

Propargyl alcohol derivatives of $\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')$ ($\text{E}, \text{E}' = \text{S}, \text{Se}$ or Te):
synthesis and spectroscopic characterization
of $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC}(\text{H})=\text{C}(\text{CH}_2\text{OH})\text{E}'\}$ ($\text{E} = \text{Se}$ or Te ; $\text{E}' = \text{S}, \text{Se}$ or Te);
Crystal structure of $(\text{CO})_5(\text{PPh}_3)\text{Fe}_2\{\mu\text{-SeC}(\text{CH}_2\text{OH})=\text{C}(\text{H})\text{Se}\}$

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Abstract

The propargyl alcohol derivatives $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC}(\text{H})=\text{C}(\text{CH}_2\text{OH})\text{E}'\}$ ($\text{E} = \text{Se}$ or Te ; $\text{E}' = \text{S}, \text{Se}$ or Te) were obtained from the room-temperature reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')$ with propargyl alcohol and were characterized by IR and ^1H , ^{13}C , ^{77}Se and ^{125}Te NMR spectroscopy. The structure of the PPh_3 -substituted derivative $(\text{CO})_5(\text{PPh}_3)\text{Fe}_2\{\mu\text{-SeC}(\text{CH}_2\text{OH})=\text{C}(\text{H})\text{Se}\}$ was established by a single-crystal X-ray diffraction study.

Keywords: Iron; Selenium; Sulfur; Tellurium; Carbonyl; Propargyl alcohol

1. Introduction

Transition metal complexes of propargyl alcohol attract considerable attention [1–3]. Addition of aromatic nucleophiles to the cations (propargyl) $\text{Co}_2(\text{CO})_6^+$ and subsequent demetallation have yielded C-propargylated aromatic derivatives [4]. The cations react with ketones to form α -(propargyl) $\text{Co}_2(\text{CO})_6$ derivatives [5], and with allylsilanes to form 1,5-enynes [6]. The use of the dicobalt hexacarbonyl unit, as well as of other metal carbonyl units as a protecting group for the C–C triple bond, is well documented. The use of the moieties containing both transition and main group metal for the same purpose has been much less studied. Owing to the presence of reactive E–E' bonds, compounds of the type $\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')$ ($\text{E}, \text{E}' = \text{S}, \text{Se}$ or Te) readily form complexes with acetylenes, and several complexes of the form $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC}(\text{R})=\text{C}(\text{R}')\text{E}'\}$ have been prepared and characterized [7–9]. As an extension of these studies, and in view of the interest in the chem-

istry of the propargyl-metal complexes, we have investigated the reaction of propargyl alcohol with $\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')$ compounds.

2. Experimental section

2.1. General procedures

All reactions and other manipulations were performed by use of standard Schlenk techniques under an argon atmosphere. All solvents were deoxygenated immediately prior to use. Infrared spectra were recorded on Nicolet 5DXB or Impact 400 Fourier transform IR spectrophotometer as dichloromethane solutions in NaCl cells at 0.1 mm path length. Elemental analyses were performed using a Carlo Erba automatic analyser. ^1H , ^{13}C , ^{31}P , ^{77}Se and ^{125}Te NMR spectra were recorded on a Varian VXR-300S spectrometer in CDCl_3 . The operating frequency for ^{77}Se NMR was 57.23 MHz with a pulse width of 15 μs and a delay of 1 s. The operating frequency for ^{125}Te NMR was 94.705 MHz with a pulse

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Table 1

Compound	Propargyl alcohol (ml(mmol))	Fe ₂ (CO) ₆ (μ-EE') (mg(mmol))	Product	Yield (mg(%))	Analysis found (calculated)	Melting point (°C)
1	0.02 (0.3)	Fe ₂ (CO) ₆ (μ-Se) ₂ , 87.6 (0.2)	Fe ₂ (CO) ₆ {μ-SeC(H)=C(CH ₂ OH)Se}	46 (47)	C, 21.93 (21.86) H, 1.03 (0.81)	92–94
2	0.02 (0.3)	Fe ₂ (CO) ₆ (μ-Te) ₂ , 107 (0.2)	Fe ₂ (CO) ₆ {μ-TeC(H)=C(CH ₂ OH)Te}	13 (11)	C, 18.35 (18.27) H, 0.89 (0.68)	148–150
3	0.02 (0.3)	Fe ₂ (CO) ₆ (μ-SSe), 78 (0.2)	Fe ₂ (CO) ₆ {μ-SeC(H)=C(CH ₂ OH)S}	38 (43)	C, 24.3 (24.16) H, 1.09 (0.89)	88–90
4	0.02 (0.3)	Fe ₂ (CO) ₆ (μ-STe), 87.9 (0.2)	Fe ₂ (CO) ₆ {μ-TeC(H)=C(CH ₂ OH)S}	28 (9)	C, 21.92 (21.79) H, 1.02 (0.81)	118–120
5 and 6	0.02 (0.3)	Fe ₂ (CO) ₆ (μ-SeTe), 97.3 (0.2)	Fe ₂ (CO) ₆ {μ-SeC(H)=C(CH ₂ OH)Te}(5) and Fe ₂ (CO) ₆ {μ-TeC(H)=C(CH ₂ OH)Se} (6)	28 (26)	C, 20.05 (19.9) H, 0.98 (0.78)	140–142

width of 9.5-μs and a delay of 1 s. ⁷⁷Se NMR spectra are referenced to Me₂Se (δ = 0 ppm) and ¹²⁵Te NMR spectra are referenced to Me₂Te (δ = 0 ppm). (CO)₆Fe₂{μ-SSe} [10], (CO)₆Fe₂{μ-Se₂} [11], (CO)₆Fe₂{μ-SeTe} [12], (CO)₆Fe₂{μ-STe} [13] and (CO)₆Fe₂{μ-Te₂} [14] were prepared as reported before.

2.2. Typical preparation of (CO)₆Fe₂{μ-EC(H)=C(CH₂OH)E'} (E = Se or Te; E' = S, Se or Te) (1–6)

Conditions used for preparation of 1–6 are summarized in Table 1. In a typical procedure, propargyl alcohol was added to a methanolic solution (50 ml) of freshly prepared (CO)₆Fe₂{μ-EE'}, where E = Se or Te and E' = S, Se or Te, and anhydrous sodium acetate (0.25 g). The mixture was stirred at room temperature for 36 h and the solvent then removed in vacuo. The

residue was dissolved in dichloromethane and the solution filtered through Celite; it was then subjected to thin layer chromatography (TLC) on silica gel plates with

Table 3
Fractional atomic coordinates and *Biso* Å² for 7

Atom	x	y	z	<i>Biso</i> (Å ²)
Se(1)	0.4250(2)	0.4377(1)	0.1924(2)	4.6(1)
Se(2)	0.4459(2)	0.1783(2)	0.3894(2)	5.6(1)
Fe(1)	0.4282(2)	0.2392(2)	0.1951(2)	2.9(1)
Fe(2)	0.2420(2)	0.3382(2)	0.3414(2)	3.7(1)
P(1)	0.6506(3)	0.1522(3)	0.1077(3)	3.0(2)
O(1)	0.304(1)	0.378(1)	-0.001(1)	5.2(7)
O(2)	0.302(1)	0.033(1)	0.267(1)	7.8(9)
O(3)	0.065(2)	0.158(1)	0.480(1)	10.1(11)
O(4)	0.046(1)	0.495(1)	0.199(1)	6.0(7)
O(5)	0.159(1)	0.473(1)	0.505(1)	6.9(8)
O(6)	0.731(2)	0.333(2)	0.409(2)	15.2(21)
C(1)	0.358(1)	0.319(1)	0.077(1)	3.5(7)
C(2)	0.354(1)	0.112(1)	0.238(1)	4.9(9)
C(3)	0.135(2)	0.231(2)	0.424(2)	6.0(11)
C(4)	0.123(2)	0.433(1)	0.254(1)	4.6(9)
C(5)	0.192(2)	0.418(2)	0.444(1)	5.1(9)
C(6)	0.549(2)	0.395(2)	0.284(2)	6.8(13)
C(7)	0.562(2)	0.291(2)	0.360(2)	7.0(13)
C(8)	0.659(3)	0.234(3)	0.440(2)	11.2(23)
C(9)	0.792(1)	0.178(1)	0.137(1)	3.1(7)
C(10)	0.808(1)	0.303(1)	0.093(1)	3.8(8)
C(11)	0.910(1)	0.326(1)	0.117(1)	4.2(8)
C(12)	0.995(2)	0.231(2)	0.184(1)	5.2(10)
C(13)	0.982(2)	0.106(2)	-0.229(2)	5.3(11)
C(14)	0.879(1)	0.085(1)	0.203(1)	4.3(9)
C(15)	0.688(1)	-0.020(1)	0.155(1)	3.0(7)
C(16)	0.830(1)	0.225(1)	-0.123(1)	4.2(8)
C(17)	0.792(2)	-0.213(1)	0.113(1)	5.0(9)
C(18)	0.750(1)	-0.279(1)	0.228(1)	4.4(9)
C(19)	0.675(1)	-0.220(1)	0.312(1)	4.5(8)
C(20)	0.646(1)	-0.087(1)	0.271(1)	4.1(8)
C(21)	0.699(1)	0.197(1)	-0.052(1)	3.4(7)
C(22)	0.608(1)	0.197(1)	-0.103(1)	4.0(8)
C(23)	0.643(2)	0.226(1)	-0.225(1)	5.1(10)
C(24)	0.772(2)	0.255(1)	-0.296(1)	5.5(11)
C(25)	0.865(2)	0.250(1)	-0.242(1)	4.6(9)
C(26)	0.764(1)	-0.081(1)	0.072(1)	4.2(9)

Table 2
Crystal data for 7

Formula	C ₂₆ H ₁₉ O ₆ Fe ₂ Se ₂ P
Formula weight	727.0
Crystal system	Triclinic
Space group	P $\bar{1}$
<i>a</i> (Å)	10.517(3)
<i>b</i> (Å)	12.216(3)
<i>c</i> (Å)	13.148(3)
α (°)	64.19(2)
β (°)	67.43(1)
γ (°)	68.82(3)
<i>V</i> (Å ³)	1365.4(6)
<i>Z</i>	2
<i>D</i> (calc) (g cm ⁻³)	1.768
μ(Mo Kα) (cm ⁻¹)	38
Temperature (K)	293
<i>hkl</i> ranges	<i>h</i> = -11 to +12, <i>k</i> = 0 to 14, <i>l</i> = -13 to +15
2θ (°)	54
<i>F</i> (000)	716
<i>R</i>	0.068
<i>R</i> _w	0.078

80:20 dichloromethane:hexane as eluant. The orange-coloured bands yielded the products **1–6**.

2.3. Synthesis of $(PPh_3)_2(CO)_5Fe_2\{\mu-SeC(CH_2OH)=C(H)Se\}$ (**7**)

The complex $Pt(PPh_3)_4$ (0.746 g, 0.6 mmol) was added to a dichloromethane solution (50 ml) of $(CO)_6Fe_2\{\mu-SeC(CH_2OH)=C(H)Se\}$ (0.198 g, 0.4 mmol) and the mixture was stirred at room temperature for 40 h. The solvent was removed in vacuo and the residue subjected to TLC on silica gel plates with 80:20 dichloromethane:hexane as eluant. This separated $(CO)_5(PPh_3)_2Fe_2\{\mu-SeC(CH_2OH)=C(H)Se\}$ (**7**) (0.125 g, (43%)) from unchanged $(CO)_6Fe_2\{\mu-SeC(CH_2OH)=C(H)Se\}$. Spectroscopic data for **7** are given in later Table 6, 7. Anal. Found: C, 42.9; H, 2.88. $C_{26}H_{19}O_6Fe_2Se_2P$ calc.: C, 42.8; H, 2.61%. Melting point 161–162°C.

2.4. Crystal structure determination

A red crystal of approximate dimensions $0.20 \times 0.20 \times 0.25$ mm was used. The data were collected on an Enraf–Nonius CAD4 diffractometer with Mo K α radiation at room temperature using the ω – 2θ scan method.

Table 4
Selected bond lengths (Å) for **7**

Se(1)–Fe(1)	2.397(2)	Fe(2)–C(5)	1.82(2)
Se(1)–Fe(2)	2.396(3)	P(1)–C(9)	1.83(1)
Se(1)–C(6)	1.89(2)	P(1)–C(15)	1.84(1)
Se(2)–Fe(1)	2.393(3)	P(1)–C(21)	1.84(1)
Se(2)–Fe(2)	2.398(3)	O(1)–C(1)	1.19(2)
Se(2)–C(7)	1.98(2)	O(2)–C(2)	1.13(2)
Fe(1)–Fe(2)	2.533(3)	O(3)–C(3)	1.17(2)
Fe(1)–P(1)	2.264(3)	O(4)–C(4)	1.14(2)
Fe(1)–C(1)	1.72(1)	O(5)–C(5)	1.14(2)
Fe(1)–C(2)	1.76(2)	O(6)–C(8)	1.49(4)
Fe(2)–C(3)	1.75(2)	C(6)–C(7)	1.22(3)
Fe(2)–C(4)	1.76(2)	C(7)–C(8)	1.52(3)

Pertinent crystallography data are listed in Table 2. Unit-cell parameters were determined from 24 randomly selected reflections. The structure was solved by direct methods and refined by least-squares methods using NRCVAX programs [15] to $R = 0.068$ and $R_w = 0.078$ for 2793 ($|F_o| > 3.5\sigma |F_o|$) reflections from 4313 unique reflections. Final ΔF synthesis showed no features above 1.1 electrons Å^{-3} . Atomic coordinates are listed in Table 3; selected bond lengths in Table 4 and selected bond angles in Table 5. Tables of thermal parameters and hydrogen atom coordinates and com-

Table 5
Selected bond angles (°) for **7**

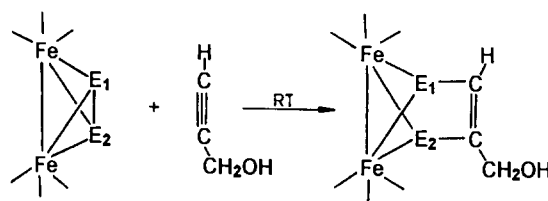
Fe(1)–Se(1)–Fe(2)	63.81(8)	Fe(1)–Fe(2)–C(4)	97.5(5)
Fe(1)–Se(1)–C(6)	103.1(5)	Fe(1)–Fe(2)–C(5)	151.0(5)
Fe(2)–Se(1)–C(6)	99.1(6)	C(3)–Fe(2)–C(4)	91.1(8)
Fe(1)–Se(2)–Fe(2)	63.84(8)	C(3)–Fe(2)–C(5)	98.5(8)
Fe(1)–Se(2)–C(7)	99.6(5)	C(4)–Fe(2)–C(5)	101.5(6)
Fe(2)–Se(2)–C(7)	96.9(5)	Fe(1)–P(1)–C(9)	114.9(4)
Se(1)–Fe(1)–Se(2)	80.55(9)	Fe(1)–P(1)–C(15)	113.6(4)
Se(1)–Fe(1)–Fe(2)	58.08(8)	Fe(1)–P(1)–C(21)	116.9(4)
Se(1)–Fe(1)–P(1)	109.02(12)	C(9)–P(1)–C(15)	103.2(6)
Se(1)–Fe(1)–C(1)	87.7(4)	C(9)–P(1)–C(21)	104.7(6)
Se(1)–Fe(1)–C(2)	154.0(5)	C(15)–P(1)–C(21)	101.8(6)
Se(2)–Fe(1)–Fe(2)	58.17(8)	Fe(1)–C(1)–O(1)	177.1(10)
Se(2)–Fe(1)–P(1)	100.74(12)	Fe(1)–C(2)–O(2)	177.7(12)
Se(2)–Fe(1)–C(1)	158.0(4)	Fe(2)–C(3)–O(3)	178.9(17)
Se(2)–Fe(1)–C(2)	90.8(6)	Fe(2)–C(4)–O(4)	179.0(12)
Fe(2)–Fe(1)–P(1)	155.22(13)	Fe(2)–C(5)–O(5)	177.0(15)
Fe(2)–Fe(1)–C(1)	99.8(4)	Se(1)–C(6)–C(7)	118.2(14)
Fe(2)–Fe(1)–C(2)	96.5(5)	Se(2)–C(7)–C(6)	119.6(13)
P(1)–Fe(1)–C(1)	100.6(4)	Se(2)–C(7)–C(8)	112.6(17)
P(1)–Fe(1)–C(2)	96.7(4)	C(6)–C(7)–C(8)	127.8(20)
C(1)–Fe(1)–C(2)	91.8(7)	O(6)–C(8)–C(7)	104.6(22)
Se(1)–Fe(2)–Se(2)	80.46(9)	P(1)–C(9)–C(10)	118.0(9)
Se(1)–Fe(2)–Fe(1)	58.11(7)	P(1)–C(9)–C(14)	123.2(10)
Se(1)–Fe(2)–C(3)	160.8(5)	C(10)–C(9)–C(14)	118.8(12)
Se(1)–Fe(2)–C(4)	89.9(5)	C(9)–C(10)–C(11)	119.6(13)
Se(1)–Fe(2)–C(5)	100.1(6)	C(10)–C(11)–C(12)	120.4(14)
Se(2)–Fe(2)–Fe(1)	57.98(7)	C(11)–C(12)–C(13)	121.6(13)
Se(2)–Fe(2)–C(3)	90.7(5)	C(12)–C(13)–C(14)	116.7(14)
Se(2)–Fe(2)–C(4)	155.2(5)	C(9)–C(14)–C(13)	122.9(14)
Se(2)–Fe(2)–C(5)	102.7(5)	P(1)–C(15)–C(20)	119.5(9)
Fe(1)–Fe(2)–C(3)	102.8(5)	P(1)–C(15)–C(26)	120.5(10)

plete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Synthesis of $Fe_2(CO)_6\{\mu-EC(H)=C(CH_2OH)E'\}$ ($E = Se$ or Te ; $E' = S, Se$ or Te) (1–6)

The propargyl derivatives of $(CO)_6Fe_2(\mu-EE')$ where $E = Se$ or Te and $E' = S, Se$ or Te were obtained by the reaction shown in Scheme 1. The propargyl derivatives were obtained within yields of 11–47%, the lowest yield being that of the Te_2 compound and the highest that of the Se_2 compound. Of the mixed-chalcogenide compounds, only for the $SeTe$ compound were two isomers observed (5 and 6). The new compounds 1–6 were characterized by IR and 1H , ^{13}C , ^{77}Se and ^{125}Te NMR spectroscopy. The PPh_3 -substituted derivative of



	E_1	E_2
1	Se	Se
2	Te	Te
3	Se	S
4	Te	S
5	Se	Te
6	Te	Se

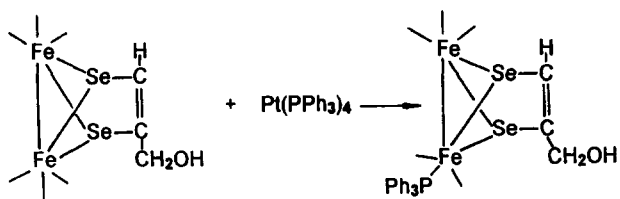
Scheme 1. Formation of 1–6.

1, i.e. 7, was prepared (Scheme 2) by treating 1 with $Pt(PPh_3)_4$ in dichloromethane at room temperature. It was also obtained by room-temperature reaction of 1

Table 6
Spectroscopic data for 1–7

Compound	IR (CH_2Cl_2), ν (cm^{-1})	1H NMR ($CDCl_3$), δ (ppm)	^{13}C NMR ($CDCl_3$), δ (ppm)	^{77}Se NMR ($CDCl_3$), δ (ppm)	^{125}Te NMR ($CDCl_3$), δ (ppm)
1	2072, 2036, 1996	7.1 (CH), 3.9 (CH_2), 1.7 (OH)	64 (CH_2), 129 (CH), 158 (CCH_2), 209 (CO)	366 (d, $^2J_{Se-H} = 54$ Hz), 391 (m)	
2	2059, 2023, 1986	8.7 (CH), 3.9 (CH_2), 1.8 (OH)	69 (CH_2), 120 (CH), 155 (CCH_2), 211 (CO)		774 (d, $^2J_{Te-H} = 131$ Hz), 830 (m)
3	2076, 2039, 1998	7.1 (CH), 4.0 (CH_2), 1.7 (OH)	63 (CH_2), 128 (CH), 163 (CCH_2), 208 (CO)	297 (d, $^2J_{Se-H} = 50$ Hz)	
4	2069, 2032, 1993	7.1 (CH), 4.0 (CH_2), 1.7 (OH)	65 (CH_2), 107 (CH), 172 (CCH_2), 209 (CO)		531 (d, $^2J_{Te-H} = 111$ Hz)
5 and 6	2065, 2029, 1991	8.0 (SeCH), 7.6 (TeCH), 4.0 (CH_2CSe), 3.8 (CH_2CSe), 1.7 (OH), 1.3 (OH)	66 (CH_2), 108 (CH), 129 (CH), 138 (CCH_2), 143 (CCH_2), 210 (CO)	434 (d, $^2J_{Se-H} = 59$ Hz), 467 (m)	696 (m), 658 (d, $^2J_{Te-H} = 120$ Hz)
7 ^a	2044, 1986, 1929	7.4–7.7 (Ph), 6.3 (CH), 3.3 (CH_2), 1.6 (OH)	64 (CH_2), 128 (CH), 130–137 (phenyl ring carbons), 155 (CCH_2), 210 (CO), 214 (CO)	330 (d, $^2J_{Se-H} = 52$ Hz), 350 (m)	

^a ^{31}P NMR data for 7 ($CDCl_3$): δ 68 ppm.



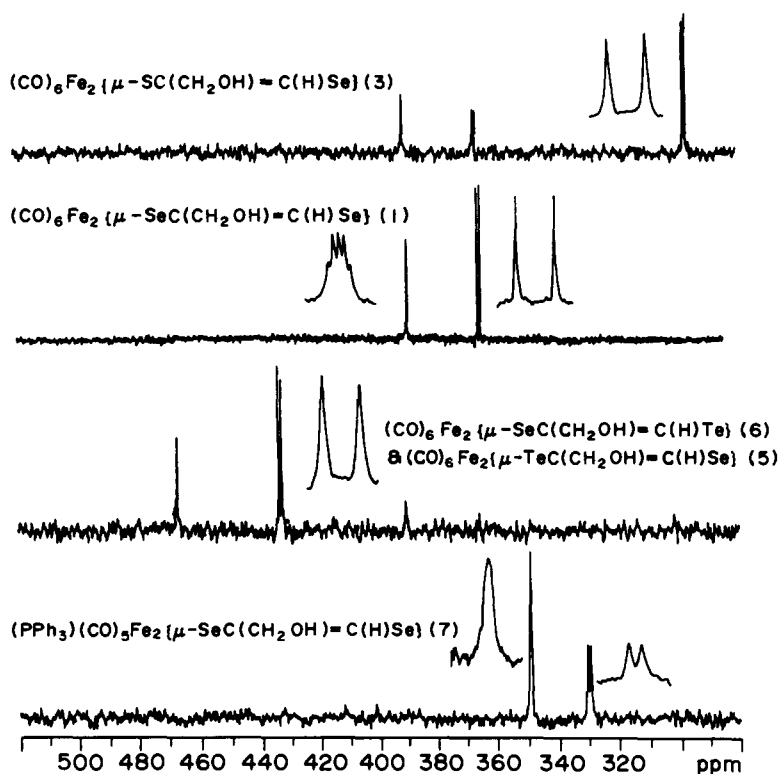
Scheme 2. Formation of 7.

with PPh_3 but with a lower yield. Its structure was established by a single-crystal X-ray diffraction study.

3.2. Spectroscopic characterization

Spectroscopic data for 1–7 are given in Table 6. The IR spectra in dichloromethane display the characteristic carbonyl stretching pattern characteristic of compounds containing the $\text{Fe}_2(\text{CO})_6$ unit. The bands shift progressively to lower $\nu(\text{CO})$ values in $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC}(\text{H})=\text{C}(\text{CH}_2\text{OH})\text{E}'\}$ as the EE' ligands are varied in the sequence SSe , Se_2 , STe , SeTe , Te_2 . ^1H NMR spectra of 1–6 show the presence of three types of proton. The farthest downfield signal is assigned to a CH proton and the farthest upfield signal is assigned to the OH proton. The presence of a mixture of isomers 5 and 6 was apparent from both the ^1H and ^{13}C NMR spectra. The ^{13}C NMR spectra of 1–6 showed the presence of four types of carbon atom and the assignment of the signals of 1–6 is based on a comparison

with the spectrum of $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{H})=\text{C}(\text{CH}_2\text{OH})\text{Se}\}$ (1). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1 showed a doublet at $\delta = 129$ ppm due to the CH carbon atom. A triplet at $\delta = 64$ ppm indicates the presence of a CH_2 carbon atom and singlet at $\delta = 158$ ppm that of a CCH_2 carbon atom. A singlet at $\delta = 209$ ppm is assigned to the carbonyl carbon atoms. By analogy, in the spectra of 1–6 the farthest upfield signal can be assigned to the CH_2 carbon atoms and the next signal downfield to the CH carbon atoms; this is followed by the signal due to the CCH_2OH carbon atoms. The CO signals appear in the usual region of $\delta = 200$ ppm. In the ^{77}Se NMR spectra of $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{H})=\text{C}(\text{CH}_2\text{OH})\text{E}\}$ (Fig. 1), the downfield shift of the signal increases in the sequence $\text{E} = \text{S}$, Se , Te . The two-bond Se-H coupling constant $^2J_{\text{Se-H}}$ increases in the same sequence. The ^{125}Te NMR spectra of $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC}(\text{H})=\text{C}(\text{CH}_2\text{OH})\text{E}\}$ (Fig. 2) showed an increase in the downfield shift in the sequence $\text{E} = \text{S}$, Se , Te and an increase in the two-bond Te-H coupling constant $^2J_{\text{Te-H}}$ in the same sequence. The ^{77}Se NMR and ^{125}Te NMR spectra served to identify the structures of the isomers 5 and 6. The ^{77}Se NMR spectrum of 1 showed two signals, a doublet and a multiplet; the Se-H coupling constant of 54 Hz for the doublet is consistent with a two-bond Se-H coupling. The multiplet arises from vinylic coupling with the CH proton and coupling with the CCH_2 protons. Similarly in the spectrum of 3, a coupling constant of 50 Hz for the

Fig. 1. ^{77}Se NMR spectra of 1, 3 and 5–7.

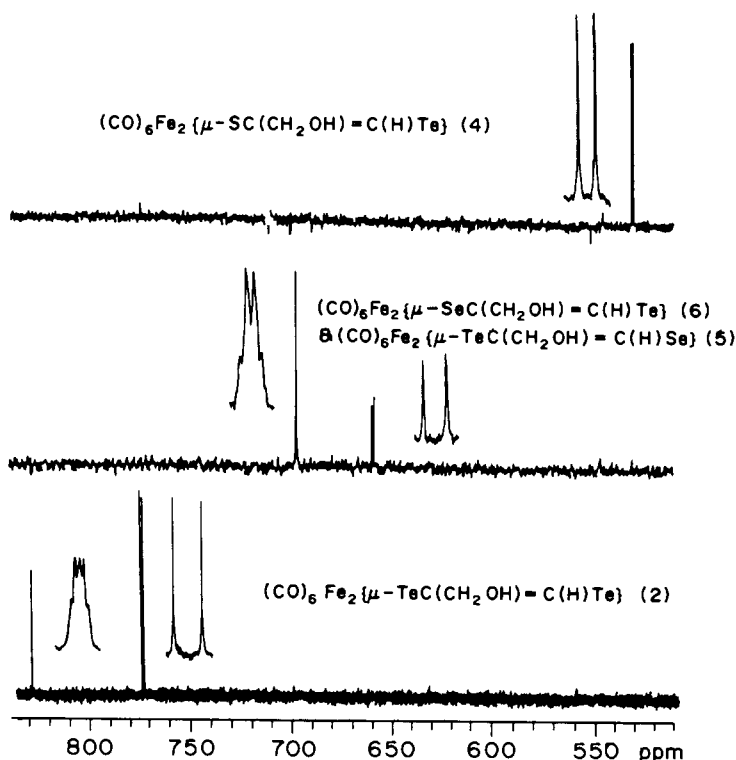


Fig. 2. ^{125}Te NMR spectra of 2 and 4–6.

doublet indicates short-range Se–H coupling and shows **3** to be the isomer that has the CH group bonded to Se. In the spectrum of the mixture of **5** and **6**, a doublet at $\delta = 434$ ppm ($J = 59$ Hz) can be assigned to **5**. No long-range coupling with the CH_2OH group was observed. Also present was a multiplet arising from coupling with CCH_2 protons and vinylic coupling with the CH proton; this indicates that Se is attached to CCH_2 and so the multiplet can be assigned to **6**. The ^{125}Te NMR spectrum of **2** shows a doublet at $\delta = 774$ ppm with a coupling constant of 131 Hz, indicating short-range coupling (Te attached to the CH group). There is also a multiplet due to coupling with CCH_2 protons and vinylic coupling with the CH proton (Te attached to CCH_2OH group). The spectrum of **4** showed a doublet ($\delta = 531$ ppm) with $J = 111$ Hz, indicating short-range coupling (Te attached to the CH group). Similarly in the spectrum of mixture of **5** and **6** there is a doublet ($\delta = 658$ ppm) with a coupling constant of 120 Hz, which indicates short-range coupling; this is due to the isomer containing a Te–CH group, i.e. $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC}(\text{H})\text{-C}(\text{CH}_2\text{OH})\text{Se}\}$ (**6**). A multiplet at $\delta = 696$ ppm shows coupling with CCH_2 protons and vinylic coupling with the CH proton, indicating the presence of the other isomer containing a Te– CCH_2OH group, i.e. $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{H})\text{-C}(\text{CH}_2\text{OH})\text{Te}\}$ (**5**).

The carbonyl stretching frequencies in the IR spectrum of **7** are lower than these for the corresponding bands that of **1**. This is consistent with replacement of

one CO group by PPh_3 ligand. The ^1H , ^{13}C and ^{31}P NMR spectra of **7** confirmed the presence of the PPh_3 group. The ^{77}Se NMR spectrum showed two signals; a doublet at $\delta = 330$ ppm with $^2J_{\text{Se-H}} = 52$ Hz from the Se atom bonded to the CH group and a multiplet at $\delta = 350$ ppm from the Se atom bonded to the CH_2OH group.

3.3. Molecular structure of 7

Brown crystals of **7** were grown from dichloromethane–hexane solution at -10°C . The molecular structure

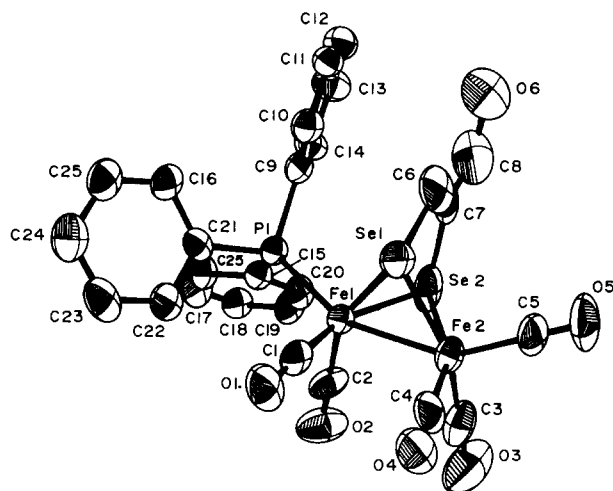


Fig. 3. Molecular structure of **7** with thermal ellipsoids at the 50% probability level.

of **7** is shown in Fig. 3. It involves an Fe₂Se₂ butterfly core and a CH=CCH₂OH group bridging the two Se atoms. One Fe atom bears three CO ligands while the other bears two CO ligands and one PPh₃ ligand. The length of the acetylenic bond in **7**, i.e. C(6)–C(7), 1.22(3) Å, is much shorter than that in the related species (CO)₆Fe₂{μ-SeC(Ph)=C(CH)Se} (1.331(7) Å) [8]. The length of the bond between one Se atom and the CH group is much shorter (Se(1)–C(6), 1.89(2) Å) than that between the other Se atom and the C atom of the CCH₂OH group (Se(2)–C(7), 1.98(2) Å). All other bond parameters are unexceptional.

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