

Synthesis and spectroscopic characterization of (CO)₆Fe₂{ μ-EC(H)=C(2-Th)E'} (E, E' = S, Se, Te; Th = C₄H₃S) Structural characterization of (CO)₆Fe₂{ μ-SeC(H)=C(2-Th)Se}

Pradeep Mathur^{a,*}, Aswini K. Dash^a, Md. Munkir Hossain^a, C.V.V. Satyanarayana^b,
Arnold L. Rheingold^c, Glenn P.A. Yap^c, Louise M. Liable-Sands^c

^a Chemistry Department, Indian Institute of Technology, Bombay 400 076, India

^b Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Bombay 400 076, India

^c Department of Chemistry, University of Delaware, Newark, DE 19716, USA

Received 10 December 1996

Abstract

Room temperature stirring of (CO)₆Fe₂(μ-EE') with 2-thiopheneacetylene (2-ThC≡CH) in methanol containing sodium acetate afforded the adducts (CO)₆Fe₂{ μ-EC(H)=C(2-Th)E'} (E = E', EE' = S (**1**), Se (**2**) and Te (**3**); E ≠ E', EE' = SeS (**4**), STe (**5**), SeTe (**6**) and TeSe (**7**)). Compounds **1**–**7** have been characterized by IR and multinuclear (¹H, ¹³C, ⁷⁷Se and ¹²⁵Te) NMR spectroscopy. The structure of (CO)₆Fe₂{ μ-SeC(H)=C(2-Th)Se} (**2**) has been established by single crystal X-ray diffraction methods. It crystallized in the triclinic space group *P* $\bar{1}$ with *a* = 7.771(2) Å, *b* = 17.051(4) Å, *c* = 20.981(5) Å, α = 67.00(2)°, β = 80.26(2)°, γ = 88.67(2)°, *V* = 2520 Å³, *Z* = 6, *D*_{calc} = 2.159 g cm⁻³. Full-matrix least squares refinement of **2** converged to *R* = 0.0635 and *R*_w = 0.0969. The structure consists of a tetrahedral butterfly core containing the thiopheneacetylene as a bridge between the two wingtip Se atoms, with three terminally bonded carbonyl groups on each Fe atom. © 1997 Elsevier Science S.A.

Keywords: Iron; Sulphur; Selenium; Tellurium; Thiopheneacetylene; Carbonyl; X-ray

1. Introduction

The coordination chemistry of thiophene with transition metals has been a topic of considerable interest with a view to understand the process of catalytic hydride-sulphurization [1]. Also, thiophene-complexes provide models for the possible modes of thiophene adsorption on metal surfaces [2]. Thiophene, the heteroaromatic organosulphur compound was first discovered as an impurity in coal-derived benzene and its occurrence is now well known in fossil fuels [3]. It adopts diverse bonding modes with metals and the coordinated thiophene displays a reactivity which can differ sharply from the behaviour of the free heterocycle [4]. Activation of thiophene by transition metals has recently received much attention [5]. The common bonding modes of thiophene to transition metal systems

include complexes containing S-bound thiophene, bonding involving the π -electrons, η^2 -, η^4 - as well as η^5 -bound, and η^5 -S- μ_2 and η^5 -S- μ_3 coordination modes, where the bridging thiophene is η^4 -coordinated through the diene to one metal and S-coordinated to one/two other metal atoms [6].

Although, there has been a large amount of work carried out on the synthesis, bonding and structural aspects of transition-metal alkyne complexes, much less is known about possible activation of alkynes on transition-metal, Main Group clusters [7]. Recent successes in the area of incorporating single atom ligands derived from certain main groups of the Periodic Table in transition-metal carbonyl complexes has evoked interest [8] in studies on the role of these ligands to act as sites of addition of alkynes. Single atom ligands derived from Group 16 elements, such as S, Se or Te, as stabilizing entities in cluster growth reactions is well established [9]. Recently, it has been demonstrated that, whereas (CO)₆Fe₂(μ-S₂) and (CO)₆Fe₂(μ-Te₂) do not

* Corresponding author.

undergo phenylacetylene addition across their S–S or Te–Te bond respectively, $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ readily adds phenylacetylene at room temperature to form $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Se}\}$ [10]. This in turn adds a second molecule of $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ and $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ to form $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-C(H)-C(Ph)}\}]_2$ [11] and $[(\text{CO})_6\text{Fe}_2\{\text{SeC(H)=C(Ph)Se}\}\{\text{Pt}(\text{PPh}_3)_2\}]$ [10] respectively, thereby facilitating the stepwise reduction of the acetylenic bond, first to a double bond and then to a single bond. Although the S and Te analogues of the olefinic derivatives, $(\text{CO})_6\text{Fe}_2\{\mu\text{-SC(H)=C(Ph)S}\}$ [12] and $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(Ph)Te}\}$ [13], have been obtained by alternative methods, they fail to add a second molecule of $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ to facilitate further reduction of the coordinated acetylenic bond. Addition of organometallic groups across the Fe–Fe bond of $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Se}\}$ can also be carried out as in the formations of triselenide Fe–Mo mixed-metal clusters, $\text{Cp}_2\text{Mo}_2(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2(\mu_4\text{-Se})$ [14]. Here we report the additions of 2-thiopheneacetylene on $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}')$ ($\text{E}, \text{E}' = \text{S}, \text{Se}, \text{Te}$) and structural characterization of the Se_2 compound, $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)Se}\}$ ($\text{Th} = \text{C}_4\text{H}_3\text{S}$).

2. Experimental section

2.1. General procedures

Reactions and manipulations were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were purified and deoxygenated immediately prior to use. Infrared spectra were recorded on a Nicolet Impact 400 Fourier transform spectrometer in a NaCl cell of 0.1 mm path length as hexane solutions. ^1H , ^{13}C , ^{77}Se , and ^{125}Te NMR spectra

were obtained on a Varian VXR-300S spectrometer in CDCl_3 solutions using appropriate references at 25 °C. The ^{77}Se NMR signals were referenced to Me_2Se ($\delta = 0$) and the spectra were obtained at an operating frequency of 57.23 MHz; 90° pulses were used with 2 s delay and 1 s acquisition time. ^{125}Te NMR measurements were made at an operating frequency of 94.705 MHz using a pulse of 90° and a delay of 1 s. The spectra were referenced to Me_2Te ($\delta = 0$). Elemental analyses were carried out using a Carlo Erba automatic analyser. $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}')$ ($\text{E} = \text{E}'$ and $\text{E} \neq \text{E}'$; $\text{E}, \text{E}' = \text{S}, \text{Se}, \text{Te}$) [15] and 2-thiopheneacetylene [16] were prepared as reported in the literature.

2.2. Typical preparation of $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E}'\}$ ($\text{E} = \text{E}'$ and $\text{E} \neq \text{E}'$; $\text{E}, \text{E}' = \text{S}, \text{Se}, \text{Te}$; $\text{Th} = \text{C}_4\text{H}_3\text{S}$)

Conditions used for preparation of **1–7** are summarized in Table 1. In a typical preparation, 0.2 ml of 2-thiopheneacetylene was added at room temperature, to a methanol solution (15 ml) containing 1–1.5 mmol of freshly prepared $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}')$ ($\text{E} = \text{E}'$; $\text{E}, \text{E}' = \text{S}, \text{Se}, \text{Te}$ and $\text{E} \neq \text{E}'$; $\text{E}, \text{E}' = \text{S}, \text{Se}, \text{Te}$) and anhydrous sodium acetate (0.25 g). The reactions were monitored by TLC and terminated when all the $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}')$ had been consumed. The reaction mixture was dried in vacuo and then dissolved in dichloromethane (15 ml). The solution was filtered through Celite to remove insoluble material. After removal of the solvent, the residue was redissolved in 5 ml of hexane and subjected to chromatographic work-up on a silica gel column. Using hexane as eluent, the compound $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E}'\}$ ($\text{E} = \text{E}'$; $\text{E}, \text{E}' = \text{S}, \text{Se}, \text{Te}$) was isolated as the major orange band. In the case of mixed-chalcogenide combinations, three closely spaced bands were collected; the major orange-red band of

Table 1
Conditions used for preparation of $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E}'\}$ ($\text{E} = \text{E}'$ and $\text{E} \neq \text{E}'$; $\text{E}, \text{E}' = \text{S}, \text{Se}, \text{Te}$; $\text{Th} = \text{C}_4\text{H}_3\text{S}$)

Compound	$\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')$ (g [mmol])	Time (h)	Product	Yield (g [%])	Analysis Calcd. (found)	M.p. (°C)
1	$(\text{CO})_6\text{Fe}_2(\mu\text{-S})_2$ 0.54 [1.57]	8	$(\text{CO})_6\text{Fe}_2\{\mu\text{-SC(H)=C(Th)S}\}$	0.23 [32]	C, 31.85 (31.97) H, 0.88 (0.92)	98 (decomp)
2	$(\text{CO})_6\text{Fe}_2(\mu\text{-Se})_2$ 0.54 [1.23]	12	$(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Th)Se}\}$	0.51 [76]	C, 26.37 (26.58) H, 0.73 (0.82)	102–104
3	$(\text{CO})_6\text{Fe}_2(\mu\text{-Te})_2$ 0.54 [1.01]	36	$(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(Th)Te}\}$	0.17 [26]	C, 20.36 (22.50) H, 0.62 (0.70)	138–140
4	$(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ 0.54 [1.38]	5	$(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Th)S}\}$	0.40 [58]	C, 28.85 (29.03) H, 0.80 (0.87)	78–80
5	$(\text{CO})_6\text{Fe}_2(\mu\text{-STe})$ 0.54 [1.23]	20	$(\text{CO})_6\text{Fe}_2\{\mu\text{-SC(H)=C(Th)Te}\}$	0.35 [52]	C, 26.27 (26.47) H, 0.72 (0.78)	104–106
6 and 7	$(\text{CO})_6\text{Fe}_2(\mu\text{-SeTe})$ 0.54 [1.11]	24	$(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Th)Te}\}$ and $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(Th)Se}\}$	0.32 [48] 0.13 [20]	C, 24.20 (24.36) H, 0.67 (0.72) C, 24.20 (24.38) H, 0.67 (0.73)	118–120 126–128

Table 2
Crystallographic data for $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)Se}\}$ (2)

Empirical formula	$\text{C}_{12}\text{H}_4\text{Fe}_2\text{O}_6\text{SSe}_2$
Formula weight	545.83
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.771(2)
b (Å)	17.051(4)
c (Å)	20.981(5)
α (deg)	67.00(2)
β (deg)	80.26(2)
γ (deg)	88.67(2)
V (Å ³)	2520
Z	6
D_{calc} (g cm ⁻³)	2.159
Limiting indices	$-9 \leq h \leq 9, -18 \leq k \leq 20,$ $0 \leq l \leq 24$
μ (mm ⁻¹)	6.208
λ (Å)	0.71073
$F(000)$	1560
Temperature (K)	297(2)
Crystal size (mm ³)	0.18 × 0.32 × 0.32
Crystal colour	red block
θ range for data collections (deg)	2.02 to 25.0
Reflections collected	9123
No. of independent reflections	8857 ($R_{\text{int}} = 0.0569$)
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	8855/0/622
GOF on F^2	1.128
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0635, wR_2 = 0.0969$
R indices (all data)	$R_1 = 0.1637, wR_2 = 0.1244$
Largest diff. peak and hole (eÅ ⁻³)	0.993 and -0.798

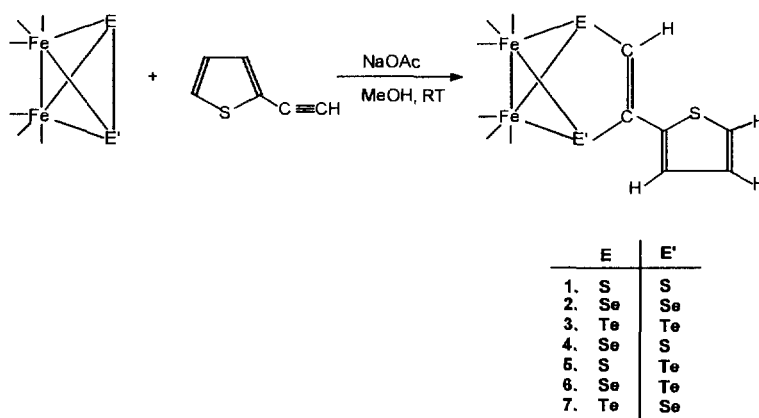
$(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E'}\}$ was eluted as the second band in each case. The first and third bands were minor and identified as the corresponding homochalcogenide compounds $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E}\}$ and $(\text{CO})_6\text{Fe}_2\{\mu\text{-E'C(H)=C(2-Th)E'}\}$.

2.3. Crystal structure determination of $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)Se}\}$ (2)

Crystallographic data for compound 2 is given in Table 2. A suitable crystal for single-crystal X-ray diffraction was selected and mounted with epoxy cement on a thin glass fibre. The unit-cell parameters were obtained by the least squares refinement of the angular settings of 24 reflections ($20 < 2\theta < 25^\circ$). No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data. E -statistics suggested the centrosymmetric space group option, $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least squares procedures. Semi-empirical ellipsoid absorption corrections were applied. The asymmetric unit consists of three independent, but chemically equivalent, molecules. There is equal carbon/sulphur compositional disorder at the thiol ring positions adjacent to C(3) for each of the three independent molecules; these disordered atoms were modelled as undersized sulphur atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were treated as idealized contributions. All soft-

Table 3
Selected bond distances and bond angles for $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)Se}\}$ (2)

Bond distances (Å)					
Se(1)–Fe(1)	2.384(2)	Se(3)–Fe(3)	2.385(2)	Se(5)–Fe(5)	2.386(2)
Se(1)–Fe(2)	2.373(2)	Se(3)–Fe(4)	2.384(2)	Se(5)–Fe(6)	2.386(2)
Se(2)–Fe(1)	2.382(2)	Se(4)–Fe(3)	2.380(2)	Se(6)–Fe(5)	2.382(2)
Se(2)–Fe(2)	2.376(2)	Se(4)–Fe(4)	2.381(2)	Se(6)–Fe(6)	2.390(2)
Fe(1)–Fe(2)	2.518(2)	Fe(3)–Fe(4)	2.512(2)	Fe(5)–Fe(6)	2.509(2)
Se(1)–C(4)	1.960(11)	Se(3)–C(15)	1.950(11)	Se(5)–C(26)	1.948(11)
Se(2)–C(5)	1.915(11)	Se(4)–C(16)	1.913(12)	Se(6)–C(27)	1.936(11)
C(4)–C(5)	1.312(14)	C(15)–C(16)	1.305(14)	C(26)–C(27)	1.303(14)
C(3)–C(4)	1.451(14)	C(14)–C(15)	1.48(2)	C(25)–C(26)	1.45(2)
Bond angles (deg)					
Fe(1)–Se(1)–Fe(2)	63.92(7)	Fe(3)–Se(3)–Fe(4)	63.54(7)	Fe(5)–Se(5)–Fe(6)	63.44(7)
Fe(1)–Se(2)–Fe(2)	63.91(7)	Fe(3)–Se(4)–Fe(4)	63.68(7)	Fe(5)–Se(6)–Fe(6)	63.44(7)
Se(1)–Fe(1)–Fe(2)	57.84(6)	Se(3)–Fe(3)–Fe(4)	58.21(6)	Se(5)–Fe(5)–Fe(6)	58.28(6)
Se(2)–Fe(1)–Fe(2)	57.91(7)	Se(4)–Fe(3)–Fe(4)	58.17(7)	Se(6)–Fe(5)–Fe(6)	58.42(7)
Se(1)–Fe(1)–Se(2)	81.46(7)	Se(3)–Fe(3)–Se(4)	81.31(7)	Se(5)–Fe(5)–Se(6)	81.01(7)
Se(1)–Fe(2)–Fe(1)	58.24(7)	Se(3)–Fe(4)–Fe(3)	58.25(6)	Se(5)–Fe(6)–Fe(5)	58.28(6)
Se(2)–Fe(2)–Fe(1)	58.18(7)	Se(4)–Fe(4)–Fe(3)	58.15(7)	Se(6)–Fe(6)–Fe(5)	58.14(7)
Se(1)–Fe(2)–Se(2)	81.81(7)	Se(3)–Fe(4)–Se(4)	81.32(7)	Se(5)–Fe(6)–Se(6)	80.86(7)
Se(1)–C(4)–C(5)	115.3(8)	Se(3)–C(15)–C(16)	115.8(9)	Se(5)–C(26)–C(27)	115.9(9)
Se(2)–C(5)–C(4)	120.0(9)	Se(4)–C(16)–C(15)	119.7(10)	Se(6)–C(27)–C(26)	119.2(9)
C(3)–C(4)–C(5)	126.7(11)	C(14)–C(15)–C(16)	126.4(11)	C(25)–C(26)–C(27)	127.7(11)

Scheme 1. Formation of $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E'}\}$ ($E, E' = \text{S, Se, Te; Th} = \text{C}_4\text{H}_3\text{S}$).Table 4
IR, ^1H and ^{13}C NMR data for $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E'}\}$ ($E, E' = \text{S, Se, Te; Th} = \text{C}_4\text{H}_3\text{S}$)

Compounds	IR (ν , cm^{-1} , hexane)	^1H NMR (δ , CDCl_3)	^{13}C (^1H) NMR (δ , CDCl_3)
$(\text{CO})_6\text{Fe}_2\{\mu\text{-SC(H)=C(2-Th)S}\}$ (1)	2080 (s), 2046 (vs), 2008 (vs), 1993 (w)	6.03 (s, CH), 6.96 (dd, $J_{\text{H-H}} = 3.6$ Hz and 5.1 Hz, 1H), 7.11 (dd, $J_{\text{H-H}} = 0.9$ Hz and 3.6 Hz, 1H), 7.31 (dd, $J_{\text{H-H}} = 0.9$ Hz and 5.1 Hz, 1H)	111.54 (d, $J_{\text{C-H}} = 188$ Hz, CH), 125.99–126.70 (m, Thiophene CH), 136.2 (s, Thiophene C), 145.8 (s, CCH), 207 (s, CO)
$(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)Se}\}$ (2)	2073 (vs), 2039 (vs), 2031 (w), 2001 (vs), 1987 (m)	6.98 (dd, $J_{\text{H-H}} = 3.6$ Hz and 5.1 Hz, 1H), 7.11 (dd, $J_{\text{H-H}} = 0.9$ Hz and 3.6 Hz, 1H), 7.19 (s, $^2J_{\text{H-Se}} = 53$ Hz, $^3J_{\text{H-Se}} = 7$ Hz, CH), 7.33 (dd, $J_{\text{H-H}} = 0.9$ Hz and 5.1 Hz, 1H)	125.1 (d, $J = 183$ Hz, CH), 127.93–128 (m, Thiophene CH), 138.87 (s, Thiophene C), 148 (s, CCH), 209 (s, CO)
$(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(2-Th)Te}\}$ (3)	2062 (vs), 2028 (vs), 1993 (vs), 1978 (w)	7.0 (dd, $J_{\text{H-H}} = 3.6$ Hz and 5.1 Hz, 1H), 7.33 (dd, $J_{\text{H-H}} = 1.2$ Hz and 5.1 Hz, 1H), 7.35 (dd, $J_{\text{H-H}} = 1.2$ Hz and 3.6 Hz, 1H), 8.71 (s, $^2J_{\text{Te-H}} = 131$ Hz, CH)	134.34 (d, $J = 174$ Hz, CH), 127.2–128.89 (m, Thiophene CH), 129.71 (s, Thiophene C), 140.82 (s, CCH), 211 (s, CO)
$(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)S}\}$ (4)	2077 (s), 2042 (vs), 2034 (w), 2004 (vs), 1991 (w)	6.81 (s, $^2J_{\text{H-Se}} = 49$ Hz, CH), 6.98 (dd, $J_{\text{H-H}} = 3.6$ Hz and 5.1 Hz, 1H), 7.15 (dd, $J_{\text{H-H}} = 0.9$ Hz and 3.6 Hz, 1H), 7.31 (dd, $J_{\text{H-H}} = 0.9$ Hz and 5.1 Hz, 1H)	123.67 (d, $J_{\text{C-H}} = 185$ Hz, CH), 126.79–127.94 (m, Thiophene CH), 137.77 (s, Thiophene C), 155.27 (s, CCH), 208 (s, CO)
$(\text{CO})_6\text{Fe}_2\{\mu\text{-SC(H)=C(2-Th)Te}\}$ (5)	2071 (vs), 2036 (vs), 2003 (s), 1996 (s), 1998 (w)	6.97 (dd, $J_{\text{H-H}} = 3.7$ Hz and 4.6 Hz, 1H), 6.98 (dq, $J_{\text{H-H}} = 0.3$ Hz, 1.65 Hz and 3.7 Hz, 1H), 7.23 (s, CH), 7.34 (dd, $J_{\text{H-H}} = 1.65$ Hz and 4.6 Hz, 1H)	127.9–129.6 (m, Thiophene CH), 135.2 (s, Thiophene C), 142.3 (d, $J = 179.6$ Hz, CH), 146 (s, CCH), 209 (s, CO)
$(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)Te}\}$ (6)	2068 (vs), 2034 (vs), 1999 (s), 1995 (s), 1984 (w)	6.97 (dd, $J_{\text{H-H}} = 3.6$ Hz and 5.1 Hz, 1H), 7.02 (dq, $J_{\text{H-H}} = 0.3$ Hz, 1.2 Hz and 3.6 Hz, 1H), 7.35 (dd, $J_{\text{H-H}} = 1.2$ Hz and 5.1 Hz, 1H), 8.01 (s, $^2J_{\text{Se-H}} = 58$ Hz, $^3J_{\text{Te-H}} = 4.2$ Hz, CH)	135.15 (d, $J = 181$ Hz, CH), 128.02–129.68 (m, Thiophene CH), 130.6 (s, Thiophene C), 142.2 (s, CCH), 210 (s, CO)
$(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(2-Th)Se}\}$ (7)	2068 (vs), 2034 (vs), 1999 (s), 1995 (s), 1984 (w)	6.97 (dd, $J = 3.6$ Hz and 5.1 Hz, 1H), 7.0 (dd, $J = 0.9$ Hz and 3.6 Hz, 1H), 7.71 (s, $^2J_{\text{Te-H}} = 119$ Hz, $^3J_{\text{Se-H}} = 9$ Hz, CH), 7.34 (dd, $J = 0.9$ Hz and 5.1 Hz, 1H)	127.22–128.92 (m, Thiophene CH), 129.8 (s, Thiophene C), 134.4 (d, $J = 179$ Hz, CH), 138.2 (s, CCH), 210 (s, CO)

ware and sources of the scattering factors are contained in the SHELXTL (5.3) program library [17]. Table 3 lists the selected bond lengths and bond angles for **2**.

3. Result and discussion

3.1. Synthesis of **1–7**

Room temperature reaction of 2-thiopheneacetylene with $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}')$ in methanol solvent containing sodium acetate afforded the adducts $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E}'\}$ ($E = E'$ and $E \neq E'$; E, E' = S, Se, Te) (**1–7**) as shown in Scheme 1. The yield of the products varies from 20–76% depending on the nature of the chalcogenide combinations used in the starting materials. In the case of $(\text{CO})_6\text{Fe}_2(\mu\text{-SeTe})$ the formation of two isomers is observed. During the isolation of the mixed-chalcogenide derivatives of 2-thiopheneacetylene, trace amounts of the corresponding homochalcogenide derivatives $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E}\}$ and $(\text{CO})_6\text{Fe}_2\{\mu\text{-E}'\text{C(H)=C(2-Th)E}'\}$ were also isolated, as confirmed by comparison of their IR spectra with phenylacetylene analogues, $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(Ph)E}'\}$, reported earlier [18]. The S_2 analogue of 2-thiopheneacetylene, **1**, could also be obtained

in a yield of 32% from the room temperature reaction of $(\text{CO})_6\text{Fe}_2(\mu\text{-S})_2$ with 2-ThC \equiv CH in methanol solvent containing sodium acetate. The exact role of sodium acetate in these reactions is not known, but when the above reactions were performed in its absence much lower yields of the products were obtained. Among the different chalcogen-combination systems, the adduct of $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$, compound **4**, is found to be the least stable; in solution, it converts slowly to $(\text{CO})_6\text{Fe}_2\{\mu\text{-SC(H)=C(Th)S}\}$ and $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Th)Se}\}$. The new compounds **1–7** have been characterized by comparison of their IR spectra with those of the previously reported analogous compounds, $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(Ph)E}'\}$, and on the basis of ^1H , ^{13}C , ^{77}Se and ^{125}Te NMR spectroscopy. The structure of **2** has been established by X-ray diffraction methods.

3.2. Spectroscopic characterization of **1–7**

Infrared and ^1H and ^{13}C NMR data of **1–7** are summarized in Table 4. The IR spectra of compounds **1–7** in hexane display the identical terminal CO stretching patterns typically observed for compounds containing an $\text{Fe}_2(\text{CO})_6$ group. Incorporation of a heavier chalcogen ligand in $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E}'\}$ shifts the corresponding bands towards lower frequen-

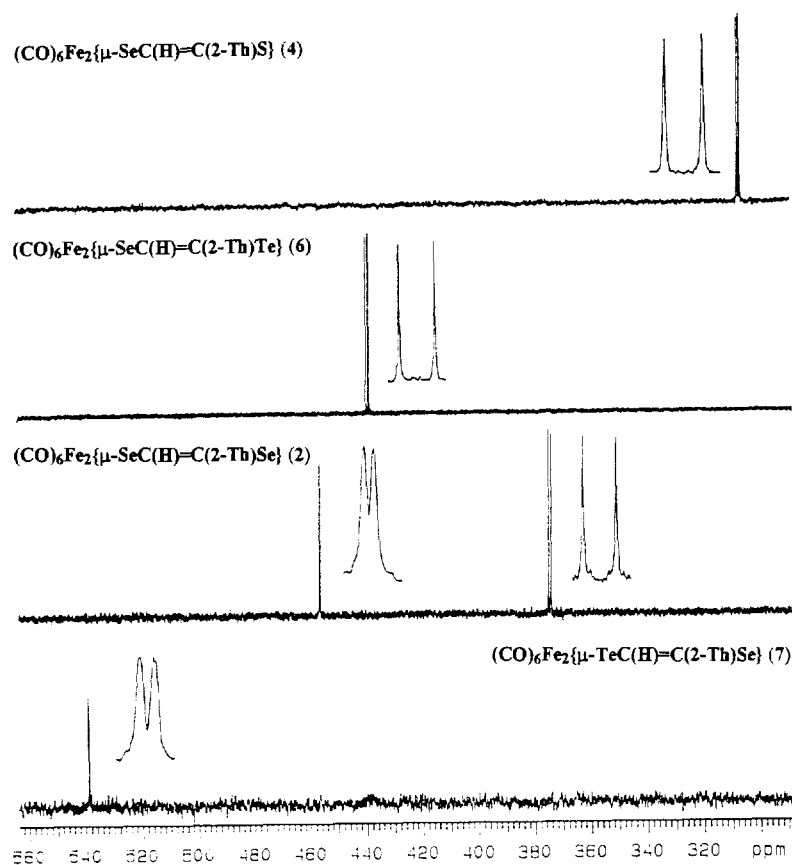
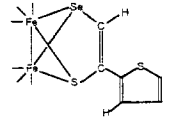
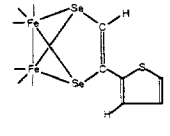
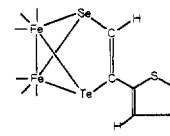
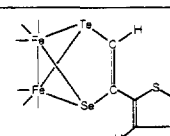


Fig. 1. ^{77}Se NMR spectra of $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E}'\}$ ($\text{EE}' = \text{SeS}$ (**4**), SeTe (**6**), SeSe (**2**), TeSe (**7**)).

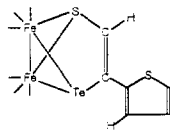
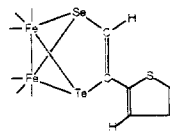
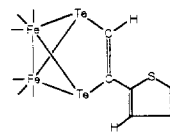
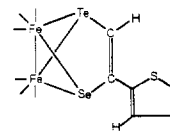
Table 5

Compounds	Two bond distance w.r.t. CH	Three bond distance w.r.t. CH
 (4)	δ 307.5 ppm d. $^2J_{\text{Se-H}} = 49$ Hz	-
 (2)	δ 374.8 ppm d. $^2J_{\text{Se-H}} = 53$ Hz	δ 456.7 ppm d. $^3J_{\text{Se-H}} = 6.8$ Hz
 (6)	δ 439.4 ppm d. $^2J_{\text{Se-H}} = 58$ Hz	-
 (7)	-	δ 539.1 ppm d. $^3J_{\text{Se-H}} = 9$ Hz

cies, as observed along the following series of EE' combinations: $S_2 > SSe > Se_2 > STE > SeTe > Te_2$. The ^1H and ^{13}C NMR spectra confirm the presence of both a thiophene group and a C_2H unit in $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC}(\text{H})=\text{C}(2\text{-Th})\text{E}'\}$. The ^1H NMR spectra of 1–7 each display four sets of signals: three signals for thiophene ring protons and a signal for the CH proton. The chemical shift of ring protons varies from δ 6.8–7.35 ppm, and each signal is split into a doublet of doublet due to coupling with three-bond- and four-bond-distance ring CH protons with coupling constants ranging from 0.9–5.1 Hz. The most upfield signal with H–H coupling constants of 5.1 Hz and 3.6 Hz can be assigned to $\gamma\text{-CH}$ followed by the $\beta\text{-CH}$ ring proton of the thiophene ring. The downfield signal can be assigned to the CH group which is bonded to S. In addition, for compounds 5 and 6, a coupling constant of 0.3 Hz is also observed due to coupling of the $\beta\text{-CH}$ ring proton with the CH proton of the acetylenic group. Each compound shows a single peak for the acetylenic CH proton with satellites due to coupling with ^{77}Se or ^{125}Te isotopes, or both, and the assignment of the signals was made on the basis of the H–Se or H–Te coupling constant. Compound $(\text{CO})_6\text{Fe}_2\{\mu\text{-}$

$\text{SeC}(\text{H})=\text{C}(2\text{-Th})\text{Te}\}$ (6) and its isomer $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC}(\text{H})=\text{C}(2\text{-Th})\text{Se}\}$ (7) both exist in solution. The signal at δ 8.01 ppm, with an H–Se coupling of 58 Hz, is comparable to the two-bond H–Se coupling of 59.5 Hz in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{H})=\text{C}(\text{Ph})\text{Te}\}$ reported earlier [18]; therefore, this signal can be assigned to the isomer $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{H})=\text{C}(2\text{-Th})\text{Te}\}$ (6). Similarly, the signal at δ 7.71 ppm, with coupling constants of 119 Hz and 9 Hz, is comparable with the two-bond distance Te–H coupling of 121.4 Hz and the three-bond distance Se–H coupling of 9.2 Hz respectively observed in $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC}(\text{H})=\text{C}(\text{Ph})\text{Se}\}$ [18]; this, therefore, can be assigned to the other isomer, $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC}(\text{H})=\text{C}(2\text{-Th})\text{Se}\}$ (7). The ^{13}C NMR spectra of 9–15 display signals for CH groups, signals for quaternary carbon atoms and a single peak in the CO region, at δ 207–211 ppm, indicating the equivalence of the carbonyl ligands on the NMR time scale at room temperature. The proton coupled ^{13}C spectra show a doublet in each case between δ 111.5–135.2 ppm for the acetylenic CH group, comparable to the corresponding phenylacetylenic derivatives reported earlier. The signal at δ 142.3 ppm with a coupling constant of 179.6 Hz is

Table 6

Compounds	Two bond distance w.r.t. CH	Three bond distance w.r.t. CH
 (5)	-	δ 644.7 ppm multiplet
 (6)	-	δ 799.8 ppm multiplet
 (3)	δ 772 ppm d. $^2J_{\text{Te-H}} = 131$ Hz	δ 940.7 ppm multiplet
 (7)	δ 662.6 ppm d. $^2J_{\text{Te-H}} = 119$ Hz	-

assigned to the acetylenic CH group of **5**, which is the most downfield signal observed in the spectra of **1–7**. The spectra also display signals for thiophene carbon atoms at δ 126.0–138.9 ppm.

The ^{77}Se NMR spectra of $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)E}\}$ (E = S (**4**), Se (**2**), Te (**6**)) and $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(2-Th)Se}\}$ (**7**) are shown in Fig. 1. Each signal is split into a doublet due to short-range or long-range Se–H coupling. The chemical shift of the ^{77}Se NMR signals are given in Table 5. Compound **2** displays two signals at δ 374.8 and 456.7 ppm, which are in the range of chemical shifts observed for $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Se}\}$ (δ 371 and 448 ppm) [18]. The upfield signal with a higher value of Se–H coupling constant of 53 Hz is due to two-bond Se–H coupling and can be assigned to SeC(H) ; the other signal, with an Se–H coupling of 6.8 Hz, can be assigned to SeC(Th) . Similarly, compounds **4**, **6** and **7** show signals at δ 307.5 ppm, δ 439.4 ppm and δ 539.1 ppm respectively. These are in the range of chemical shifts observed for previously reported compounds of phenylacetylene analogues. Both compound **6** and its isomer **7** show a doublet in the ^{77}Se NMR spectrum and were distinguished on the basis of the Se–H coupling constant. An Se–H coupling of 58 Hz observed at δ 439.4 ppm is due to a two-bond distance coupling and can be assigned to $(\text{CO})_6\text{Fe}_2\{\mu\text{-$

$\text{SeC(H)=C(Th)Te}\}$ (**6**). The signal at δ 539.1 ppm with a long-range Se–H coupling of 9 Hz can be assigned to the other isomer, $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(2-Th)Se}\}$ (**7**). Fig. 1 shows that introducing a more electropositive chalcogen ligand in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)E}\}$ or $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)Se}\}$ shifts the signals downfield along the series E = S, Se, Te. Likewise, $^2J_{\text{Se-H}}$ and $^3J_{\text{Se-H}}$ coupling constants also increase along the same series.

The ^{125}Te NMR data for $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)Te}\}$ (E = S (**5**), Se (**6**), Te (**3**)) and $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(2-Th)Se}\}$ (**8**) are given in Table 6. Compound **3** displays two signals: a doublet at δ 772 ppm and a multiplet at δ 940.7 ppm. The Te–H coupling constant of 131 Hz for the doublet is consistent with a two-bond Te–H coupling observed in $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(Ph)Te}\}$ (δ 769.2 ppm, $^2J_{\text{Te-H}} = 132.8$ Hz). Similarly, compounds **5** and **6** each show a multiplet centred at δ 644.7 ppm and δ 799.8 ppm respectively, as shown in Fig. 2. These are in the range of chemical shifts observed in the following compounds: δ 620 ppm in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SC(H)=C(Ph)Te}\}$ and δ 782 ppm in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Te}\}$. The multiplet nature of the signal is due to the coupling of ^{125}Te isotope with the three-bond distance acetylenic proton accompanied by a coupling with the β -CH proton of the thiophene ring, i.e. a four-bond Te–H coupling. Similar types of

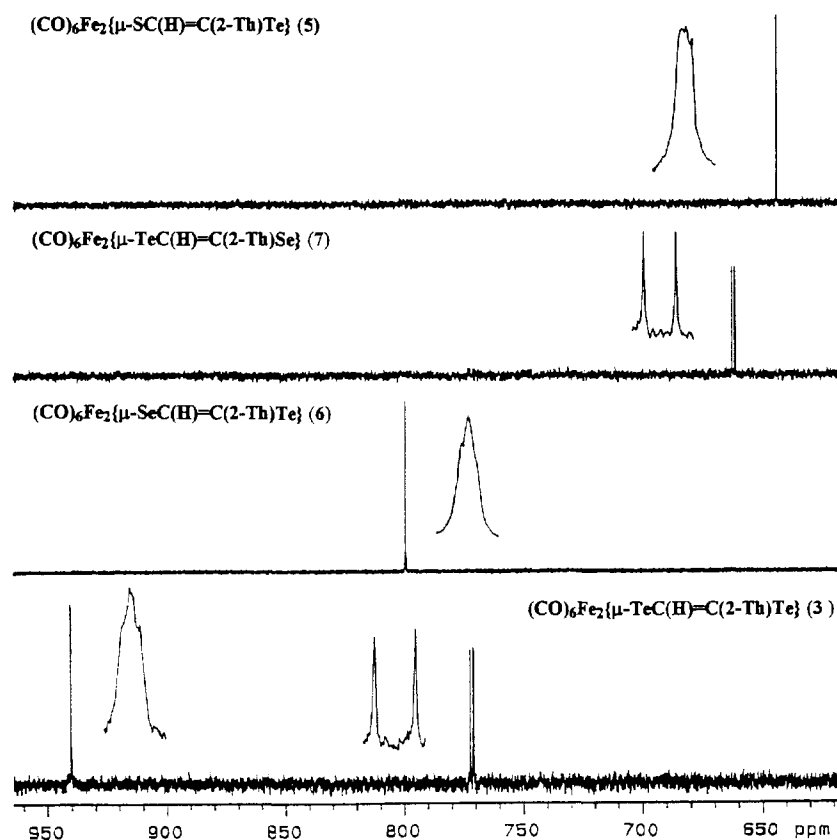


Fig. 2. ^{125}Te NMR spectra of $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E'}\}$ (EE' = STe (**5**), TeSe (**7**), SeTe (**6**), TeTe (**3**)).

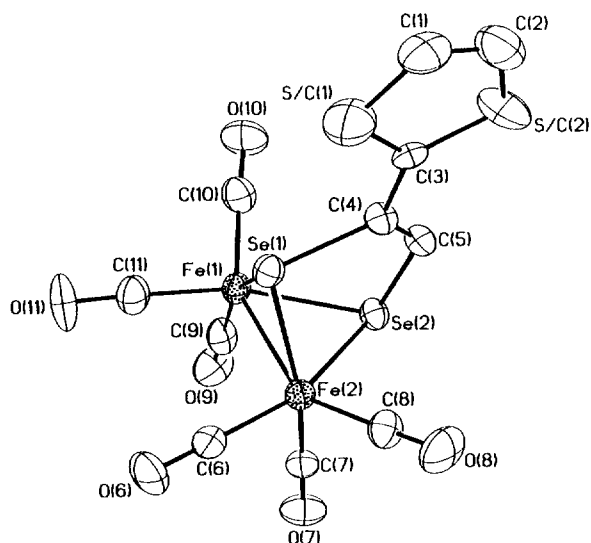


Fig. 3. Molecular structure of $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)Se}\}$ (**2**).

long-distance coupling are also observed in the ^1H NMR spectra of compounds **5** and **6** with a five-bond distance H–H coupling of 0.3 Hz. The doublet at δ 662.6 ppm for **7** is due to short-range Te–H coupling of 119 Hz. Examination of the ^{125}Te NMR spectra for the series of compounds $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC(H)=C(2-Th)E}\}$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) and $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(2-Th)E}\}$ ($\text{E} = \text{Se}, \text{Te}$) shows that the chemical shift values for the signals increase along the series $\text{E} = \text{S}, \text{Se}, \text{Te}$. Similar trends of increasing short-range and long-range Te–H coupling were also observed along the series $\text{E} = \text{S}, \text{Se}, \text{Te}$, consistent with the general trend observed in the ^{77}Se NMR spectrum.

3.3. Molecular structure of $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(2-Th)Se}\}$ (**2**)

Red, block-shaped single crystals of **2** were obtained from its hexane– CH_2Cl_2 solution at -10°C and an X-ray diffraction study was undertaken. Fig. 3 shows the ORTEP diagram of the molecular structure of **2**. The structure consists of an Fe_2Se_2 butterfly core, and the thiopheneacetylene molecule is bonded to the wingtips of the Fe_2Se_2 butterfly tetrahedral core geometry. Each Fe atom has three terminally bonded carbonyl groups. The three CO groups, the $\mu_3\text{-Se}$ ligands and the Fe–Fe bond define a distorted octahedral geometry around each Fe atom. Overall the structure of **2** is similar to $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)E}\}$ ($\text{E} = \text{S}$ [19], Se [11], Te [18]) and $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(Ph)Te}\}$ [13]. The average C–C bond distance of 1.306(14) Å in **2** indicates the reduction of the acetylenic triple bond to an olefinic bond order. It is similar to the corresponding bond distance of the coordinated acetylenic bond in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Se}\}$ (1.331(7) Å) [11], $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)S}\}$ (1.293(19) Å) [19],

$(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Te}\}$ (1.31(3) Å) [18] and $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(Ph)Te}\}$ (1.34(1) Å) [13]. The average Fe–Fe bond distance of 2.513(2) Å is shorter than the corresponding distance in $(\text{CO})_6\text{Fe}_2\{\mu\text{-TeC(H)=C(Ph)Te}\}$ (2.571(4) Å) and in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Te}\}$ (2.539(5) Å), but it is comparable with the 2.501(3) Å in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)S}\}$ and 2.512(1) Å in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Se}\}$. The average Fe–Se bond length in **2** is 2.382(2) Å, which is similar to the Fe–Se bond distance of 2.384(9) Å in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Se}\}$. The average Se–Fe–Se bond angle of 81.3° in **2** is similar to the average Se–Fe–Se bond angle of 81.4° in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(Ph)Se}\}$, but it is greater than the average Se–Fe–Se angle of 58° in $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ [20]; this is consistent with an opening of the Fe_2Se_2 butterfly core to accommodate the thiopheneacetylene molecule.

Acknowledgements

We thank the Council of Scientific and Industrial Research, Government of India, for financial support. AKD is grateful to CSIR for the award of Senior Research Fellow.

References

- [1] A. Gellman, M.E. Bussell, G.A. Somorjai, *J. Catal.* 107 (1987) 103. M.C. Zonneville, R. Hoffmann, S. Harris, *Surf. Sci.* 199 (1988) 320. B.C. Gates, J.R. Katzer, G.C.A. Schuit, *Chemistry of Catalytic Processes*, McGraw-Hill, New York, 1997.
- [2] K.M. Rao, C.L. Day, R.A. Jacobson, R.J. Angelici, *Inorg. Chem.* 11 (1992) 3328. C.-M.J. Wang, R.J. Angelici, *Organometallics* 9 (1990) 1770.
- [3] G.D. Galpern, in: S. Gronowitz (Ed.), *Thiophene and Its Derivatives*, vol. 44, part 1, Wiley, New York, 1986, p. 325.
- [4] R.J. Angelici, *Acc. Chem. Res.* 21 (1988) 387.
- [5] T.B. Rauchfuss, *Prog. Inorg. Chem.* 39 (1991) 259. R.M. Chin, W.D. Jones, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 357. S. Luo, T.B. Rauchfuss, A.L. Rheingold, S.R. Wilson, *Organometallics* 10 (1991) 1002. J. Chen, L.M. Daniels, R.J. Angelici, *J. Am. Chem. Soc.* 112 (1990) 199. M.-G. Choi, R.J. Angelici, *Organometallics* 11 (1992) 992.
- [6] R.J. Angelici, *Coord. Chem. Rev.* 105 (1990) 61 and references cited therein.
- [7] A.J. Deeming, *Adv. Organomet. Chem.* 26 (1986) 1. (b) D. Braga, F. Grepioni, B.F.G. Johnson, J. Lewis, J.A. Luniss, *J. Chem. Soc. Dalton Trans.* (1992) 1101. H. Bonnemann, *Angew. Chem. Int. Ed. Engl.* 24 (1985) 248. E. Sappa, A. Tiripicchio, P. Braunstein, *Chem. Rev.* 83 (1983) 1081. M.D. Vargas, J.N. Nicholls, *Adv. Inorg. Chem. Radiochem.* 30 (1986) 123.
- [8] H. Vahrenkamp, *Angew. Chem. Int. Ed. Engl.* 14 (1975) 322. K.H. Whitmire, *J. Coord. Chem.* 17 (1988) 95. L.C. Roof, J.W. Kolis, *Chem. Rev.* 93 (1993) 1037. M.A. Ansari, J.A. Ibers, *Coord. Chem. Rev.* 100 (1990) 223. R.D. Adams, in: D.F. Shriver, H.D. Kaesz, R.D. Adams (Eds.), *The Chemistry of Metal Cluster Complexes*, VCH, New York, 1990, Chapter 3. P. Mathur, I.J. Mavunkal, A.L. Rheingold, *J. Chem. Soc. Chem. Commun.* (1989) 382.

- [9] P. Mathur, D. Chakrabarty, I.J. Mavunkal, J. Cluster Sci. 4 (1993) 351. P. Mathur, B. Manimaran, Md.M. Hossain, R. Shanbag, J. Murthy, I.S. Saranathan, C.V.V. Satyanarayana, Md.M. Bhadbhade, J. Organomet. Chem. 490 (1995) 173. P. Mathur, Md.M. Hossain, A.L. Rheingold, Organometallics 13 (1994) 3909. P. Mathur, P. Sekar, C.V.V. Satyanarayana, M.F. Mahon, Organometallics 14 (1995) 2115. P. Mathur, Md.M. Hossain, S.B. Umbarkar, C.V.V. Satyanarayana, A.L. Rheingold, L.M. Liable-Sands, G.P.A. Yap, Organometallics 15 (1996) 1898.
- [10] P. Mathur, Md.M. Hossain, K. Das, U.C. Sinha, J. Chem. Soc. Chem. Commun. (1993) 46.
- [11] P. Mathur, Md.M. Hossain, Organometallics 12 (1993) 2398.
- [12] D. Seyferth, G.B. Womack, Organometallics 5 (1986) 2360.
- [13] T. Fassler, D. Buchholz, G. Huttner, L. Zsolnai, J. Organomet. Chem. 369 (1989) 297.
- [14] P. Mathur, Md.M. Hossain, A.L. Rheingold, Organometallics 12 (1993) 5029.
- [15] P. Mathur, D. Chakrabarty, Md.M. Hossain, J. Organomet. Chem. 401 (1991) 167. P. Mathur, D. Chakrabarty, Md.M. Hossain, J. Organomet. Chem. 418 (1991) 415. L.E. Bogan, D.A. Lesch, T.B. Rauchfuss, J. Organomet. Chem. 250 (1983) 429. D.A. Lesch, T.B. Rauchfuss, Inorg. Chem. 20 (1981) 3583. P. Mathur, D. Chakrabarty, Md.M. Hossain, R.S. Rashid, V. Rugmini, A.L. Rheingold, Inorg. Chem. 31 (1992) 1106.
- [16] J.P. Beny, S.N. Dhawan, J. Kagan, S. Sundlass, J. Org. Chem. 47 (1982) 2201. A. Sarkar, P. Sekher, M.B. Kamath, L. Bhagwat, K.N. Babu, K. Rajalakshmi, S.S. Talwar, Indian J. Chem. B: 30 (1991) 360.
- [17] G. Sheldrick, Siemens XRD, Madison, WI.
- [18] P. Mathur, Md.M. Hossain, S.B. Umbarkar, C.V.V. Satyanarayana, S.S. Tavale, V.G. Puranik, Organometallics 14 (1995) 959.
- [19] P. Mathur, A.K. Dash, Md.M. Hossain, S.B. Umbarkar, C.V.V. Satyanarayana, Y.-S. Chen, E.M. Holt, S.N. Rao, M. Soriano, Organometallics 15 (1996) 1356.
- [20] C.F. Campana, F.W.-K. Lo, L.F. Dahl, Inorg. Chem. 18 (1979) 3060.