Synthesis and reaction chemistry of [(μ-SeR)(μ-σ,π-C≡CPh)]Fe$_2$(CO)$_6$

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Abstract

RSeC≡CPh (**1a**, R = Et; **1b**, R = n-Bu; **1c**, R = Ph; **1d**, R = 2,4,6-Me$_3$C$_6$H$_2$) reacts with equimolar amounts of Fe$_2$(CO)$_9$ (**2**) to give [(μ-SeR)(μ-σ,π-C≡CPh)]Fe$_2$(CO)$_6$ (**3a**, R = Et; **3b**, R = n-Bu; **3c**, R = Ph; **3d**, R = 2,4,6-Me$_3$C$_6$H$_2$).Complexes **3a**–**3d** exist as two isomers, depending on the axial or equatorial position of R at selenium.Addition of P(O^{i}C$_3$H$_7$)$_3$ (**4**) to **3d** affords {(μ-Se-2,4,6-Me$_3$C$_6$H$_2$)[μ-η^1-C≡CPh(P(O^{i}C$_3$H$_7$)$_3$)]}Fe$_2$(CO)$_6$ (**5**) along with {(μ-Se-2,4,6-Me$_3$C$_6$H$_2$)[μ-η^1:η^1-PhC=C(P(O^{i}C$_3$H$_7$)$_3$)]}Fe$_2$(CO)$_6$ (**6**).

The solid-state structures of **3d**, **5** and **6** were determined by single X-ray structure analysis.In mononuclear **3d** the Fe(CO)$_3$ fragments are bridged by a μ-Se-2,4,6-Me$_3$C$_6$H$_2$ and a μ-σ,π-C≡CPh unit, resulting in an over-all butterfly arrangement.Due to steric reasons, the mesityl group is pointing away from the PhC≡C entity and hence, is located in an equatorial position.Compounds **5** and **6**, which co-crystallise in the ratio of 7:93, feature aμ-bridging 2,4,6-Me$_3$C$_6$H$_2$Se unit and either a vinylidenic C=CPh(P(O^{i}C$_3$H$_7$)$_3$) (complex **5**) or a olefinic PhC=C(P(O^{i}C$_3$H$_7$)$_3$) (complex **6**) building block of which the latter entity is part of a diiron cyclobutene ring.
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1. Introduction

Recently, Seyferth et al. [1,2] reported on the synthesis and reaction chemistry of [(μ-SR)(μ-σ,π-C≡CR′)]-Fe$_2$(CO)$_6$ (R = R′, R ≠ R′; R,R′ = singly bound organic ligand) (type **A** molecule) by reacting Fe$_2$(CO)$_9$ with RSC≡CR′. A further possibility to prepare structural type **A** molecules is given by the reaction of [Et$_3$NH][(μ-SR)(μ-CO)Fe$_2$(CO)$_6$] with allylic or propargylic halides [1–3].

A
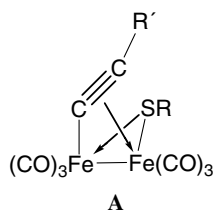
Replacement of the RS moiety by isolobal R$_2$P entities gives [(μ-PR$_2$)(μ-σ,π-C≡CR′)]Fe$_2$(CO)$_6$ [4]. The reaction chemistry of related thio- and phosphido-bridged acetylide diiron hexacarbonyl complexes was explored [1,4–7]. For example, the reactions of structural type **A** molecules with diverse transition metal carbonyls, such as Fe(CO)$_5$, Fe$_2$(CO)$_9$ and Co$_2$(CO)$_8$, respectively, were used to good advantage for the preparation of higher nuclearity, homo- and heterometallic acetylide clusters [1,3]. These multimetallic species possess novel properties [1–7]. Included in these studies were also the reaction behaviour of molecules of type [(μ-ER$_n$)(μ-σ,π-C≡CR′)]Fe$_2$(CO)$_6$ (E = P, n = 2; E = S, n = 1) towards diverse Lewis-bases L (L = amines, phosphines and phosphites) which revealed a varied and exciting organometallic chemistry with particularly relevant applications to organic synthesis, whereby numerous examples of unusual reactivity patterns have been reported [7].

This prompted us to synthesise complexes of structural type [(μ-SeR)(μ-σ,π-C≡CPh)]Fe$_2$(CO)$_6$ and to study their reaction chemistry towards Lewis-bases, such as phosphites.
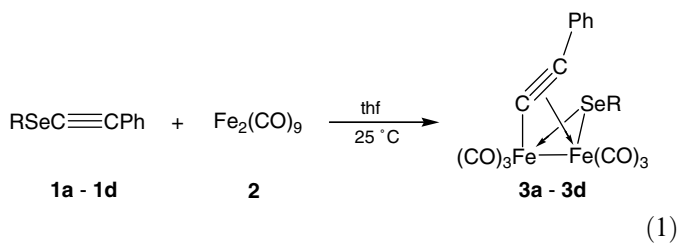
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2. Results and discussion

The reaction of RSeC≡CPh (**1a**, R = Et; **1b**, R = *n*-Bu; **1c**, R = Ph; **1d**, R = 2,4,6-Me$_3$C$_6$H$_2$) with equimolar amounts of Fe$_2$(CO)$_9$ (**2**) produces, upon evolution of CO and colour change from yellow to dark red, the diiron hexacarbonyl complexes [(μ-SeR)(μ-σ,π-C≡CPh)]Fe$_2$-(CO)$_6$ (**3a**, R = Et; **3b**, R = *n*-Bu; **3c**, R = Ph; **3d**, R = 2,4,6-Me$_3$C$_6$H$_2$) in tetrahydrofuran at 25 °C (Eq. (1)). After appropriate work-up, **3a**–**3d** can be isolated in yields between 40% and 60% as dark red oils (Section 3). Complex **3d** solidifies upon cooling to 0 °C.

$$RSeC\equiv CPh \ + \ Fe_2(CO)_9 \ \xrightarrow[25\,°C]{thf} \ \begin{array}{c} Ph \\ \| \\ C \\ \diagdown \\ C\!\!-\!\!SeR \\ (CO)_3Fe\!\!-\!\!Fe(CO)_3 \end{array}$$

1a - 1d   **2**   **3a - 3d**

(1)

Air stable **3a**–**3d** are soluble in most common organic solvents, such as petroleum ether, toluene and dichloromethane. They were characterised by elemental analysis, IR, ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy and EI-MS spectrometry.

The IR spectra of **3a**–**3d** show the characteristic vibration patterns for Fe$_2$(CO)$_6$ units with ν_{CO} absorptions at ca. 2075, 2035 and 2000 cm^{-1} (Section 3) [1].

The ^{1}H- and ^{13}C{^{1}H}-NMR spectra of **3a**–**3d** reveal that they exist in two isomeric forms. These isomers arise either from an equatorial (*eq*, isomer **I**) or axial (*ax*, isomer **II**) orientation of the organic substituents R and the lone-pair of electrons at selenium with respect to their orientation to the Fe$_2$C$_2$/Fe$_2$Se plane (Fig. 1, Section 3).

The ^{1}H NMR spectra of **3a**–**3d** show that the resonance signals of the major isomer **I** are slightly shifted downfield, when compared with the respective signals for isomer **II**. The ratio of these signals resembles to 3:1. This finding is in agreement with previously reported data for similar RS μ-bridged diiron hexacarbonyl complexes [1,8].

The sp-hybridised PhC$_\beta$≡C$_\alpha$ carbon atoms of **3a**–**3d** appear in the ^{13}C{^{1}H} NMR spectra between 90 and 115 ppm, whereby the C$_\alpha$ carbons resonate at ca. 115 ppm and the C$_\beta$ ones at ca. 90 ppm. In contrast to **1a**–**1d** (**1a**: C$_\alpha$ 70.1, C$_\beta$ 99.9; **1b**: C$_\alpha$ 70.8, C$_\beta$ 99.5; **1c**: C$_\alpha$ 69.8, C$_\beta$ 103.7; **1d**: C$_\alpha$ 71.9, C$_\beta$ 97.8 ppm) the signals for
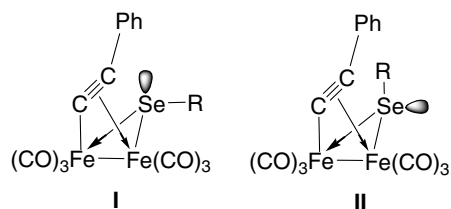
3a–**3d** are shifted to higher field upon their coordination to the Fe$_2$(CO)$_6$ unit [1,2,9]. The resonance signal at ca. 200 ppm can be assigned to the Fe(CO)$_3$ units [10].

Complex **3d** could additionally be characterised by single X-ray structure analysis. Red crystals of **3d** were obtained by cooling a saturated petroleum ether solution containing **3d** to −30 °C. The molecular solid-state structure of **3d** is depicted in Fig. 2. Selected bond distances (Å) and angles (°) are listed in the legend of Fig. 2. Intensity collection parameters are given in Table 1.

Complex **3d** represent a diiron hexacarbonyl species with a μ-Se-2,4,6-Me$_3$C$_6$H$_2$ and a μ-σ,π-C≡CPh ligand. While the mesityl selenide unit is symmetrically orientated across the two iron atoms Fe(1) and Fe(2) (Fe(1)–Se(1) 2.4181(3), Fe(2)–Se(1) 2.4253(4) Å) (Fig. 2), the PhC≡C entity is σ-bound to Fe(1) (Fe(1)–C(1) 1.902(2) Å) and η^2-coordinated to Fe(2) with separations of 2.297(2) Å (Fe(2)–C(2)) and 2.117(2) Å (Fe(2)–C(1)). These distances are in the range typical for these bonding motifs [11,5]. The C(1)–C(2) bond length with 1.346(2) Å is representative for diiron μ$_2$-vinylidene complexes (1.266(6)–1.358(5) Å) [12], and is close to the accepted C$_{sp^2}$–C$_{sp^2}$ separation of 1.34 Å for olefinic ligands [5].

As discussed earlier, complexes of structural type [(μ-ER)(μ-σ,π-C≡CPh)]Fe$_2$(CO)$_6$ (ER = S^{t}Bu, PPh$_2$) show a versatile reaction chemistry towards diverse amines and phosphanes. For example, Et$_2$NH adds at C$_\beta$ to form [(μ-ER)(μ-CH=C(Ph)(NEt$_2$))]Fe$_2$(CO)$_6$ [1]. In a similar way, we reacted **3d** with the phosphite P(O^{i}C$_3$H$_7$)$_3$ (**4**) in a 1:1 molar ratio in tetrahydrofuran at 25 °C. After appropriate work-up, {(μ-Se-2,4,6-Me$_3$C$_6$H$_2$)[μ-η^1-C=CPh(P(O^{i}C$_3$–H$_7$)$_3$)]}Fe$_2$(CO)$_6$ (**5**) along with {(μ-Se-
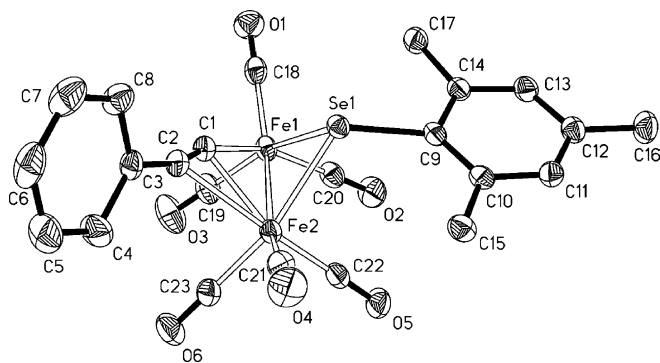

Fig. 2. XP-plot (with 50% probability level) and atom numbering scheme of **3d**. The estimated standard deviations of the last significant digits are shown in parentheses. Selected bond distances (Å) and angles (°): Fe(1)–C(1) 1.902(2), Fe(1)–Se(1) 2.4181(3), Fe(1)–Fe(2) 2.5241(4), Fe(2)–C(1) 2.117(2), Fe(2)–C(2) 2.297(2), Fe(2)–Se(1) 2.4253(4), Se(1)–C(9) 1.950(2), C(1)–C(2) 1.346(2) and C(1)–Fe(1)–Se(1) 75.15(5), C(1)–Fe(1)–Fe(2) 55.01(5), Se(1)–Fe(1)–Fe(2) 58.73(1), C(1)–Fe(2)–C(2) 32.15(6), C(1)–Fe(2)–Se(1) 71.50(4), C(2)–Fe(2)–Se(1) 85.37(4), C(1)–Fe(2)–Fe(1) 47.38(4), C(2)–Fe(2)–Fe(1) 47.38(4), Se(1)–Fe(2)–Fe(1) 58.450(8), C(9)–Se(1)–Fe(1) 113.79(5), C(9)–Se(1)–Fe(2) 117.74(5), Fe(1)–Se(1)–Fe(2) 62.82(1), C(2)–C(1)–Fe(1) 159.1(2), C(2)–C(1)–Fe(2) 82.0(2), Fe(1)–C(1)–Fe(2) 77.61(6), C(1)–C(2)–C(3) 165.(2), C(1)–C(2)–Fe(2) 65.9(1), C(3)–C(2)–Fe(2) 129.0(2).

Fig. 1. Isomers **I** and **II** of **3a**–**3d**.

Table 1
Crystal and intensity collection data for **3d**, **5** and **6**

	3d	**5/6**
Formula weight	579.02	787.25
Chemical formula	$C_{23}H_{16}Fe_2O_6Se$	$C_{32}H_{37}Fe_2O_9Pse$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	7.7750(8)	10.4248(5)
b (Å)	10.5107(11)	17.9885(8)
c (Å)	14.4784(15)	18.4563(8)
α (°)	103.773(2)	90
β (°)	98.457(2)	97.8710(10)
γ (°)	95.413(2)	90
V (Å^3)	1118.5(2)	3428.4(3)
ρ_{calc} (g cm^{-3})	1.719	1.525
$F(000)$	576	1608
Crystal dimensions (mm)	$0.45 \times 0.35 \times 0.24$	$0.22 \times 0.18 \times 0.10$
Z	2	4
Maximum and minimum transition	0.5368, 0.3492	0.8247, 0.6668
Absorption coefficient (λ, mm^{-1})	2.961	2.005
Scan range (°)	1.48–30.81	1.59–32.01
Index ranges	$-11 \leqslant h \leqslant 10$	$-15 \leqslant h \leqslant 15$
	$-11 \leqslant k \leqslant 15$	$0 \leqslant k \leqslant 26$
	$-19 \leqslant l \leqslant 20$	$0 \leqslant l \leqslant 27$
Total reflections	11 175	60469
Unique reflections	6298	11792
R_{int}	0.0237	0.0411
Data/restraints/parameter	6298/0/353	11 788/197/599
Goodness-of-fit on F^2	1.039	1.056
R_1[a], wR_2[a] $[I \geqslant 2\sigma(I)]$	0.0245, 0.0608	0.0277, 0.0671
R_1[a], wR_2[a] (all data)	0.0300, 0.0630	0.0371, 0.0717
Maximum and minimum peak in final Fourier map (e Å^{-3})	0.391, −0.494	0.917, −0.260

[a] $R_1 = [\sum(\|F_o\| - |F_c\|)/\sum|F_o|]$; $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$; $P = (\max(F_o^2, 0) + 2F_c^2)/3$; $S = [\sum w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$; n = number of reflections, p = parameters used; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

2,-4,6-Me$_3$C$_6$H$_2$)[μ-η^1:η^1-PhC=C(P(O^{i}C$_3$H$_7$)$_3$)]}Fe$_2$(CO)$_6$ (**6**) could be isolated in 50% yield (Eq. (2)).

$$(2)$$
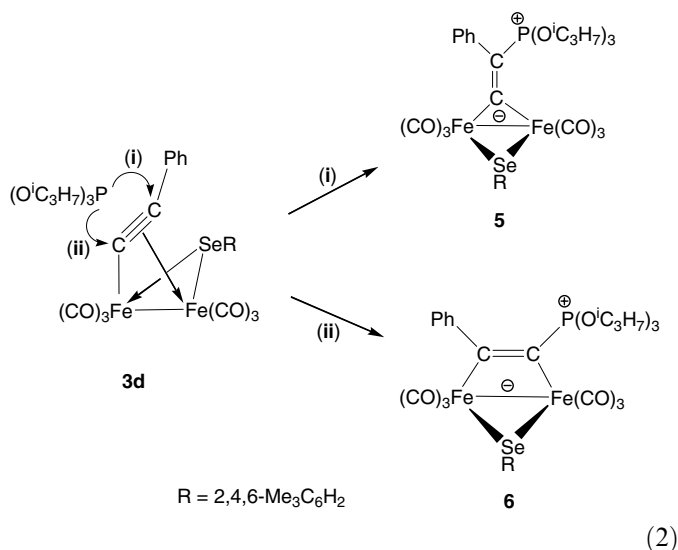
However, complex **5** could not totally be separated from **6**, either by column chromatography or fractional crystallisation. Solid red **5** and **6** are, like **3a**–**3d**, stable to air

for a long period of time. However, in solution they slowly start to decompose to form insoluble materials. They nicely dissolve in, for example, toluene, dichloromethane and tetrahydrofuran, whereas in petroleum ether and *n*-hexane they are not soluble.

In the IR spectrum a total of five ν_{CO} absorptions are found between 1936 and 2041 cm^{-1}, indicating that only terminal-bound carbonyls are present.

The ^{1}H and ^{13}C\{^{1}H\} NMR spectra of **6** show the characteristic resonance signals expected (Section 3).

That in **6** a phosphenium cation is present can nicely be concluded from ^{31}P\{^{1}H\} NMR spectroscopic studies. A very distinct signal at 5.0 ppm is observed, which is compared to free P(O^{i}C$_3$H$_7$)$_3$ shifted to higher field. A similar trend was observed for {(μ-Ph$_2$P)[μ-η^1:η^1-(CH$_3$)C=C-(P(NMe$_2$)$_3$)]}Fe$_2$(CO)$_6$ [7].

To establish the molecular structures of **5** and **6** X-ray crystallographic studies were undertaken. They co-crystallise in the monoclinic space group $P2_1/c$ in the ratio of 7:93 by slowly cooling a *n*-hexane–dichloromethane solution (ratio 5:1) to −30 °C. For clarity and distinction the molecular structures of **5** and **6** are described separately and are independently shown in Fig. 3 (complex **5**) and 4 (complex **6**). Selected bond distances (Å) and angles (°) for both molecules are given in the legend of Figs. 3 and 4. Crystal data and structure refinement details for **5** and **6** are presented in Table 1.

In **5** the Fe$_2$(CO)$_6$ unit is symmetrically bridged by the selenium atom Se(1) (Fe(1)–Se(1) 2.3887(2), Fe(2)–Se(1) 2.3923(2) Å) and a one-atom asymmetrically bridging

Fig. 3. XP-plot (with 50% probability level) and atom numbering scheme of **5**. The hydrogen atoms are omitted for clarity. The estimated standard deviations of the last significant digits are shown in parentheses. Selected bond distances (Å) and angles (°): Se(1)–C(15) 1.952(1), Se(1)–Fe(1) 2.3887(2), Se(1)–Fe(2) 2.3923(3), Fe(1)–Fe(2) 2.5891(3), Fe(1)–C(1′) 1.792(17), Fe(2)–C(1′) 2.009(19), P(1′)–C(2′) 1.807(18), C(1′)–C(2′) 1.29(2), C(2′)–C(3′) 1.57(2) and C(1′)–Fe(2)–Fe(1) 43.7(5), Se(1)–Fe(2)–Fe(1) 57.144(6), Fe(1)–Se(1)–Fe(2) 65.577(7), C(1′)–Fe(2)–Se(1) 70.0(5), Se(1)–Fe(1)–Fe(2) 57.279(7), C(1′)–Fe(1)–Se(1) 73.4(6), C(1′)–Fe(1)–Fe(2) 50.7(6), C(15)–Se(1)–Fe(2) 113.56(4), C(15)–Se(1)–Fe(1) 113.56(4), C(2′)–C(1′)–Fe(1) 143.7(15), C(2′)–C(1′)–Fe(2) 130.4(14), Fe(1)–C(1′)–Fe(2) 85.6(8), C(1′)–C(2′)–C(3′) 125.1(15), C(1′)–C(2′)–P(1′) 123.6(15), C(3′)–C(2′)–P(1′) 111.2(12).
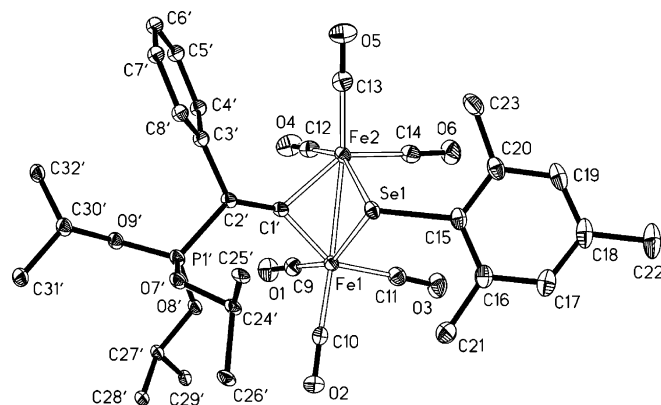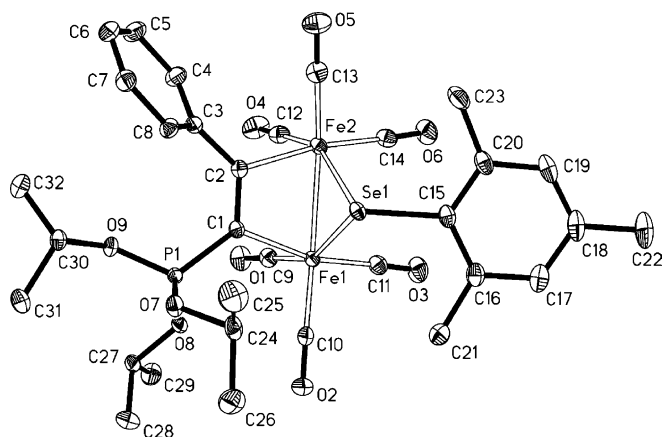
Fig. 4. XP-plot (with 50% probability level) and atom numbering scheme of **6**. The hydrogen atoms are omitted for clarity. The estimated standard deviations of the last significant digits are shown in parentheses. Selected bond distances (Å) and angles (°): Se(1)–C(15) 1.9519(13), Se(1)–Fe(1) 2.3887(2), Se(1)–Fe(2) 2.3923(2), Fe(1)–Fe(2) 2.5891(3), Fe(1)–C(1) 2.0576(14), Fe(2)–C(2) 2.0256(14), P(1)–C(1) 1.7430(15), C(2)–C(3) 1.4772(19), C(1)–C(2) 1.3445(19) and C(2)–C(1)–P(1) 127.22(11), C(1)–C(2)–C(3) 128.87(13), O(9)–P(1)–C(1) 116.81(7), C(1)–C(2)–Fe(2) 107.13(10), C(3)–C(2)–Fe(2) 123.95(10), C(1)–Fe(1)–Fe(2) 71.27(4), C(2)–Fe(2)–Fe(1) 73.23(4), C(2)–C(1)–Fe(1) 108.31(10), P(1)–C(1)–Fe(1) 124.22(7), C(15)–Se(1)–Fe(1) 113.56(4), C(15)–Se(1)–Fe(2) 113.47(4), Fe(1)–Se(1)–Fe(2) 65.577(7), C(1)–Fe(1)–Se(1) 79.65(4), Se(1)–Fe(1)–Fe(2) 57.279(7), C(2)–Fe(2)–Se(1) 81.66(4), Se(1)–Fe(2)–Fe(1) 57.144(6).

vinylidene ligand (Fe(1)–C(1′) 1.792(17), Fe(2)–C(1′) 2.009(19) Å). The Fe(1)–C(1′) separation is slightly shorter than previously reported values (1.874–1.969 Å) [11]. The C(1′)–C(2′) distance with 1.29(2) Å resembles to typical C=C separations in similar species (1.266 and 1.358 Å) [12,13]. As expected for a vinylidene-bridged dimer, the carbon atom C(2′) is essentially sp²-hybridised, since all the angles at C(2′) are close to 120° (Fig. 3). Although C(1′) is distorted from a trigonal geometry, with angles of 143.7(15)°, 130.4(14)° and 85.6(8)° (Fig. 3). The short P(1′)–C(2′) bond length of 1.807(18) Å, with the asymmetry in the vinylidene-iron connectivity suggests that the electron density is partially delocalised through the bonds between P(1′), C(2′), C(1′) and Fe(1). The dihedral angle between the plane formed by P(1′), C(2′), C(1′) and Fe(1), Fe(2), C(1′) is 4.0° and the angle subtended by the metal atom at the μ-C=CPh(P(O^{i}C$_3$H$_7$)$_3$) bridge of 85.7(8)° is characteristic for a binuclear vinylidene species [7,14,15].

The molecular structure shown in Fig. 4 identifies the 2nd molecule in the crystal as the diferra-cylobutene derivative {(μ-Se-2,4,6-Me₃C₆H₂)[μ-η¹:η¹-PhC=C(P(O^{i}C$_3$-H$_7$)$_3$)]}Fe₂(CO)₆ (**6**), an isomer of **5**, that contains a zwitterionic μ-η¹:η¹-acetylenic unit formally derived by the addition of P(O^{i}C$_3$H$_7$)$_3$ to the C$_\alpha$ carbon atom of the bridging acetylide in **3d**. The C(1)–C(2) separation of 1.3445(19) Å is close to that expected for a carbon–carbon double bond (1.337 Å) [12]. The P(1)–C(1) distance of 1.7430(15) Å is shorter than that in **5**, but similar to that expected for a compound with zwitterionic phosphorus

ylide character [6a,7,14,15], with a significant contribution from the μ-η¹:η¹-PhC=C(P(O^{i}C$_3$H$_7$)$_3$) unit. The Fe(1)–C(1) and Fe(2)–C(2) distances of 2.0576(14) and 2.0256(14) Å are different, which suggest some contributions from a ylide-carbene substructure as also found in [(μ-PPh₂)(μ-η¹:η¹-MeC=C(P(NMe₂)₃))]Fe₂(CO)₆ [7,15].

3. Experimental

3.1. General methods

All reactions were carried out in an atmosphere of purified nitrogen (O₂ traces: CuO catalyst, BASF AG, Ludwigshafen, Germany; H₂O traces: molecular sieve, 4 Å, Roth company) using standard Schlenk techniques. Solvents were purified by distillation (petroleum ether and dichloromethane: calcium hydride; toluene: sodium; tetrahydrofuran: sodium/benzophenone ketyl). FT-IR spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer (KBr pellets or as film between NaCl plates). NMR spectra were recorded with a Bruker Avance 250 spectrometer operating in the Fourier transform mode. ¹H NMR spectra were recorded at 250.123 MHz (internal standard, relative to CDCl₃, δ 7.26). ¹³C{¹H} NMR spectra were recorded at 67.890 MHz (internal standard, relative to CDCl₃, δ 77.00). Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane with the solvent signal as reference signal. ³¹P{¹H} NMR were recorded at 101.202 MHz in CDCl₃ with P(OMe)₃ as external standard (δ 139.0, relative to 85% H₃PO₄, δ 0.00). Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 melting point apparatus. Microanalyses were performed by the Organic Department at Chemnitz, the Technical University, and the Institute of Organic Chemistry at the University of Heidelberg.

3.2. General remarks

The starting materials RSeC≡CPh (**1a**–**1d**) [9] and Fe₂(CO)₉ [16] were prepared following published procedures. All other chemical were purchased from commercial suppliers and were used as received.

3.3. Synthesis of 3a

EtSeC≡CPh (**1a**) (500 mg, 1.67 mmol) is dissolved in tetrahydrofuran (80 mL). Equimolar amounts of Fe₂(CO)₉ (**2**) (607 mg, 1.67 mmol) are added in one portion at 25 °C. Carbon monoxide evolution is observed and the colour of the reaction mixture changes from yellow to cheery red. After 12 h of stirring at 25 °C all volatiles are removed in *oil-pump vacuum* and the residue obtained is purified by column chromatography (column size: 20 × 2.5 cm, petroleum ether, Silica gel, 25 °C). Eluation with petroleum

ether gives a dark red fraction. After removal of the solvent in *oil-pump vacuum*, **3a** can be isolated as a dark red, air stable oil. Yield: 0.70 g (1.43 mmol, 60% based on **1a**).

Anal. Found: C, 40.06; H, 2.35; $C_{16}H_{10}Fe_2O_6Se$ (488.90). Calcd.: C, 39.31; H, 2.06%. IR (NaCl, neat): v_{CO} 2074 (vs), 2036 (vs), 1996 (sh) cm^{-1}. ^{1}H NMR: δ 1.08 (t, 3H, $J_{HH} = 7.5$ Hz, CH$_3$, isomer II), 1.29 (t, 3H, $J_{HH} = 7.53$ Hz, CH$_3$, isomer I), 2.27 (q, 2H, $J_{HH} = 7.5$ Hz, CH$_2$, isomer II), 2.42 (q, 2H, $J_{HH} = 7.53$ Hz, CH$_3$, isomer I), 7.2–7.4 (m, 5H, C$_6$H$_5$, isomers I and II); ratio I:II = 3:1. ^{13}C{^{1}H} NMR:[a] δ 17.4 (CH$_3$, isomer II), 17.7 (CH$_3$, isomer I), 24.8 (CH$_2$, isomer II), 25.1 (CH$_2$, isomer I), 91.6 (C≡C, isomer I), 115.4 (C≡C, isomer I), 122.0 (^{i}C/Ph), 125.9 (^{i}C/Ph), 128.1 (Ph), 128.8 (Ph), 128.9 (Ph), 129.1 (Ph), 130.0 (Ph), 132.3 (Ph), 132.6 (Ph), 209.6 (CO). (a) For isomer II the C≡C resonance signals could not be detected. EI-MS [m/e (rel. intens.)]: 489 (M$^+$, 56), 461 (M$^+$ – CO, 18), 433 (M$^+$ – 2CO, 32), 405 (M$^+$ – 3CO, 17), 377 (M$^+$ – 4CO, 21), 349 (M$^+$ – 5CO, 19), 321 (M$^+$ – 6CO, 44), 293 (Fe$_2$SeC$_2$Ph$^+$, 50), 216 (Fe$_2$SeC$_2^+$, 25), 191 (Fe$_2$Se$^+$, 100), 157 (FeC$_2^+$, 34), 136 (FeSe$^+$, 20).

3.4. Synthesis of 3b

500 mg (2.10 mmol) of *n*-BuSeC≡CPh (**1b**) is reacted with 764 mg (2.10 mmol) of Fe$_2$(CO)$_9$ (**2**) as described for the preparation of **3a** (see above). After appropriate work up, **3b** could be isolated as a dark red, air stable oil. Yield: 597 mg (1.15 mmol, 55% based on **1 b**).

Anal. Found: C, 42.01; H, 2.80; $C_{18}H_{14}Fe_2O_6Se$ (516.95). Calcd.: C, 41.73; H, 2.73%. IR (NaCl, neat): v_{CO} 2074 (s), 2036 (vs), 1995 (vs), 1945 (w) cm^{-1}. ^{1}H NMR: δ 0.74 (t, 3H, $J_{HH} = 7.11$, CH$_3$, isomer II), 0.85 (t, 3H, $J_{HH} = 7.25$, CH$_3$, isomer I), 1.32 (m, 2H, CH$_3$C*H$_2$*CH$_2$CH$_2$, isomers I and II), 1.53 (m, 2H, CH$_3$-CH$_2$C*H$_2$*CH$_2$, isomers I and II), 2.24 (t, 2H, $J_{HH} = 7.30$, CH$_3$CH$_2$CH$_2$C*H$_2$*, isomer II), 2.45 (t, 2H, $J_{HH} = 7.50$ Hz, CH$_3$CH$_2$CH$_2$C*H$_2$*, isomer I). ^{13}C{^{1}H} NMR:[a] δ 13.2 (*C*H$_3$CH$_2$CH$_2$CH$_2$, isomer II), 13.5 (*C*H$_3$CH$_2$CH$_2$CH$_2$, isomer I), 22.4 (CH$_3$*C*H$_2$CH$_2$CH$_2$, isomer II), 22.8 (CH$_3$*C*H$_2$CH$_2$CH$_2$, isomer I), 30.5 (CH$_3$CH$_2$*C*H$_2$CH$_2$, isomer II), 30.9 (CH$_3$CH$_2$*C*H$_2$CH$_2$, isomer I), 33.8 (CH$_3$CH$_2$CH$_2$*C*H$_2$, isomer II), 34.2 (CH$_3$CH$_2$CH$_2$*C*H$_2$, isomer I), 91.3 (C≡C, isomer I), 115.144 (C≡C, isomer I), 125.5 (^{i}C/Ph), 128.9 (Ph), 128.7 (Ph), 131.88 (Ph), 132.3 (Ph). (a) For isomer II the C≡C resonance signals could not be detected. EI-MS [m/e (rel. intens.)]: 517 (M$^+$, 18), 489 (M$^+$ – CO, 15), 432 (M$^+$ – 3CO, 17), 349 (M$^+$ – 6CO, 13), 293 (HSeFe$_2$C$_2$CPh$^+$, 50), 216 (SeFe$_2$C$_2$H$_2^+$, 25), 191 (HSeFe$_2^+$, 100).

3.5. Synthesis of 3c

300 mg (1.16 mmol) of PhSeC≡CPh (**1c**) are treated with 422 mg (1.16 mmol) of **2** as described for the preparation of **3a**. After appropriate work-up, complex **3c** could be isolated as a dark red oil. Yield: 280 mg (0.52 mmol, 45% based on **1c**).

Anal. Found: C, 44.88; H, 1.90; $C_{16}H_{10}Fe_2O_6Se$ (536.94). Calcd.: C, 44.74; H, 188%. IR (NaCl, neat): v_{CO} 2076 (vs), 2039 (vs), 2000 (sh) cm^{-1}. ^{1}H NMR: δ 7.1–7.4 (m, 10H, CH$_5$). ^{13}C{^{1}H} NMR:[a] δ 92.7 (C≡C, isomer I), 116.06 (C≡C, isomer I), 122.0 (^{i}C/Ph), 125.9 (^{i}C/Ph), 127.0 (Ph), 128.2 (Ph), 128.3 (Ph), 128.6 (Ph), 129.5 (Ph), 132.3 (Ph), 209.7 (CO). (a) For isomer II the resonance signals of the C≡C unit could not be detected. EI-MS [m/e (rel. intens.)]: 537 (M$^+$ – CO, 18), 453 (M$^+$ – 3CO, 17), 397 (M$^+$ – 5CO, 19), 293 (HSeFe$_2$C$_2$Ph, 50), 216 (SeFe$_2$C$_2$H$_2^+$, 25), 191 (HSeFe$_2^+$, 100), 157 (FeC$_2$H$^+$, 34), 136 (HSeFe$^+$, 20).

3.6. Synthesis of 3d

500 mg (1.67 mmol) of (2,4,6-Me$_3$C$_6$H$_2$)SeC≡CPh (**1d**) is reacted with 607 mg (1.67 mmol) of **2** as described earlier (synthesis of **3a**). After appropriate work-up, **3d** can be isolated as a dark red solid. Yield: 390 mg (0.67 mmol, 40% based on **1d**).

Anal. Found: C, 47.68; H, 2.71; $C_{23}H_{16}Fe_2O_6Se$ (579.02). Calcd.: C, 47.71; H, 2.79%. M.p: 130 °C. IR (KBr): v_{CO} 2074 (s), 2040 (vs), 2000 (vs) cm^{-1}. ^{1}H NMR: δ 2.15 (s, 3H, Me, isomer I), 2.21 (s, 3H, Me, isomer II), 2.39 (s, 6H, Me, isomer I), 2.54 (s, 6H, Me, isomer II), 6.68 (s, 2H, C$_6$H$_2$, isomer I), 6.95 (s, 2H, C$_6$H$_2$, isomer II), 7.27–7.46 (m, 5H, C$_6$H$_5$, isomers I and II). ^{13}C{^{1}H} NMR:[a] δ 20.5 (Me, isomer II), 20.7 (Me, isomer I), 25.5 (Me, isomer II), 25.8 (Me, isomer I), 92.8 (C≡C, isomer I), 116.2 (C≡C, isomer I), 125.4 (^{i}C/Ph), 128.7 (Ph), 129.6 (Ph), 132.4 (Ph), 137.8 (Ph), 139.7 (Ph), 207.2 (CO). (a) For isomer II the C≡C resonance signals could not be detected. EI-MS [m/e (rel. intens.)]: 580 (M$^+$, 10), 524 (M$^+$ – 2CO, 12), 412 (M$^+$ – 4CO, 100).

3.7. Synthesis of 5 and 6

Complex **3d** (0.169 g, 0.292 mmol) is dissolved in tetrahydrofuran (20 mL) and P(O^{i}C$_3$H$_7$)$_3$ (**4**) (0.61 g, 0.292 mmol) is added in one portion at 25 °C. The reaction mixture is stirred for 14 h at this temperature. All volatiles are removed in *oil-pump vacuum* to leave an orange-red oil, which is dissolved in 5 mL of *n*-hexane and is chromatographed (column size: 10 × 1.25 cm, Silica gel, *n*-hexane, 25 °C). With *n*-hexane–dichloromethane (ratio 10:1) a red zone could be eluted. Evaporation of the solvent in *oil-pump vacuum* affords a red solid. Crystallisation from *n*-hexane–dichloromethane (ratio 10:2) gives red crystals of **5** and **6** in 50% yield (0.085 g, 0.146 mmol based on **3d**).

Anal. Found: C, 47.68; H, 2.71; $C_{23}H_{16}Fe_2O_6Se$ (579.02). Calcd.: C, 47.71; H, 2.79%. IR (KBr): v_{CO} 2041 (s), 1997 (vs), 1965 (vs), 1950 (vs), 1936 (s) cm^{-1}.

Complex **5**. ^{1}H NMR: δ 0.90 (dd, 18H, $J_{HH} = 6.92$, $J_{HP} = 13.72$, Me/P(O^{i}C$_3$H$_7$)$_3$), 1.96 (s, 3H, Me/C$_6$H$_2$), 2.43 (s, 6H, Me/C$_6$H$_2$), 3.66 (m, 3H, CH/P(O^{i}C$_3$H$_7$)$_3$,

6.46 (s, 2H, C_6H_2), 7.1–7.2 (m, 5H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ 21.4 (CH_3/C_6H_2), 22.6 ($^2J_{PC} = 16.4$ Hz, Me/$P(O^iC_3H_7)_3$), 26.6 (Me/C_6H_2), 77.3 (d, $^2J_{PC} = 9.4$ Hz, CH/$P(O^iC_3H_7)_3$), 112.8 (d, $^1J_{PC}$ = Hz, C(1)), 122–129 (Ph), 129.8 (C_6H_2), 133.5 (C_6H_2), 136.3 (C_6H_2), 140.8 (C_6H_2), 212.1–212.6 (CO), 214.5 (d, $^2J_{PC} = 3.7$ Hz, C(2)). $^{31}P\{^1H\}$ NMR: δ 5.0. EI-MS [m/e (rel. intens.): 788 (M^+, 10), 704 (M^+ $-3CO$, 38), 676 ($M^+ - 4CO$, 36), 620 ($M^+ - 6CO$, 100).

Complex 6. ^1H NMR: δ 1.27 (dd, 18H, $J_{HH} = 6.12$, $J_{HP} = 9.5$, Me/$P(O^iC_3H_7)_3$), 2.13 (s, 3H, Me/C_6H_2), 2.56 (s, 6H, Me/C_6H_2), 4.63 (m, 3H, CH/$P(O^iC_3H_7)_3$), 6.74 (s, 2H, Me/C_6H_2), 7.1–7.2 (m, 5H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ 20.7 (Me/C_6H_2), 23,6 (dd, $^2J_{PC} = 16.4$ Hz, Me/$P(O^iC_3H_7)_3$), 26.4 (Me/C_6H_2), 75.9 (d, $^2J_{PC} = 9.2$ Hz, CH/$P(O^iC_3H_7)_3$), 113.6 (d, $^1J_{PC} = 66.6$ Hz, C(1)), 122–129 (Ph), 129.1 (C_6H_2), 133.2 (C_6H_2), 136.2 (C_6H_2), 140.1 (C_6H_2), 212 (CO, broad), 214.5 (d, $^2J_{PC} = 3.7$ Hz, C(2)). $^{31}P\{^1H\}$ NMR: δ 5.0.

4. Crystal structure determination of 3d, 5 and 6

The crystal data for **3d**, **5** and **6** are presented in Table 1. The experimental data for **3d** were collected on a Bruker Smart CCD 1k and for **5** and **6** on a Bruker Smart 1000 System at 173(2) K (**3d**) or 103(2) K (**5/6**) using oil-coated shock-cooled crystals [18]. Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97 [18]) and refined by full-matrix least-squares procedures on F^2 using SHELXL-97 [19]. All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. The two co-crystallised complexes **5** and **6** have been refined to a split occupancy of 7/93 and the $P(O^iC_3H_7)_3$ substituents have been equalised by similarity restraints.

Other crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication (CCDC Nos.: **3d**, 273460; **5/6**, 273459). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat.): +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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