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A new entry into ferraborane chemistry: Synthesis and characterization of heteroferraborane complexes

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Dedicated to Professor S.S. Krishnamurthy on the occasion of his 70th birthday.

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ABSTRACT

Reaction of [CpFe(CO)₂I], **1** (Cp = η^5 -C₅H₅) and di(organyl)dichalcogenides, E₂R₂ (E = S, Se; R = Ph, CH₂Ph, 2,6-(^tBu)₂-C₆H₂OH) with [LiBH₄·thf] at -70 °C in toluene, followed by stirring at room temperature for 18 h yielded heteroferraboranes, [CpFe(CO)B₂H₄(µ-L)], **2-4** (**2**: L = SePh; **3**: SeCH₂Ph and **4**: S(2,6-(^tBu)₂-C₆H₂OH). Compounds **2-4** are highly unstable and concurrent lose of boron atoms yielded organochalcogenolato-bridged complexes, [CpFe(CO)(µ-L)]₂, **5-7**, respectively (**5**: L = SePh; **6**: SeCH₂Ph and **7**: S(2,6-(^tBu)₂-C₆H₂OH). In contrast, the reaction of **1** with di(2-furyl)ditelluride, (C₄H₃O)₂Te₂, yielded organotellurato-bridged complex, [CpFe(CO)(µ-TeC₄H₃O)]₂, **8** and all of our attempts to isolate the boron precursor [CpFe(CO)B₂H₄(µ-TeC₄H₃O)] in pure form failed. The accuracy of these predictions in each case is established by IR, ¹H, ¹¹B, ¹³C, ⁷⁷Se, ¹²⁵Te NMR and mass spectrometry and complex **8** is further structurally confirmed by X-ray crystallography.

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1. Introduction

Metallaborane [1,2] and metallaheteroborane [3,4] chemistry is widespread and has historically developed largely by the incorporation of one, two, or three atoms other than boron into the borane cluster. Syntheses of metallaheteroborane clusters are typically affected by the addition of metal complexes to heteroborane clusters [5], and as a result there is substantial interest in the nature of the chemistry that may typically result while the transition metals are from the first row. Metallaheteroborane compounds containing group 16 elements as cluster constituents [6,7] have mostly been generated from the reaction of metal centers with preformed polyhedral heteroborane substrates [8], and very little attention has been given to the idea of producing metallaheteroborane by the addition of the heteroatom to metallaborane clusters [9].

As a part of our interest in synthesizing metallaboranes of group 5–9 from various metal precursors and small metallaboranes, recently we have reported several novel metallaborane and metallaheteroborane compounds of group 5 and 6 transition metals [10–14]. Accordingly, in our continuing search for different metal precursors, containing Cp*M (Cp* = η^5 -C₅Me₅) fragment, we found that mono(halo)(cyclopentadienyl)metal carbonyl, [Cp*M(CO)_nX], (when M = Mo or W, X = Cl and *n* = 3; M = Fe, X = I and *n* = 2), are very useful to group 6 and 8 metallaboranes [15]. After it had been discovered that the reaction of [Cp*MoCl₄] with [LiBH₄·thf] in presence of dichalcogenide ligands yielded a new class of open-cage

dimolybdaheteroborane clusters [16], an investigation of metallaheterobaranes containing group 8 metal, became of interest. As ferraboranes are rare [17], and known heteroferraboranes [18,19,6b,20] even more so, we have begun to investigate the use of different chalcogen sources which generally may result new types of cluster systems. In this paper, we present a set of small monometallic heteroferraborane compounds generated from the reaction of dichalcogenide ligands and an in situ generated intermediate ([CpFe(CO)B₃H₈]) [21], produced from the reaction between [CpFe(CO)₂I] **1** and [LiBH₄·thf].

2. Results and discussion

2.1. Isolation and characterization of 2-4

As shown in Scheme 1, compounds **2–4** have been isolated in good yields as red brown solids. The ¹H and ¹¹B NMR spectra provided convincing evidence for the structure and bonding of these complexes. The ¹¹B NMR spectra of **2–4** are very identical consisting of a triplet, which indicates the presence of BH₂ group. The IR spectra show bands due to terminal carbonyl groups. Descriptions of the characterization of **2–4** from mass spectrometry and IR, ¹H, ¹¹B, ¹³C NMR spectroscopic studies follow.

2.1.1. arachno-[CpFe(CO)B₂H₄(μ -SePh)] (**2**)

The composition and structure of **2** is established in comparison of the spectroscopic data with *arachno*-[Cp*Fe(CO)B₃H₈] [15] and related species [22–25]. The composition of **2** is defined by the mass, an isotopic distribution pattern characteristic of one Fe,



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Scheme 1. Synthesis of heteroferraboranes, 2-4.

two B and one Se atom. It is also evident by the loss of one CO from the parent ion mass of 330. The ¹¹B NMR spectrum reveals one equivalent of boron environment associated with one terminal hydrogen and one bridging hydrogen at $\delta = -25.1$ ppm. The chemical shift and multiplicity of ¹¹B NMR resonance is characteristic of those observed for metal-B₃H₈ complexes [22] and $[Cp*Ru(PMe_3)(\eta^2-B_2H_7)]$ [23]. Besides the Cp protons, ¹H NMR spectrum reveals four protons associated with boron cage with a ratio of 1:1. The resonances appeared at $\delta = -16.12$ and 1.83 ppm have been assigned to two equivalents each of Fe-H-B and B-H terminal protons, respectively. The ⁷⁷Se NMR of **2** shows single resonance at δ = 336 ppm for the bridged µ-SePh group. In addition, the IR spectrum shows band corresponding to terminal carbonyl group at 1965 cm⁻¹. All the spectroscopic data suggest a seven skeletal electron pair (sep) 2 with molecular formula [CpFe $(CO)B_2H_4(\mu-SePh)].$

2.1.2. arachno-[CpFe(CO)B₂H₄(μ -SeCH₂Ph)] (**3**)

The parent ion in the mass spectrum fragments by the loss of CO molecule and the molecular mass corresponds to [CpFe(CO) $B_2H_4(SeCH_2Ph)$]. The IR spectrum of compound **3** supports the presence of a terminal carbonyl ligand appeared at 1953 cm⁻¹. The ¹¹B NMR spectrum of **3** shows a singlet resonance at δ = -24.1 ppm approximating to a triplet and the chemical shift is similar to that observed for 2. The ¹H NMR spectrum reveals the presence of one Cp resonance and a single broad resonance at $\delta = -16.1$ ppm due to Fe–H–B. The terminal boron hydrogen atoms resonate at δ = 1.78 ppm. The ¹³C NMR spectrum indicates the presence of carbonyl ligand appeared at δ = 216.4 ppm. The ⁷⁷Se NMR spectrum of **3** shows a single peak, in the region normally associated with μ -Se ligand (δ = 332 ppm). Despite many attempts to grow X-ray-quality crystals of 3 were unsuccessful, however, the molecular formula as well as the spectroscopic properties of 3 are best fit with the proposed structure as shown in Scheme 1.

Comparision of selected spectroscopic parameters of compounds 2-4, 6-8 and related species

2.1.3. arachno-[CpFe(CO)B₂H₄(μ -S(2,6-(^tBu)₂-C₆H₂OH)] (**4**)

The mass spectrum of **4** in the high m/z range shows a molecular ion peak at 412 corroborating the composition of $C_{20}H_{30}B_2$ Fe₁O₂S₁ and a single resonance at $\delta = -28.4$ ppm in the ¹¹B NMR spectrum indicates a highly symmetrical structure in solution. The ¹¹B chemical shift is consistent with hydrogen-bridged rather than direct Fe–B linkages and the ¹H chemical shift with the intensity ratio of 5:2:2, attributed to the Cp, Fe–H–B and B–H protons, respectively. The IR spectrum of **4** shows a band at 1966 cm⁻¹ which is characteristic of terminal carbonyl ligand. However, spectroscopic analysis were used to assign **4** as an *arachno*-metallaheteroborane, similar to that of [B₄H₁₀], where one of the wing-tips, that is BH₂, has been replaced by [CpFe(CO)] fragment and another wing-tip BH₄ by [S(2,6-(^fBu)₂-C₆H₂OH)] fragment.

The existence of compounds 2-4 permit comparison of the spectroscopic parameters with other metal-B₃H₈ complexes, which are listed in Table 1. The ¹¹B resonances, on going from the lighter to the heavier metal atom, appeared at low field, whereas the ¹H chemical shifts (M–H–B) appear at high field. Difference in the ¹H and ¹¹B NMR chemical shift correlation of 2-4 with other related compounds may due to the perturbation of the electronic environment of the boron atoms both by the metal and the chalcogen ligands.

2.2. Isolation and characterization of (5-8)

Up to date significant attention has been devoted to the metal complexes with chalcogenolate ligands [26,27]. The keen interest in this area stems from the richness of their structural, bonding and reactivity features [28,29] and their relevance to materials science [30,31]. In contrast to the larger number of sulfur containing clusters, those containing selenium and tellurium have been less explored [32,33].

Compounds **2–4** are highly unstable and sensitive to both air and moisture. As a result they slowly converted to corresponding organochalcogenolato-bridged complexes, **5–7** from a hexane solution (Scheme 2, vide infra) even at low temperature. Identification of **5** is based on a comparison of its spectral features and a solid state X-ray structure which is reported earlier [34]. The mass spectrometry measurements of **6** and **7** gave molecular ions corresponding to $C_{26}H_{24}Fe_2O_2Se_2$ and $C_{40}H_{52}Fe_2O_4S_2$, respectively. The IR spectra of **6** and **7** (**6**: 1955; **7**: 1956 cm⁻¹) are indicative of terminal CO groups. The ¹H spectra show Cp resonances at $\delta = 4.68$ and 5.25 ppm for **6** and **7**, respectively. Consistent with this observation, the ¹³C NMR spectra of **6** and **7** show resonances corresponds to the Cp and CO groups.

2.3. Compound 8

In an attempt to synthesize telluroferraborane [CpFe(CO)B₂H₄ $(\mu$ -TeC₄H₃O)], **1** was treated with [LiBH₄·thf] and di(2-furyl)ditellu-

Compound ¹H NMR (ppm)[M–H–B] ¹¹B NMR (ppm)^a ⁷⁷Se NMR (ppm) $v_{CO} (cm^{-1})$ Ref. 2 -16.12 -25.1 336 1965 This work This work 3 -16.10-24.1332 1953 4 -15.66-2841966 This work [Cp*Fe(CO)B₃H₈] -15.4-41.31967 _ [15] $[Cp*Ru(PMe_3)(\eta^2-B_2H_7)]$ -11.1 -21.4[23] _ [Cp*Ru(PMe₃)B₃H₈] -12.01-34.6[24] _ _ $[(\eta^6 - C_6 Me_6)Ru(Cl)B_3H_8)]$ -9.50 -36.5_ _ [22a] $[Cp*Re(H_3)B_3H_8]$ -10.3-39.9[25] 333 1955 6 This work 1956 This work 7 _ 373^b 8 1923 This work _ _

^{a 11}B NMR of hinge boron (M-H-B).

^b ¹²⁵Te NMR.

Table 1



Scheme 2. Reaction pathway for the formation of 5-7 from heteroferraboranes, 2-4.

ride in toluene for 4 h. However, a rather unexpected observation, not seen with analogous S and Se systems, was the direct formation of organotellurato-bridged complex **8**. Compound **8** has been characterized spectroscopically, as well as by a single crystal X-ray diffraction study. Mass spectral data of **8** suggest a molecular formula of $C_{20}H_{16}Fe_2O_4Te_2$. The IR spectrum of **8** in the carbonyl region displays band at 1923(m) cm⁻¹ due to terminal carbonyl groups. The ¹H NMR shows single resonance for Cp ligands at $\delta = 4.89$ ppm. The ¹³C NMR spectrum shows four resonances at $\delta = 108.4, 110.2, 143.7$ and 144.6 ppm for furyl ligands. In addition to these, resonances at $\delta = 213.6$ and 210.2 ppm are due to the CO groups. The ¹²⁵Te NMR spectrum of **8** shows a signal at $\delta = 373$ ppm, which is in well agreement with the reported organotellurato-bridged complex [35].

The definitive assignment of the structure of **8** was obtained by X-ray crystallography (Fig. 1). The iron atom is bonded to a carbonyl and cyclopentadienyl ligand, which together with the two Te contacts yield a distorted tetrahedral environment (82.42–127.31°) about Fe. On the other hand, the tellurium atom is also bonded to a 2-furyl ligand, which together with the two iron contacts, gives rise to a distorted trigonal–pyramidal arrangement (93.30–106.64°) in which Te lies at the apex of the pyramid. The cyclopentadienyl ligands on the iron atoms are *trans* disposed with respect to each other and 2-furyl ligands on the tellurium atoms are also in *trans* configuration.

An interesting piece of structural data can be found by comparing the geometry of 8 with different organotellurato-bridged complexes [35–37]. The Fe. .. Fe separations are found to be 3.721 Å and apparently depend mainly on the size of the chalcogen atoms. It is reasonable to assume that interaction and communication between the two metals is essentially transferred through the two Te(2-furyl) bridges. The Te-Te bond distance is too long to consider the existence of any Te...Te bonding interaction. The angles at the metal (Te-Fe-Te, 81-82°) are generally more acute than those at the chalcogen (Fe-Te-Fe, 93°), although they are comparable $(93-94^{\circ})$ in the *p*-ethoxyphenyltellurolato complex, [CpFe(CO) $(TeC_6H_4OC_2H_5)]_2$ [37]. The mean Fe–Te bond distance (2.5574 Å) is slightly longer than the Fe-Te bond distance of 2.5495 Å in $[Fe_2(CO)_6(\mu-TeCH_3)_2]$ [38]. The Fe-C (carbonyl) distances of 1.748(6) Å and the Fe-C (Cp) distances of 2.07-2.10 Å are comparable with distances in similar iron compounds. The carbonyl groups in **8** are very close to linear. Tellurium–carbon (furyl)



Fig. 1. Molecular structure and labeling diagram for $[CpFe(CO)(\mu-TeC_4H_3O)]_2$ 8. Relevant bond lengths (Å) and angles (°): Fe(1)–Te(1) 2.5567(9), Fe(1)–Te(2) 2.5435(8), Fe(2)–Te(1) 2.5606(9), Fe(2)–Te(2) 2.5690(9), C(11)–Te(1) 2.108(5), C(15)–Te(2) 2.121(5); Fe(1)–Te(1)–Fe(2) 93.30(3), Fe(1)–Te(2)–Fe(2) 93.42(3), C(11)–Te(1)–Fe(1) 102.68(14), C(15)–Te(2)–Fe(1) 106.57(15), C(11)–Te(1)–Fe(2) 102.50(14), C(15)–Te(2)–Fe(2) 106.83(16).

distances of 2.108(5) and 2.121(5) Å, compare favorably with other Te–C distances, e.g., 2.136(8) Å in 2-biphenyltellurium tribromide [39].

2.4. Reaction pathways

The mechanism for the formation of **5–7** is not fully implicit; however a plausible sequence of actions is shown in Scheme 2. It is reasonable to consider that compounds **2–4** are the primary products of the oxidative attack of dichalcogenide ligands to the ferraborane, *arachno*-[CpFe(CO)B₃H₈] [21]. The ER (E = S, Se) in **2– 4** is a five-skeletal electron donor isoelectronic with the BH₄ unit; therefore the replacement of wing-tip boron hydride in ferraborane necessitates the formation of **2–4**. As shown in Scheme 2, a three-step mechanism has been suggested to account for the formation **5–7** from **1**. Further, to evaluate the ultimate fate of the released boron atoms in the last step, low temperature reaction of **2–4** was performed in the presence of Lewis base, PMe₂Ph. The reaction was monitored by ¹¹B NMR spectroscopy, which revealed the formation of borane base adduct (BH₃ PMe₂Ph), as indicated by the presence of a single resonance in the ¹¹B{¹H} NMR spectrum at δ = -36.2 ppm [40]. Thus it is possible that upon slow release of BH₃ from **2** to **4**, compounds **5–7** are formed. On the other hand, in order to verify further the formation of telluroferraborane, $[CpFe(CO)B_2H_4(\mu-TeC_4H_3O)]$ as an intermediate in the formation of **8**, low temperature reaction of **1** and di(2-furyl)ditelluride with [LiBH₄ thf] was monitored by ¹¹B NMR spectroscopy, which revealed the formation (almost immediately) of a new boron containing compound, as indicated by the presence of a resonance at δ = -29.2 ppm. The peak at δ = -29.2 ppm slowly decreases as the reaction progresses and finally disappears after the reaction mixture stirred for 4 h at room temperature. Thus, we assume that telluroferraborane is an intermediate in the formation of **8**.

3. Conclusions

In conclusion, the synthesis and characterization of heteroferraboranes have been described, which on slow decomposition generate organochalcogenolato-bridged complexes, **5–8**. Apparently, these results highlight the possibility of practical application in the synthesis of a new class of mixed transition metal/chalcogen/ boron complexes. Efforts to assess the scope, limitations, as well the solid state structure of these novel heteroferraboranes **2–4** are now in process.

4. Experimental

4.1. General procedures and instrumentation

All the operations were conducted under an Ar/N₂ atmosphere using standard Schlenk techniques and glove box. Solvent were distilled prior to use under Argon. [CpFe(CO)₂]₂, [LiBH₄·thf] (Aldrich) were used as received. The external reference $[Bu_4N(B_3H_8)]$ for the ¹¹B NMR, was synthesized with the literature method [41]. The [CpFe(CO)₂I] [42], (C₄H₃O)₂Te₂ [43], (PhCH₂)₂Se₂ [44], Ph₂Se₂ [45] and $(2,6-({}^{t}Bu)_{2}-C_{6}H_{2}OH)_{2}S_{2}$ [46] were prepared as described in the literature. Thin layer chromatography was carried on 250 mm diameter aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ , ppm, CDCl₃, 7.26), while a sealed tube containing $[Bu_4N(B_3H_8)]$ in C₆D₆ (δ_B , ppm, -30.07) was used as an external reference for the ¹¹B NMR. Microanalyses for C, H and N were performed on Perkin-Elmer Instruments series II model 2400. Infrared spectra were obtained on a Nicolet 6700 FT-IR spectrometer. Mass spectra were obtained on ESI Q-Tof Micro mass Spectrometer and Jeol SX 102/Da-600 mass spectrometer/Data System using Argon/Xenon (6kv, 10 mÅ) as the FAB gas.

4.2. General procedure for the synthesis of 2-4

In a typical reaction, **1** (0.120 g, 0.39 mmol) was loaded in a 100 mL Schlenk tube and freshly distilled toluene (10 mL) was added to generate a brown solution and the mixture cooled to -70 °C. LiBH₄ (0.78 mL, 1.56 mmol) was added dropwise and stirred at room temperature in presence of an excess of PhSe–SePh (0.48 g, 1.54 mmol) for 18 h. The solvent was dried and the residue was extracted into hexane and passed through Celite. After removal of solvent, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (95:05 v/v) mixture yielded reddish brown **2** (0.06 g, 46%). Under

the similar reaction conditions, PhCH₂Se–SeCH₂Ph (0.52 g, 1.53 mmol) and $(2,6-({}^{t}Bu)_{2}-C_{6}H_{2}OH)_{2}S_{2}$ (0.74 g, 1.56 mmol) yielded **3** (0.07 g, 51%) and **4** (0.05 g, 30%), respectively. Note that, reaction of **1** with [LiBH₄·thf] and (C₄H₃O)₂Te₂ (0.6 g, 1.54 mmol) in toluene for 4 h, under the same reaction conditions yielded **8** (0.08 g, 29%).

Compound **2**. ¹¹B NMR (128 MHz, CDCl₃, 22 °C): δ –25.1 (br s, 2B); ¹H{¹¹B} NMR (400 MHz, CDCl₃, 22 °C): δ 7.60–7.01(m, 5H, Ph), 4.63 (s, 5H, Cp), 1.83 (partially collapsed quartet (pcq), 2 BH_t), –16.12 (s, 2Fe–H–B); ¹³C NMR (100 MHz, CDCl₃, 22 °C): δ 223.3 (s, Fe–CO), 131.6, 129.3, 128.6, 127.8 (s, C₆H₅), 78.7 (s, C₅H₅); ⁷⁷Se NMR (95.38 MHz, CDCl₃, 22 °C): δ 336 (s, Se); MS (FAB⁺): m/z (%) = 330 [M]⁺, 302 [M–CO]⁺; IR (hexane cm⁻¹): 2496 (w, BH_t), 1965 (s, Fe–CO); C₁₂H₁₄B₂FeOSe: Calc. C, 43.59; H, 4.27. Found: C, 44.06; H, 4.64.

Compound **3.** ¹¹B NMR (128 MHz, CDCl₃, 22 °C): δ –24.1 (br s, 2B); ¹H{¹¹B} NMR (400 MHz, CDCl₃, 22 °C): δ 7.69–7.26 (m, 5H, Ph), 4.61 (s, 5H, Cp), 2.76 (s, PhCH₂Se), 1.78 (pcq, 2 BH_t), –16.10 (s, 2Fe–H–B); ¹³C NMR (100 MHz, CDCl₃, 22 °C): δ 216.4 (s, Fe–CO), 129.2, 128.8, 128.5, 128.3 (s, C₆H₅), 79.8 (s, C₅H₅), 34.5 (s, PhCH₂Se); ⁷⁷Se NMR (95.38 MHz, CDCl₃, 22 °C): δ 332 (s, Se); MS (FAB⁺): *m/z* (%) = 344 [M]⁺, 316 [M–CO]⁺; IR (hexane cm⁻¹): 2417 (w, BH_t), 1953 (s, Fe–CO).

Compound **4**. ¹¹B NMR (128 MHz, CDCl₃, 22 °C): δ –28.4 (br s, 2B); ¹H{¹¹B} NMR (400 MHz, CDCl₃, 22 °C): δ 7.04 (s, 2H, C₆H₂OH), 5.08 (s, C₆H₂OH), 4.79 (s, 5H, Cp), 2.08 (br, 2BH_t), 1.35 (s, 18H, (CH₃)₃C), -15.66 (s, 2Fe-H–B); ¹³C NMR (100 MHz, CDCl₃, 22 °C): δ 221.1 (s, Fe-CO), 154.3, 136.8, 127.8 (s, C₆H₂OH), 79.4 (s, C₅H₅), 34.6 (s, -C(CH₃)₃), 30.3 (s, C(CH₃)₃); MS (FAB⁺): *m/z* (%) = 412 [M]⁺, 384 [M–CO]⁺; IR (hexane cm⁻¹): 2432 (w, BH_t), 1966 (s, Fe-CO).

Compound **8**. 1H NMR (400 MHz, CDCl₃, 22 °C): δ 7.72–6.55 (s, 3H, C₄H₃O), 4.89 (s, 5H, Cp); ¹³C NMR (100 MHz, CDCl₃, 22 °C): δ 213.6, 210.2 (s, Fe–CO), 144.6, 143.7, 110.2, 108.4 (s, C₄H₃O), 80.1 (s, C₅H₅); ¹²⁵Te NMR: δ 373 (s, 2Te); MS (ESI⁺): *m/z* (%) = 688 [M]⁺, 660 [M–CO]⁺, 632 [M–2CO]⁺; IR (hexane cm⁻¹): 1923 (s, Fe–CO). C₂₀H₁₆Fe₂O₄Te₂: Calc. C, 34.95; H, 2.35. Found: C, 34.41; H, 2.06.

4.3. Generation of 5-7 from 2 to 4

In a 50 mL Schlenk tube, containing 0.2 g (0.6 mmol) of **2** in 3 mL of hexane was kept at 4 °C for 5 days. The solvent was dried and the residue was extracted into hexane and passed through Celite. After removal of solvent, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (95:05 v/v) mixture yielded reddish brown **5** (0.24 g, 65%). Under identical conditions, **3** (0.3 g, 0.87 mmol) and **4** (0.2 g, 0.49 mmol) yielded **6** (0.26 g, 47%) and **7** (0.18 g, 48%), respectively. Note that the optimized reaction time for the conversion of **2–4** into the respective organochalcogenolato-bridged complexes **5–7** was 5 days.Compound **5** was characterized by comparison of its spectroscopic data and an X-ray structure reported earlier [34].

Compound **6**. ¹H NMR (400 MHz, CDCl₃, 22 °C): δ 7.43–7.25 (s, 10H, C₆H₅CH₂), 4.68 (s, 10H, Cp), 2.43 (s, 4H, C₆H₅CH₂); ¹³C NMR (100 MHz, CDCl₃, 22 °C): δ 218.1, 213.6 (s, Fe–CO), 137.8, 129.4, 128.3, 125.4 (s, C₆H₅CH₂), 91.1 (s, C₅H₅), 25.3 (s, C₆H₅CH₂); ⁷⁷Se NMR (95.38 MHz, CDCl₃, 22 °C): δ 333 (s, 2Se); MS (FAB⁺): *m/z* (%) = 638 [M]⁺, 610 [M–CO]⁺, 582 [M–2CO]⁺; IR (hexane cm⁻¹): 1955 (s, Fe–CO). C₂₆H₂₄Fe₂O₂Se₂: Calc. C, 48.94; H, 3.79. Found: C, 49.16; H, 4.18.

Compound **7**. ¹H NMR (400 MHz, CDCl₃, 22 °C): δ 7.19 (s, 4H, C₆H₂OH), 5.25 (s, 10H, Cp), 5.18 (s, 2H, C₆H₂OH), 1.35–1.32 (s, 36H, (*C*H₃)₃C); ¹³C NMR (100 MHz, CDCl₃, 22 °C): δ 214.1 (s, Fe–CO), 136.8, 127.9, 127.0 (s, C₆H₂OH), 82.1 (s, C₅H₅), 34.6 (s,

 $-C(CH_3)_3$, 30.29 (s, $C(CH_3)_3$); MS (FAB⁺): m/z (%) = 772 [M]⁺, 744 [M-CO]⁺, 716 [M-2CO]⁺; IR (hexane cm⁻¹): 1956 (s, Fe–CO). C₄₀H₅₂Fe₂O₄S₂: Calc. C, 62.18; H, 6.78. Found: C, 62.86; H, 7.27.

4.4. X-ray structure determination

Crystal data were collected and integrated using Bruker Apex II CCD area detector system equipped with graphite monochromated Mo K α (λ = 0.71073 Å) radiation at 173 K. The structure was solved by heavy atom methods using SHELXS-97 [47] and refined using SHELXL-97 [48] (G.M. Sheldrick, University of Göttingen). X-ray quality crystal was grown by slow diffusion of a hexane: CH₂Cl₂ (9.5:0.5 v/v) solution of **8**.

Crystal data for **8**: formula, $C_{20}H_{16}Fe_2O_4Te_2$; M = 687.23 g/mol; crystal system, space group: orthorhombic, Pbca; unit cell dimensions: a = 13.234(3) Å, b = 17.198(3) Å, c = 18.514(4) Å; Z = 8; density (calculated) 2.167 Mg/m³; final *R* indices $[I > 2\sigma(I)]$ $R_1 = 0.0329$, $wR_2 = 0.0925$; index ranges: $-12 \le h \le 17$, $-15 \le k \le 22$, $-24 \le l \le 20$; crystal size: $0.22 \times 0.16 \times 0.09$ mm³; reflections collected 17,415; independent reflections: 5145; [R(int) = 0.0405], goodness-of-fit on F^2 0.737.

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Appendix A. Supplementary material

CCDC 789116 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.033.

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