent mixture as eluant. The following compounds were isolated in order of elution: $\text{Re}_3(\text{CO})_{10}(\mu\text{-H})_3(\mu\text{-S}(\text{CH}_2)_3\text{CHCH}=\text{CH}_2)$, **1** (25.9 mg, 50%), and $\text{Re}_3(\text{CO})_9(\mu\text{-H})_3(\mu\text{-}\eta^3\text{-S}(\text{CH}_2)_3\text{CHCHCH}_2)$, **2** (6.1 mg, 12%). Analytical and spectral data for **1**: IR ν_{CO} (cm^{-1} in hexane): 2102 (m), 2047 (m), 2031 (vs), 2015 (s), 1988 (vs), 1976 (s), 1959 (s), 1947 (m), 1939 (sh). $^1\text{H-NMR}$ spectrum of **1** (δ in CD_2Cl_2): major isomer: 5.74 (ddd, $J_{\text{H-H}} = 10.0$ Hz, $J_{\text{H-H}} = 10.0$ Hz, $J_{\text{H-H}} = 16.5$, 1H), 5.55 (d, $J_{\text{H-H}} = 10.0$ Hz, 1H), 5.49 (d, $J_{\text{H-H}} = 17.0$ Hz, 1H), 3.93 (m, 1H), 3.49 (m, 1H), 3.30 (ddd, $J_{\text{H-H}} = 5.0$ Hz, $J_{\text{H-H}} = 7.5$ Hz, $J_{\text{H-H}} = 12.5$ Hz, 1H), 2.56–2.17 (m, 4H), –13.27 (s, 1H), –16.19 (s, 1H), –16.35 (s, 1H); minor isomer: 5.86 (ddd, $J_{\text{H-H}} = 7.0$ Hz, $J_{\text{H-H}} = 10.5$ Hz, $J_{\text{H-H}} = 17.5$ Hz, 1H), 5.49 (dd, $J_{\text{H-H}} = 1.0$ Hz, $J_{\text{H-H}} = 10.5$ Hz, 1H), 5.40 (dd, $J_{\text{H-H}} = 1.0$ Hz, $J_{\text{H-H}} = 17.5$ Hz, 1H), 3.84 (m, 1H), 3.49 (m, 1H), 3.21 (ddd, $J_{\text{H-H}} = 7.0$ Hz, $J_{\text{H-H}} = 7.5$ Hz, $J_{\text{H-H}} = 13.0$ Hz, 1H), 2.56–2.17 (m, 4H), –13.26 (s, 1H), –16.20 (s, 1H), –16.35 (s, 1H). The ratio of major isomer **1** to the minor isomer is 2.6/1. Anal. Calc. for **1**: C, 20.10; H, 1.37. Found: C, 20.31; H, 1.10%. Analytical and spectral data for **2**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2063 (s), 2033 (vs), 2025 (vs), 1976 (m), 1949 (s), 1935 (sh). $^1\text{H-NMR}$ (δ in CD_2Cl_2): 4.35 (dd, $J_{\text{H-H}} = 1.2$ Hz, $J_{\text{H-H}} = 8.0$ Hz, 1H), 4.02 (m, 1H), 3.89 (dd, $J_{\text{H-H}} = 0.4$

Hz, $J_{\text{H-H}} = 13.6$ Hz, 1H), 3.34 (m, 2H), 2.97 (m, 1H), 2.73 (m, 1H), 2.46 (m, 1H), 2.34 (m, 1H), 2.06 (m, 1H), –13.95 (s, 1H), –14.66 (s, 1H), –16.04 (s, 1H). Anal. Calc. for **2**: C, 19.42; H, 1.41. Found: C, 19.44; H, 1.32%.

3.3. Interconversion of the isomers of **1**

An 8.0 mg amount of **1** was dissolved in 1 ml of CDCl_3 . This solution was transferred to a serum capped NMR tube under nitrogen. Chemical exchange spectra of the sample were recorded by using the standard Varian NOESY sequence on a Varian Inova 500 MHz spectrometer. The chemical exchange was monitored by $^1\text{H-NMR}$ at 500.154 MHz at 25°C. A 9 ppm window centered at 4.5 ppm was collected with 2048 FIDs and 16 scans per FID using a 2 s recycle time and a 800 ms mixing time. Data were zero filled to 4096 points in both dimensions and weighted with a matched Gaussian filter.

3.4. Transformation of **1** to **2**

A 7.5 mg amount of **1** (0.0079 mmol) was dissolved in 5 ml of distilled CH_2Cl_2 and the solution was refluxed under nitrogen. The reaction was monitored by IR and after 18 h, only **2** was present in the mixture. The solvent was evaporated and the product was separated by TLC using a hexane–methylene chloride (2:1) solvent mixture to yield **2** (7.1 mg, 98%).

3.5. Crystallographic analyses

Crystals of **1** and **2** suitable for X-ray diffraction measurements were obtained by slow evaporation of solvent from solutions in hexane–methylenechloride solvent mixtures at 25°C. The crystals used in data collection were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data-collection parameters, and results of the analyses are listed in Table 5. All data processing was performed on a Silicon Graphics Indigo² computer by using the texsan structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX, USA. Neutral atom scattering factors were calculated by the standard procedures [13a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [13b]. An absorption correction (DIFABS) was applied in each analysis. Full matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_{\text{obs}}^2)/2F_{\text{obs}}$ and $\sigma(F_{\text{obs}}^2) = [\sigma(I_{\text{raw}})^2 + (0.06I_{\text{net}})^2]^{1/2}/L_p$.

Table 5
Crystallographic data for compounds **1** and **2**

Compound	1	2
Formula	Re ₃ SO ₁₀ C ₁₆ H ₁₃	Re ₃ SO ₉ C ₁₅ H ₁₃
Formula weight	955.95	927.94
Crystal system	Monoclinic	Monoclinic
Unit cell dimensions		
<i>a</i> (Å)	9.349(2)	8.418(3)
<i>b</i> (Å)	17.318(5)	26.11(1)
<i>c</i> (Å)	14.542(6)	19.643(7)
α (°)	90	90
β (°)	91.52(2)	94.41(3)
γ (°)	90	90
<i>V</i> (Å ³)	2353.5(8)	4304(2)
Space group	<i>P</i> 2 ₁ / <i>n</i> (# 14)	<i>P</i> 2 ₁ / <i>c</i> (# 14)
<i>Z</i>	4	8
<i>D</i> _{calc} (g cm ⁻³)	2.70	2.86
μ (Mo–K α) (cm ⁻¹)	155.3	166.8
Temperature (°C)	20	20
2 θ _{max} (°)	47	41
No. of observations (<i>I</i> > 3 σ (<i>I</i>))	2803	3120
No. of variables	272	190
Goodness-of-fit (GoF)	1.26	1.15
Max shift in final cycle	0.00	0.01
Residuals ^a : <i>R</i> , <i>R</i> _w	0.041, 0.058	0.037, 0.057
Absorption correction	DIFABS	DIFABS
Transmission coefficient (max.–min.)	1.000–0.40	1.00–0.63
Largest peak in final difference Fourier analysis (e Å ⁻³)	2.05	1.03

$$^a R = \frac{\sum_{hkl} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{hkl} |F_{\text{obs}}|}{\sum_{hkl} |F_{\text{obs}}|^{1/2}}, \quad R_w = \frac{[\sum_{hkl} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2]}{[\sum_{hkl} w |F_{\text{obs}}|]}, \quad w = 1/\sigma^2(F_{\text{obs}}), \quad \text{GoF} = \frac{[\sum_{hkl} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sigma(F_{\text{obs}})]}{(n_{\text{data}} - n_{\text{vari}})}$$

Compounds **1** and **2** crystallized in the monoclinic crystal system. The space group settings *P*2₁/*n* and *P*2₁/*c*, respectively, were identified on the basis of the systematic absences observed in the intensity data. Both structures were solved by a combination of direct methods (SIR92) and difference Fourier syntheses. For **1**, all of the nonhydrogen atoms were refined with anisotropic thermal parameters. Because of the limited amount of data, only the atoms heavier than carbon were refined anisotropically for **2**. The hydride ligands were located and partially refined in each analysis and were then fixed on the final cycles of refinement. All hydrogen atom positions on the ligands were calculated by assuming idealized geometries with C–H distances of 0.95 Å. These hydrogen atoms were included in the structure factor calculations without refinement.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 133002 and CCDC no. 133003 for compounds **1** and **2**, respectively. Copies of

this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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