A chalcogen-stabilized cluster containing a s-*trans*-1,3-diene ligand: synthesis and structural characterization of $\{(CO)_6Fe_2Se_2\}_2(\mu\text{-s-trans-}C_4H_2)$

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Abstract

Reaction of $(CO)_6Fe_2(\mu\text{-Se})_2$ with $HC\equiv CC\equiv CR$ (R = $SiMe_3$ or Sn^nBu_3) at room temperature in methanol containing sodium acetate yielded the unexpected product $\{(CO)_6Fe_2Se_2\}_2(\mu\text{-s-trans-}C_4H_2)$ in which a 1,3-butadiene ligand is coordinated to the Fe_2Se_2 core in a *trans* conformation as determined by a single-crystal X-ray diffraction studies. The complex was also obtained with a low yield by reaction of $(CO)_6Fe_2(\mu\text{-Se})_2$ with $HC\equiv CC\equiv CH$ under similar conditions.

Keywords: Iron; Carbonyl; Cluster; Butadiene; Selenium; Crystal structure

1. Introduction

Transition metal complexes of conjugated dienes are of considerable interest as substrates or reagents in many catalytic processes and organic syntheses [1]. 1,3-Butadiene, the simplest acyclic conjugated diene, exists in two conformations, planar s-*cis* and s-*trans* forms, which are separated by an activation barrier of only 4 kcal mole [2]. At ambient temperature, free butadiene adopts the more stable s-*trans* conformation, but the other conformation when is bonded to a metal centre. Most mononuclear and polynuclear metal complexes prefer η^4 complexation with the less stable but readily available s-*cis*-butadiene conformer [3]. There is currently a resurgence of interest in acyclic(diene) $Fe(CO)_3$ complexes as organic intermediates [4]. In such complexes, the $Fe(CO)_3$ moiety activates the coordinated dienes towards both electrophiles and nucleophiles, giving rise to highly stereospecific and regiospecific products [5]. It stabilizes allyl and dienyl carbonium ions and may act as a protecting, activating or directing group in various reactions [6].

During our investigation of the reactivity of the chalocogen-stabilized compounds $(CO)_6Fe_2(\mu\text{-EE}')$ where E,E' = S, Se, or Te, the facile addition of acetylenes [7] and diacetylenes [8] was observed. In the compound $(CO)_6Fe_2\{\mu\text{-SeC(H)} = C(Ph)Se\}$ the reactive Se sites are blocked, thus enabling cluster growth to occur across the Fe–Fe bond to give $Cp_2Mo_2(CO)_6$-$Fe_2(\mu_4\text{-Se})$ $(\mu_3\text{-Se})_2$ [9]. We report here the synthesis of a symmetrical diacetylene adduct of $(CO)_6Fe_2(\mu\text{-Se})_2$ and its characterization by spectroscopic and X-ray diffraction methods.

2. Experimental details

Reactions and manipulations were carried out under an atmosphere of argon or nitrogen by use of standard Schlenk techniques. Solvents were deoxygenated immediately prior to use. IR spectra were recorded on a Nicolet Impact 400 Fourier transform spectrometer for hexane solutions in 0.1 mm path length NaCl cells. The ^1H, ^{13}C and ^{77}Se NMR spectra were recorded in $CDCl_3$ on a Varian VXR-300S spectrometer at 25°C. The ^{77}Se NMR signals were referenced to Me_2Se (δ = 0 ppm); the spectra were obtained at an operating frequency of

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Table 1
Crystal data and structure refinement for $\{(CO)_6Fe_2Se_2\}_2(\mu\text{-s-}trans\text{-}C_4H_2)$

Empirical formula	$C_{16}H_2Fe_4O_{12}Se_4$
Formula weight	925.42
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.7764(2)
b (Å)	15.9229(6)
c (Å)	9.1431(10)
β (°)	90.355(8)
Volume (Å^3)	1277.7(2)
Z	2
D_c (g cm^{-3})	2.405
Absorption coefficient (cm^{-1})	7.979
$F(000)$	868
Crystal size (mm)	0.3 × 0.2 × 0.2
θ range for data collection (°)	2.56–24.98
Index range	$h = -10$ to $+10$, $k = 0$ to $+18$, $l = 0$ to $+10$
Number of reflections collected	2240
Number of independent reflections	2240 (R(int) = 0.0000)
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Number of data	2240
Number of restraints	0
Number of parameters	164
Goodness of fit on F^2	1.024
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0408$, $wR_2 = 0.1000$
R indices (all data)	$R_1 = 0.0516$, $wR_2 = 0.1034$
Extinction coefficient	0.0000(4)
Largest difference peak and hole (electron Å^{-3})	0.278 and -0.598

57.23 MHz using a pulse width of 15 µs and a delay of 2 s. Elemental analysis was earned out with a Carlo Erba automatic analyzer. The compounds $(CO)_6Fe_2(\mu\text{-}Se)_2$ [10] and $HC\equiv CC\equiv CR$ (R = H, SiMe$_3$, or Sn^{n}Bu$_3$) [11] were prepared as previously described.

2.1. Reaction of $(CO)_6Fe_2(\mu\text{-}Se)_2$ with $HC\equiv CC\equiv CR$ (R = SiMe$_3$ or Sn^{n}Bu$_3$)

A methanol solution (15 ml) of freshly prepared $(CO)_6Fe_2(\mu\text{-}Se)_2$ (0.54 g, 1.23 mmol), anhydrous sodium acetate (0.25 g) and $HC\equiv CC\equiv CSiMe_3$ (0.6 ml, 9.57 mmol) was stirred at room temperature for 16 h. The solvent was evaporated in vacuo and the residue dissolved in 5 ml of dichloromethane. The solution was filtered through Celite to remove insoluble material, the solvent removed, and the residue dissolved in 5 ml of hexane. Chromatographic separation on a silica gel column with hexane as eluant gave the dark-red complex $\{(CO)_6Fe_2Se_2\}_2(\mu\text{-s-}trans\text{-}C_4H_2)$ (0.27 g, (47%)). IR: ν (CO), 2073 (vs), 2040 (s), 2002 (vs), 1989 (m) cm^{-1} ^{1}H NMR: δ 7.39 (s, CH, $^2J_{H-Se} = 52$ Hz, $^3J_{H-Se} = 5.4$ Hz) ppm. ^{13}C (^{1}H) NMR: δ 137.1 (d, CH, $J_{C-H} = 184.42$ Hz), 149.77 (s, CCH), 208 (CO) ppm. ^{77}Se NMR: δ 369.28 (d, $^2J_{Se-H} = 52$ Hz), 458.8 (d,

$^3J_{Se-H} = 6$ Hz) ppm. Melting point, 154–156°C (decomposition). Anal. $C_{16}H_2Fe_2O_{12}Se_4$ Calc.: C, 21.02; H, 0.56. Found: C, 20.73; H, 0.21%.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $\{(CO)_6Fe_2Se_2\}_2(\mu\text{-s-}trans\text{-}C_4H_2)$, where U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3}$ Å^2)
Se(1)	580(1)	9628(1)	7546(1)	32(1)
Se(2)	2592(1)	8368(1)	9286(1)	34(1)
Fe(1)	1050(1)	8171(1)	7159(1)	31(1)
Fe(2)	3168(1)	9226(1)	7219(1)	33(1)
O(1)	-28(7)	8375(4)	4163(6)	65(2)
O(2)	-1581(7)	7287(5)	8362(7)	81(2)
O(3)	2907(7)	6718(3)	6329(7)	64(2)
O(4)	3025(7)	9845(5)	4225(6)	81(2)
O(5)	4891(7)	10599(4)	8575(7)	82(2)
O(6)	5789(6)	8180(4)	6493(8)	84(2)
C(1)	373(8)	8291(4)	5303(8)	43(2)
C(2)	-615(8)	7638(5)	7905(7)	45(2)
C(3)	2158(8)	7277(5)	6679(8)	46(2)
C(4)	3077(8)	9610(5)	5376(9)	51(2)
C(5)	4176(7)	10065(4)	8042(8)	43(2)
C(6)	4816(7)	8578(5)	6809(8)	45(2)
C(7)	493(6)	9690(4)	9702(6)	29(1)
C(8)	1354(6)	9143(4)	10386(7)	32(1)

By a similar procedure, the complex $\{(CO)_6Fe_2Se_2\}_2$-(μ-s-*trans*-C_4H_2) was obtained with a yield of 0.25 g (45%) from the reaction of $(CO)_6Fe_2(\mu$-Se$)_2$ (0.54 g, 1.23 mmol) with $HC{\equiv}CC{\equiv}CSn^nBu_3$ (2.16 ml, 9.57 mmol) in the presence of sodium acetate (0.25 g).

2.2. Reaction of $(CO)_6Fe_2(\mu$-Se$)_2$ with $HC{\equiv}CC{\equiv}CH$

Diacetylene gas was prepared and condensed in dry methanol (30 ml) at $-78°C$. A portion of the solution containing 0.54 g (1.23 mol) of the diacetylene was added to a methanol solution (15 ml) containing freshly prepared $(CO)_6Fe_2(\mu$-Se$)_2$ (0.54 g, 1.23 mmol) and anhydrous sodium acetate (0.25 g). The mixture was stirred at room temperature for 16 h, and the solvent then removed in vacuo. The residue was dissolved in 5

ml of dichloromethane and the solution was filtered through Celite, the solvent was evaporated off, and the residue redissolved in 5 ml of hexane. Chromatography on a silica gel column with hexane as eluant yielded $\{(CO)_6Fe_2Se_2\}_2(\mu$-s-*trans*-C_4H_2) (0.068 g (12%)).

2.3. Crystal structure determination of $\{(CO)_6Fe_2Se_2\}_2$-(μ-s-*trans*-C_4H_2)

A dark-red hexagonal single crystal of approximate dimensions $0.3 \times 0.2 \times 0.2$ mm^3 was used. The data were collected on a Enraf–Nonius CAD 4 diffractometer generating Mo $K\alpha$ radiation at room temperature by use of the ω–2θ scan method. Pertinent crystallographic data are listed in Table 1. The structure was solved by the heavy atom method by locating the

Table 3
Bond lengths and angles for $\{(CO)_6Fe_2Se_2\}_2(\mu$-s-*trans*-C_4H_2)

Bond lengths

Se(1)–C(7)	1.976(5)	O(1)–C(1)	1.106(8)
Se(1)–Fe(2)	2.3809(10)	O(2)–C(2)	1.100(8)
Se(1)–Fe(1)	2.3837(10)	O(3)–C(3)	1.152(8)
Se(2)–C(8)	1.932(5)	O(4)–C(4)	1.118(9)
Se(2)–Fe(1)	2.3828(11)	O(5)–C(5)	1.162(8)
Se(2)–Fe(2)	2.3883(11)	O(6)–C(6)	1.103(8)
Fe(1)–C(3)	1.781(8)	C(7)–C(8)	1.309(9)
Fe(1)–C(1)	1.805(7)	C(7)–C(7′)	1.423(11)
Fe(1)–C(2)	1.826(6)		
Fe(1)–Fe(2)	2.5055(12)		
Fe(2)–C(5)	1.769(7)		
Fe(2)–C(4)	1.794(8)		
Fe(2)–C(6)	1.817(6)		

Bond angles

C(7)–Se(1)–Fe(2)	100.4(2)	C(5)–Fe(2)–C(4)	99.3(3)
C(7)–Se(1)–Fe(1)	101.8(2)	C(5)–Fe(2)–C(6)	96.9(3)
Fe(2)–Se(1)–Fe(1)	63.45(3)	C(4)–Fe(2)–C(6)	91.8(3)
C(8)–Se(2)–Fe(1)	101.0(2)	C(5)–Fe(2)–Se(1)	102.6(2)
C(8)–Se(2)–Fe(2)	99.7(2)	C(4)–Fe(2)–Se(1)	89.4(2)
C(3)–Fe(1)–C(1)	91.7(3)	C(6)–Fe(2)–Se(1)	160.0(2)
C(3)–Fe(1)–C(2)	99.2(3)	C(5)–Fe(2)–Se(2)	101.7(2)
C(1)–Fe(1)–C(2)	98.1(3)	C(4)–Fe(2)–Se(2)	158.4(2)
C(3)–Fe(1)–Se(2)	89.9(2)	C(6)–Fe(2)–Se(2)	90.6(2)
C(1)–Fe(1)–Se(2)	159.3(2)	Se(1)–Fe(2)–Se(2)	81.26(3)
C(2)–Fe(1)–Se(2)	102.0(2)	C(5)–Fe(2)–Fe(1)	152.3(2)
C(3)–Fe(1)–Se(1)	155.6(2)	C(4)–Fe(2)–Fe(1)	100.3(2)
C(1)–Fe(1)–Se(1)	88.9(2)	C(6)–Fe(2)–Fe(1)	101.9(2)
C(2)–Fe(1)–Se(1)	104.9(2)	Se(1)–Fe(2)–Fe(1)	58.33(3)
Se(2)–Fe(1)–Se(1)	81.31(3)	Se(2)–Fe(2)–Fe(1)	58.21(3)
C(3)–Fe(1)–Fe(2)	97.8(2)	O(1)–C(1)–Fe(1)	178.9(6)
C(1)–Fe(1)–Fe(2)	100.9(2)	O(2)–C(2)–Fe(1)	176.9(8)
C(2)–Fe(1)–Fe(2)	154.0(2)	O(3)–C(3)–Fe(1)	177.2(6)
Se(2)–Fe(1)–Fe(2)	58.43(3)	O(4)–C(4)–Fe(2)	179.6(7)
Se(1)–Fe(1)–Fe(2)	58.22(3)	O(5)–C(5)–Fe(2)	177.3(7)
		C(8)–C(7)–C(7′)	128.9(7)
		C(8)–C(7)–Se(1)	114.7(4)
		C(7′)–C(7)–Se(1)	116.4(6)
		C(7)–C(8)–Se(2)	120.1(4)

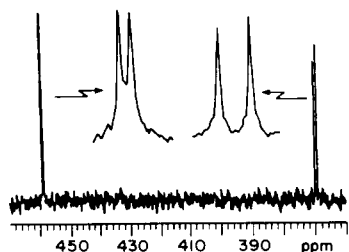Symmetry transformations used to generate equivalent atoms: $-x, -y + 2, -z + 2$.
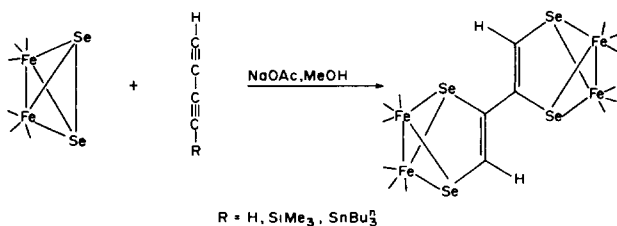
Scheme 1. Preparation of {(CO)$_6$Fe$_2$Se$_2$}$_2$(μ-s-trans-C$_4$H$_2$)}.

heaviest atom Se in the Patterson map. Unit-cell parameters were determined and refined from 24 randomly selected reflections with the maximum θ of 25° by the least-squares method. The full-matrix least-squares refinement of all the atoms converged to an R_1 index of 0.0408 ($wR_2 = 0.1034$). Data processing and refinement was carried out using the SHELXL-93 package [12]. Table 2 lists the atomic coordinates, and Table 3 lists the bond lengths and angles. A list of thermal parameters has been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

When a methanol solution of (CO)$_6$Fe$_2$(μ-Se)$_2$ and HC≡CC≡CR (R = SiMe$_3$ or Sn^{n}Bu$_3$) was stirred at room temperature in the presence of sodium acetate for 16 h, the new compound {(CO)$_6$Fe$_2$Se$_2$}$_2$(μ-s-trans-C$_4$H$_2$) was obtained with a 47% yield. It was also obtained with a 12% yield by the direct addition of (CO)$_6$Fe$_2$(μ-Se)$_2$ and HC≡CC≡CH (Scheme 1). The product was characterized by IR and ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy. The IR spectrum of {(CO)$_6$Fe$_2$-Se$_2$}$_2$(μ-s-trans-C$_4$H$_2$) indicated the presence of only terminally bonded carbonyl groups with a carbonyl stretching pattern typically found for compounds containing Fe$_2$(CO)$_6$ groups. The ^{1}H NMR spectrum showed a single peak with two pairs of ^{77}Se satellites ($^2J_{H-Se}$ = 52 Hz and $^3J_{H-Se}$ = 5.5 Hz). The proton-coupled ^{13}C NMR spectrum showed a single peak in the

CO region, indicating the equivalence of the carbonyl ligands on the NMR time scale at room temperature, as well as two other signals, a doublet (J_{C-H} = 184.5 Hz) for the CH carbon atoms and a singlet for the C=CH carbon atoms. The ^{77}Se NMR spectrum showed two doublets (J_{Se-H} = 52 Hz and 6 Hz) (Fig. 1). The higher field signal has the larger coupling and therefore can be assigned to the Se atom which is bonded to the CH group and the downfield signal with smaller Se–H coupling can be assigned to the Se atom which is farther away from CH group.

3.2. Molecular structure of {(CO)$_6$Fe$_2$Se$_2$}$_2$(μ-s-trans-C$_4$H$_2$)

Dark-red air-stable crystals of {(CO)$_6$Fe$_2$Se$_2$}$_2$(μ-s-trans-C$_4$H$_2$) were obtained from a hexane–CH$_2$Cl$_2$ solution at −10°C and an X-ray diffraction study was undertaken. An ORTEP diagram of the molecular structure of {(CO)$_6$Fe$_2$Se$_2$}$_2$(μ-s-trans-C$_4$H$_2$) is shown in Fig. 2. The structure consists of two Fe$_2$Se$_2$ butterfly tetrahedra connected by a s-trans-1,3-butadiene moiety. Each Fe atom has three terminally bonded carbonyl groups. The bridging butadiene group is attached to both the Se atoms of each (CO)$_6$Fe$_2$(μ-Se)$_2$ group such that the molecule is centrosymmetric with a crystallographic inversion centre at midpoint of C(7)–C(7') bond. The three terminally bonded CO groups, two μ_3-Se atoms and the Fe–Fe bond define a distorted octahedral geometry around each Fe atom. The C(7)–C(8) bond distance of 1.309(9) Å indicates reduction of the acetylenic triple bond to an olefinic bond. It is similar to the corresponding bond distances of coordinated

Fig. 1. ^{77}Se NMR spectrum of {(CO)$_6$Fe$_2$Se$_2$}$_2$(μ-s-trans-C$_4$H$_2$)}.
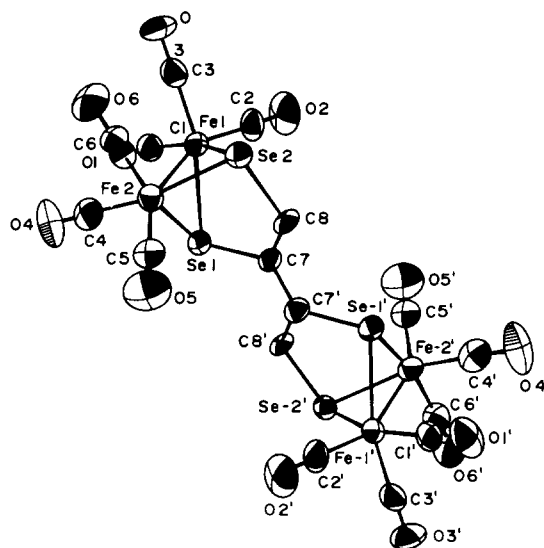
Fig. 2. ORTEP drawing of the molecular structure of {(CO)$_6$Fe$_2$Se$_2$}$_2$(μ-s-trans-C$_4$H$_2$)}.

acetylenic bonds in $(CO)_6Fe_2\{\mu\text{-SeC(H)}=C(Ph)Se\}$ (1.331(7) Å), $(CO)_6Fe_2\{\mu\text{-SeC(H)}=C(C\equiv CMe)Se\}$ (1.303(7) Å), $(CO)_6Fe_2\{\mu\text{-TeC(H)}=C(Ph)Te\}$ (1.34(1) Å) [13] and $(CO)_6Fe_2\{\mu\text{-TeC(H)}=C(C\equiv CMe)S\}$ (1.31(1) Å). It also compares well with the corresponding bond distances in compounds containing s-trans-1,3-butadiene ligands: $Os_3(CO)_{10}(s\text{-trans-}C_4H_6)$ (average, 1.33(4) Å) [14], $\{Cp(CO)_2Fe\}_2(\mu\text{-s-trans-}C_4H_4)$ (1.34(7) Å) [15] but is shorter than the corresponding bond distances in the following compounds: $Cp_2Zr(s\text{-trans-PhCH}=CHCH=CHPh)$ (average, 1.379 Å) [16], $Mn_2(CO)_8(s\text{-trans-}C_4H_6)$ (1.387(14) Å) [17], $Cp(NO)Mo(s\text{-trans-Me}_2C=CHCH=CMe_2)$ (average, 1.409(4) Å) [18], $\{Cp(CO)_2Mn\}_2(s\text{-trans-}C_4H_6)$ (average, 1.43 Å) [19] and $Cp_2(CO)_2Ru_2(s\text{-trans-}C_4H_6)$ (1.423(11) Å) [20]. The terminal carbon atoms in the butadiene moiety are slightly closer to the Fe_2Se_2 core (1.932(5) Å) than the internal carbon atoms (1.976(5) Å). A reverse order is seen in the compounds $Cp(NO)Mo(s\text{-trans-Me}_2C=CHCH=CMe_2)$ and $Cp_2Zr(s\text{-trans-PhCH}=CHCH=CHPh)$ in which the central carbon atoms of the butadiene group are closer to the metal centres. The Se–Fe (2.3809(10)–2.3883(11) Å) and Fe–Fe (2.5055(12) Å) bond distances are shorter than the corresponding distance reported for $(CO)_6Fe_2(\mu\text{-Se})_2(Se\text{-Fe}$, average 2.363 Å; Fe–Fe, 2.575(2) Å) [21] but are comparable to with those reported for other acetylenic derivatives of $(CO)_6Fe_2(\mu\text{-Se})_2$: $(CO)_6Fe_2\{\mu\text{-SeC(H)}=C(C\equiv CMe)Se\}$ (Se–Fe, 2.381(2)–2.386(2) Å; Fe–Fe, 2.507(2) Å); $(CO)_6Fe_2\{\mu\text{-SeC(H)}=C(Ph)Se\}$ (Se–Fe, 2.379(9)–2.385(9) Å; Fe–Fe, 2.512(1) Å); $(CO)_6Fe_2\{\mu\text{-TeC(H)}=C(C\equiv CMe)S\}$ (Fe–Fe, 2.538(2) Å). The average Se–Fe–Se angle in $\{(CO)_6Fe_2Se_2\}_2(\mu\text{-s-trans-}C_4H_2)$ is 81.3° and is similar to the average Se–Fe–Se angles of 81.4° in $(CO)_6Fe_2\{\mu\text{-SeC(H)}=C(Ph)Se\}$ and 81.9° in $(CO)_6Fe_2\{\mu\text{-SeC(H)}=C(C\equiv CMe)Se\}$ but greater than the average Se–Fe–Se angle of 58° in $(CO)_6Fe_2(\mu\text{-Se})_2$, consistent with an opening of the Fe_2Se_2 butterfly core to accommodate the s-trans-C_4H_2 molecule. The C(7)–C(7') bond distance in $\{(CO)_6Fe_2Se_2\}_2(\mu\text{-s-trans-}C_4H_2)$ of 1.423(11) Å is similar to the corresponding carbon–carbon bond distance of 1.423(15) Å in $[(CO)_6Fe_2Pt(PPh_3)_2\{\mu\text{-SeC(H)}-C(Ph)\}]$ which indicates electron delocalization on the butadiene fragment.

Although there are several methods to generate metal-diene complexes, here we have reported a new route for the synthesis of s-trans-1,3-butadiene complex from diacetylene. To our knowledge this is the first example of a chalcogen-stabilized cluster containing a s-trans-butadiene moiety. To determine whether the preference of the s-trans isomer over the cis form is due to steric or electronic factors a theoretical analysis is required. This and the characteristic reactivity of the bound diene towards different nucleophiles and electrophiles is currently under investigation.

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