

Synthesis of [1'-(diphenylthiophosphoryl)ferrocenyl]ethyne and alkyne-metal complexes thereof

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Abstract

The novel functionalized ferrocene alkyne $\text{Ph}_2\text{P}(\text{S})\text{fcC}\equiv\text{CH}$ (**1**; fc = ferrocene-1,1'-diyl) was synthesized from $\text{Ph}_2\text{P}(\text{S})\text{fcCHO}$ (**6**) via the Corey–Fuchs reaction. It was further reacted with $\text{K}_2[\text{HgI}_4]/\text{KOH}$ to give mercury(II) acetylide $\text{Hg}\{\text{C}\equiv\text{CfcP}(\text{S})\text{Ph}_2\}_2$ (**8**), and with $[\text{Co}_2(\text{CO})_8]$ to afford the trimetallic Co_2Fe complex $[(\mu-\eta^2:\eta^2-1)\{\text{Co}(\text{CO})_3\}_2](\text{Co}-\text{Co})$ (**9**). All compounds were characterized by spectral methods (IR, NMR, and MS) and by combustion or high-resolution MS elemental analyses. In addition, the crystal structures of **1**, Ph_2PfcBr (**5**), **6**, $\text{Ph}_2\text{P}(\text{S})\text{fcCH}=\text{CBr}_2$ (**7**), and **9** were determined by single-crystal X-ray diffraction.

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1. Introduction

Ferrocene alkynes represent valuable ligands and building blocks for organometallic synthesis and material science [1]. The area of their possible application can be further widened by introducing one or more functional groups into their molecules. For instance, functionalized ferrocene alkynes have been utilized in the preparation of redox-active organometallic oligo- and polymers [2,3] and their precursors [4], and as precursors to materials with non-linear optical properties [5] and nucleobase receptors [6]. Besides, ferrocene alkynes modified with polar groups hold great potential for the synthesis of other ferrocene derivatives [7]. In view of these facts, it appears somewhat surprising that there was only little effort devoted to the synthesis of ferrocene alkynes substituted with standard donor groups (e.g., N-donor groups and phosphines) and their coordination behaviour [8]. In an effort to extend the chemistry of ferrocene alkynes modified with potentially coordinating groups, we decided to study [1'-(diphenylthiophosphoryl)ferrocenyl]ethyne, $\text{Ph}_2\text{P}(\text{S})\text{fcC}\equiv\text{CH}$ (**1**;

fc = ferrocene-1,1'-diyl). This contribution deals with the synthesis and coordination behaviour towards selected metals of this 'semi-masked' phosphinoalkyne.

2. Results and discussion

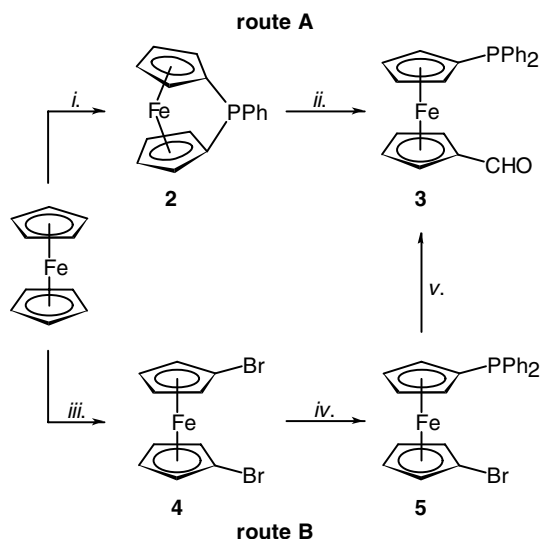
2.1. Synthesis of the ligand **1**

For the preparation of alkyne **1**, we made use of the known precursor 1'-(diphenylphosphino)ferrocenecarboxaldehyde (**3**). This compound, which was originally prepared by stepwise metallation/functionalization of 1,1'-bis(tributylstannyl)ferrocene [9], is more conveniently obtained from ring-opening of 1-phenyl-[1]-phosphaferrocenophane (**2**) with phenyl lithium and quenching the lithiated intermediate with *N,N*-dimethylformamide (Scheme 1, route A) [10] or, alternatively, by sequential lithiation/functionalization of 1,1'-dibromoferrocene (route B) [11].

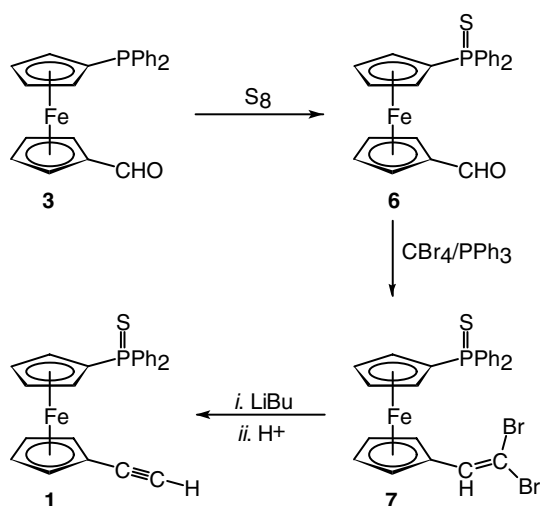
Aldehyde **3** was reacted with elemental sulfur to give the corresponding phosphine sulphide **6**, which was subsequently converted to the desired alkyne **1** by applying the Corey–Fuchs methodology [12] (Scheme 2). Aldehyde **6** was first reacted with $\text{CBr}_4/\text{PPh}_3$ mixture to give 1'-(diphenylthiophosphoryl)-1-(2,2-dibromovinyl)ferrocene (**7**).

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Scheme 1. Synthetic routes to (phosphino)aldehyde **3**. Legend: (i) 1. LiBu/TMEDA, 2. PhPCl₂. (ii) 1. LiPh, 2. Me₂NCHO. (iii) 1. LiBu/TMEDA, 2. 1,2-C₂F₄Br₂ (or C₂Cl₄Br₂). (iv) 1. LiBu, 2. PhPCl₂. (v) 1. LiBu, 2. Me₂NCHO; TMEDA = *N,N,N',N'*-tetramethyl-1,2-diaminoethane.



Scheme 2. The synthesis of alkyne **1**.

A subsequent eliminative dehalogenation of the latter compound with butyl lithium followed by aqueous work-up and crystallization gave alkyne **1** as an air-stable, orange crystalline solid in 60% overall yield with respect to **3**.

All new compounds were characterized by standard spectral methods (NMR, IR, and MS) and gave correct elemental analyses. In addition, the solid-state structures of **1** and **5–7** were determined by single-crystal X-diffraction analysis.

2.2. Crystal structures of **1** and **5–7**

Views of the molecular structures of **1** and **5–7** are shown in Figs. 1–4 together with the relevant geometric data. Compounds **1** and **6** crystallize with two molecules within

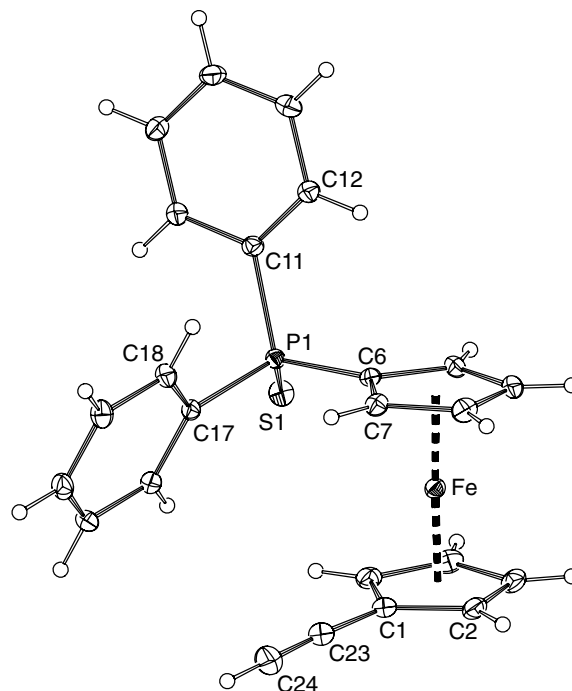


Fig. 1. View of molecule **1** in the structure of alkyne **1**. Displacement ellipsoids are shown at 30% probability level. Note. Atom-labelling scheme for molecule **2** is similar: the respective atom labels are obtained by adding 30 the respective atom label in molecule **1**. Selected geometric data; molecule **1**: Fe(1)–Cg(1) 1.6492(9), Fe(1)–Cg(2) 1.6394(9), P(1)–S(1) 1.9543(7), P(1)–C(6) 1.790(2), P(1)–C(11) 1.817(2), P(1)–C(17) 1.812(2), C(1)–C(23) 1.432(3), C(23)–C(24) 1.185(3) Å, ∠Cp1,Cp2 2.2(1), C(1)–C(23)–C(24) 176.2(2)°; molecule **2**: Fe(2)–Cg(3) 1.6514(9), Fe(2)–Cg(4) 1.6406(9), P(2)–S(2) 1.9531(7), P(2)–C(36) 1.792(2), P(2)–C(41) 1.821(2), P(2)–C(47) 1.812(2), C(31)–C(53) 1.431(3), C(53)–C(54) 1.181(3) Å, ∠Cp3,Cp4 0.5(1), C(31)–C(53)–C(54) 175.6(2)°. Definition of the ring planes: Cp1: C(1–5), Cp2: C(6–10); C(31–35), Cp2: C(36–40); Cg(1–4) are the respective ring centroids.

the asymmetric unit. In both cases, however, the independent molecules are practically identical, showing only minor conformational differences in the pairs (**1** in the conformation of the ferrocene unit and the phosphorus substituent while **6** only very slightly in the orientation of the phenyl rings) [13].

The structures corroborate the expected structures and their geometric parameters compare favourably with those in the related, structurally characterized compounds [14]. For instance, the geometry of the alkynyl moiety in **1** corresponds nicely to that in (ethynyl)ferrocene [15], the C–Br bond length in **5** is very similar to those in, e.g., 1-bromo-1'-(2-chloroethen-1-yl)ferrocene (1.887 Å [16]) and 1,1'-dibromoferrocene (1.866 and 1.882 Å [17]), whereas the molecular structure of aldehyde **6** differs only marginally from that of its phosphane precursor **3** (C=O 1.213 Å). Notably, the carbonyl group in **6** is twisted from a position coplanar with its parent cyclopentadienyl ring, the deviation from the cyclopentadienyl plane being higher for the carbonyl carbon than for the oxygen atom (cf. perpendicular distances from the least-squares cyclopentadienyl planes; molecule **1**: C(23) 0.105(2) and O(1) 0.042(2) Å;

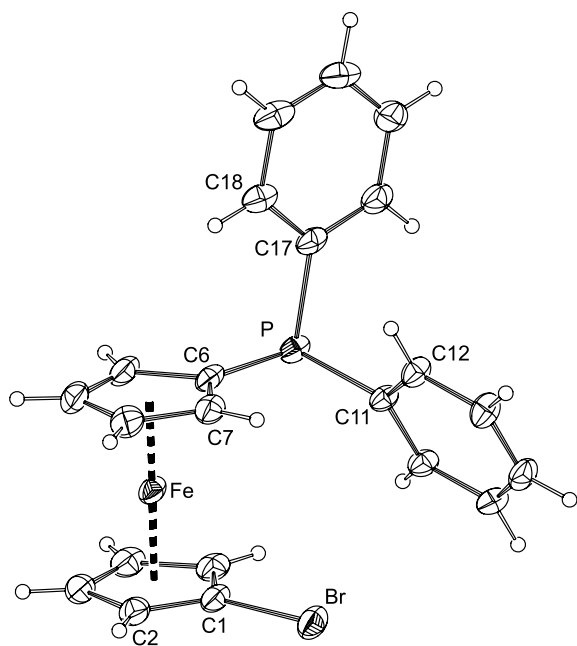


Fig. 2. Molecular structure of **5**. Displacement ellipsoids are scaled to the 30% probability level. Selected geometric data: Fe–Cg(1) 1.647(2), Fe–Cg(2) 1.642(2), C(1)–Br 1.883(4), P–C(6) 1.813(4), P–C(11) 1.833(4), P–C(17) 1.839(4) Å; \angle Cp1,Cp2 0.6(2)° (the ring planes are defined as for **1**, see Fig. 1).

molecule **2**: C(53) $-0.116(2)$ and O(2) $-0.025(2)$ Å). Likewise, the dibromovinyl group in **7** is rotated with respect to the adjacent cyclopentadienyl ring at the dihedral angle of the {C(23)C(24)Br(1)Br(2)} and Cp1 least-square planes of $29.6(2)^\circ$. However, the dibromovinyl group itself is almost perfectly planar and its overall geometry matches that in 1,1-dibromo-2-[3,5-bis(benzyloxy)phenyl]ethene [18].

A noteworthy feature of the whole series is the similarity of the overall molecular arrangement (Scheme 3). Ferrocene units in all molecules (**1**, **5**–**7**) show well balanced Fe–Cg(1,2) distances (relative differences are lower than 1%) and negligible tilts of the cyclopentadienyl rings (cf. the maximum tilt angle of 3.1° for **6**, molecule **2**). As indicated by the torsion angle C(1)–Cg(1)–Cg(2)–C(6) (τ), all compounds adopt similar conformations at the ferrocene unit; **1**: $\tau = 78.5(2)^\circ$ and $-73.7(1)^\circ$ (two independent molecules), **5**: $\tau = 70.7(3)^\circ$, **6**: $\tau = -75.0(1)^\circ$ and $77.3(1)^\circ$ (two symmetrically non-equivalent molecules), and **7**: $\tau = 66.0(2)^\circ$. The τ angles are scattered around the value characteristic for the ideal *syn*-eclipsed conformation ($\tau = 72^\circ$). In addition, all compounds have similarly oriented phosphorus groups. The Ph₂P(S) moieties, where E is sulfur atom (**1**, **6**, and **7**) or lone electron pair (**5**), are oriented so that one phenyl ring is directed outwards the ferrocene unit with the pivotal C(fc)–C(Ph¹) bond practically parallel to the axis of the ferrocene framework whilst the E-substituent and the other phenyl ring point towards it with the ferrocene axis approximately bisecting the E–P–C(Ph²) angle. Moreover, the second substituent at the ferrocene unit (X = C \equiv CH, Br, CHO, and CH=CBr₂) is always located at the side of the phenyl group. Such an arrangement leads to relatively com-

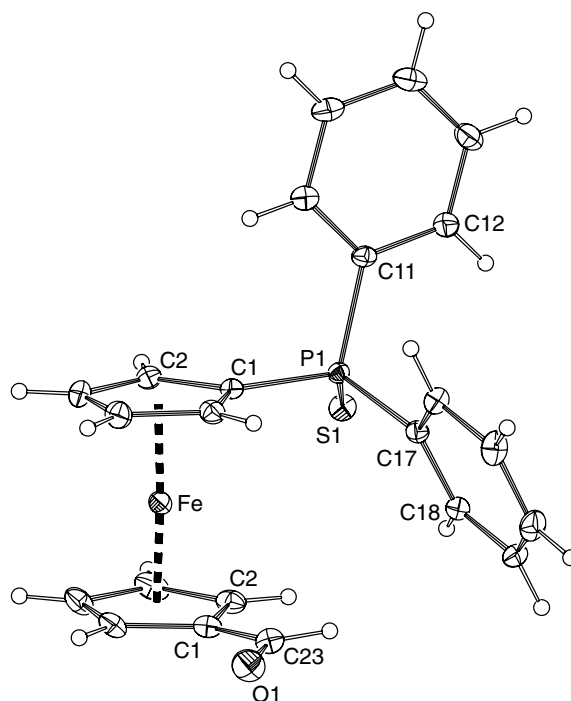


Fig. 3. A view of molecule **1** in the structure of **6** showing displacement ellipsoids with 30% probability. Molecule **2** is practically identical; atom labels for molecule **2** are obtained by adding 30 to the respective atom label in molecule **1** (except for Fe(2), P(2), and S(2)). Selected geometric data; molecule **1**: Fe(1)–Cg(1) 1.6530(9), Fe(1)–Cg(2) 1.6450(9), P(1)–S(1) 1.9506(7), P(1)–C(6) 1.793(2), P(1)–C(11) 1.816(2), P(1)–C(17) 1.818(2), C(1)–C(23) 1.452(3), C(23)–O(1) 1.217(3) Å, \angle Cp1,Cp2 2.2(1), C(1)–C(23)–O(1) $124.1(2)^\circ$; molecule **2**: Fe(2)–Cg(3) 1.6474(9), Fe(2)–Cg(4) 1.6485(9), P(2)–S(2) 1.9474(7), P(2)–C(36) 1.792(2), P(2)–C(41) 1.811(2), P(2)–C(47) 1.818(2), C(31)–C(53) 1.453(3), C(53)–O(2) 1.216(3) Å, \angle Cp3,Cp4 3.1(1), C(31)–C(53)–O(2) $125.4(2)^\circ$ (the ring planes are defined as for **1**, see Fig. 1).

pact (though perhaps sterically congested) structures and my thus facilitate the crystal assembly that, due to a lack of stronger intermolecular interactions, seems to be dictated largely by dipolar interactions and intermolecular forces at the van der Waals level (with occasional support from the weak hydrogen bonds, e.g., C–H \cdots S/O).

2.3. Preparation of complexes

Similarly to simple alkynes [19], ethanol–acetone solution of alkyne **1** reacts smoothly with alkalic solution of potassium tetraiodomercurate(II) to give the appropriate mercury(II) acetylide **8** in good yield (Scheme 4). Unfortunately, the crystallized acetylide is only sparingly soluble in common organic solvents which makes it impractical for further synthetic utilization.

The compound was characterized by spectral methods and elemental analysis. Its NMR spectra are in accordance with the formulation, showing signals due Ph₂P(S)-substituted ferrocene framework. The σ -coordination of the triple bond is clearly reflected by an absence of the signal due to the terminal \equiv CH group (¹H NMR), and further by changes in the region of triple bond C–13 resonances:

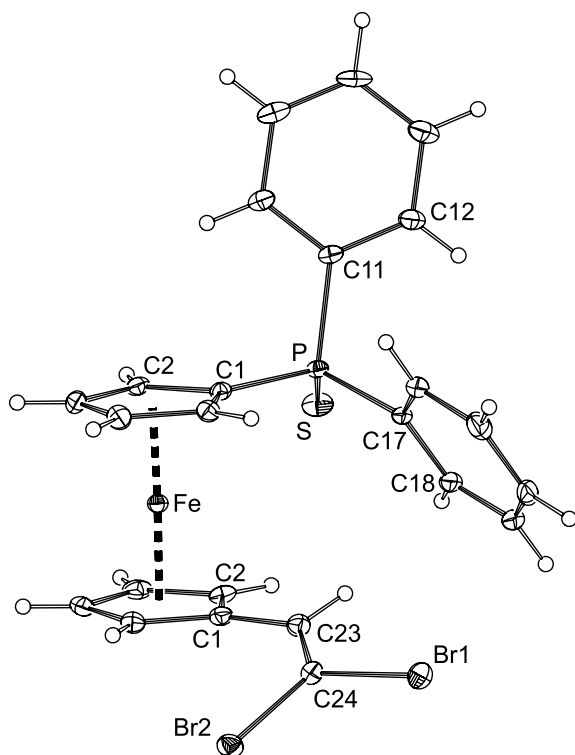
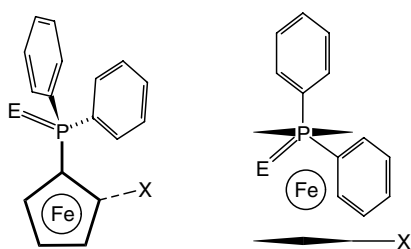
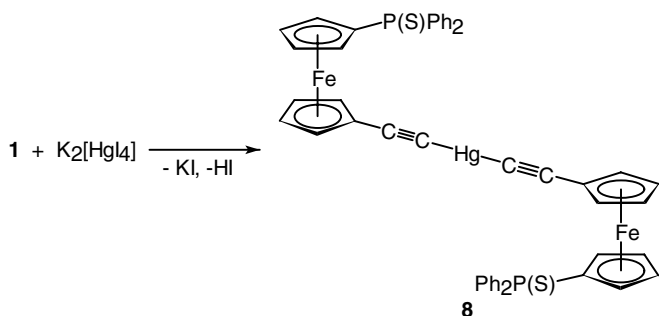


Fig. 4. Molecular structure of **7** showing the displacement ellipsoids at the 30% probability level. Selected geometric data: Fe–Cg(1) 1.649(2), Fe–Cg(2) 1.641(2), C(24)–Br(1) 1.891(3), C(24)–Br(2) 1.893(3), P–S 1.955(1), P–C(6) 1.788(3), P–C(11) 1.819(3), P–C(17) 1.812(3), C(1)–C(23) 1.460(4), C(23)–C(24) 1.322(4) Å; \angle Cp1,Cp2 1.6(2), C(1)–C(23)–C(24) 129.0(3), C(23)–C(24)–Br(1) 120.9(2), C(23)–C(24)–Br(2) 124.9(2), Br(1)–C(24)–Br(2) 114.2(2)° (for the definition of the ring planes see Fig. 1).



Scheme 3. A schematic drawing of the molecular conformation adopted by **1** and **5–7** in the solid state as viewed along (left) and perpendicular (right) to the axis of the ferrocene unit.



Scheme 4.

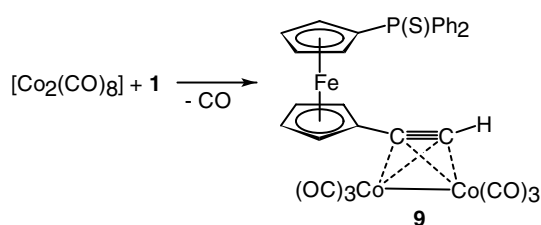
whereas the C^B is influenced only marginally, the $\equiv CH$ resonance is replaced with a signal of the mercury-bonded carbon (C^A) at lower field. In IR spectrum, the $\nu(C\equiv C)$ stretching vibration of **8** appears as a composite band, shifted by around 50 cm^{-1} to higher energies as compared with the parent alkyne.

Alkyne **1** also reacted smoothly with one-molar equivalent of $[\text{Co}_2(\text{CO})_8]$ in benzene at room temperature to give $(\mu\text{-alkyne})\text{hexacarbonyldicobalt}$ complex **9** as a brown dichroic crystalline solid in a 88% yield after chromatographic purification (Scheme 5). A comparison of the spectral data (NMR and IR) obtained for **9** with those reported for similar complexes [20] as well as identical δ_P values for **1** and **8** indicate that even in this case the phosphine sulphide moiety remains uncoordinated. The $\text{CH}[\text{Co}]$ signal in ^1H NMR spectrum of **8** appears at δ_H 6.03 (cf. δ_H 6.27 for the analogue without the phosphorus substituent, $[(\mu\text{-}\eta^2\text{-}\eta^2\text{-FeCCH})\{\text{Co}(\text{CO})_3\}_2(\text{Co-Co})$ (**10**) [20a]), while the CO resonance in ^{13}C NMR spectrum is observed at a slightly higher field as compared to the same reference compound (δ_C 199 and 203, respectively [20e]). The FAB mass spectrum of **9** shows the molecular ion $[\text{M}+\text{H}]^+$ and fragments resulting from successive loss of the carbonyl ligands.

Crystallization of **9** from toluene to hexane gave single crystals suitable for X-ray diffraction analysis. The molecular structure is depicted in Fig. 5 and the relevant geometric parameters are given in Table 1. The geometry of the alkyne-bridged $\text{Co}_2(\text{CO})_6$ moiety in **9** compares favourably with those in other structurally characterized dicobalt hexacarbonyl complexes featuring ferrocene alkynes [20b,20d,20e], particularly, with **10** [21].

The coordination of **1** leads to an elongation of the triple bond, consistent with donation from bonding π -electron systems. Furthermore, the loss of triple bond character and rehybridization is reflected by the bond lengths and angles at the vertexes of the dicobaltatetrahedrane (Table 1; see also the torsion angle C(1)–C(23)–C(24)–H(24) of $-15(3)^\circ$). The Co_2C_2 core is slightly asymmetric (less than in **10**), showing somewhat varying Co–C bond lengths (the Co(2)–C(23) bond is by ca. 0.04 Å shorter than the remaining three bonds).

The ferrocene unit in **9** is rotated with respect to the Co_2C_2 framework so that the dihedral angle subtended by the $\{\text{Co}(1), \text{C}(23), \text{C}(24)\}$ and $\{\text{Co}(1), \text{C}(23), \text{C}(24)\}$ planes and the Cp1 ring (see Fig. 5) are $14.9(2)^\circ$ and



Scheme 5.

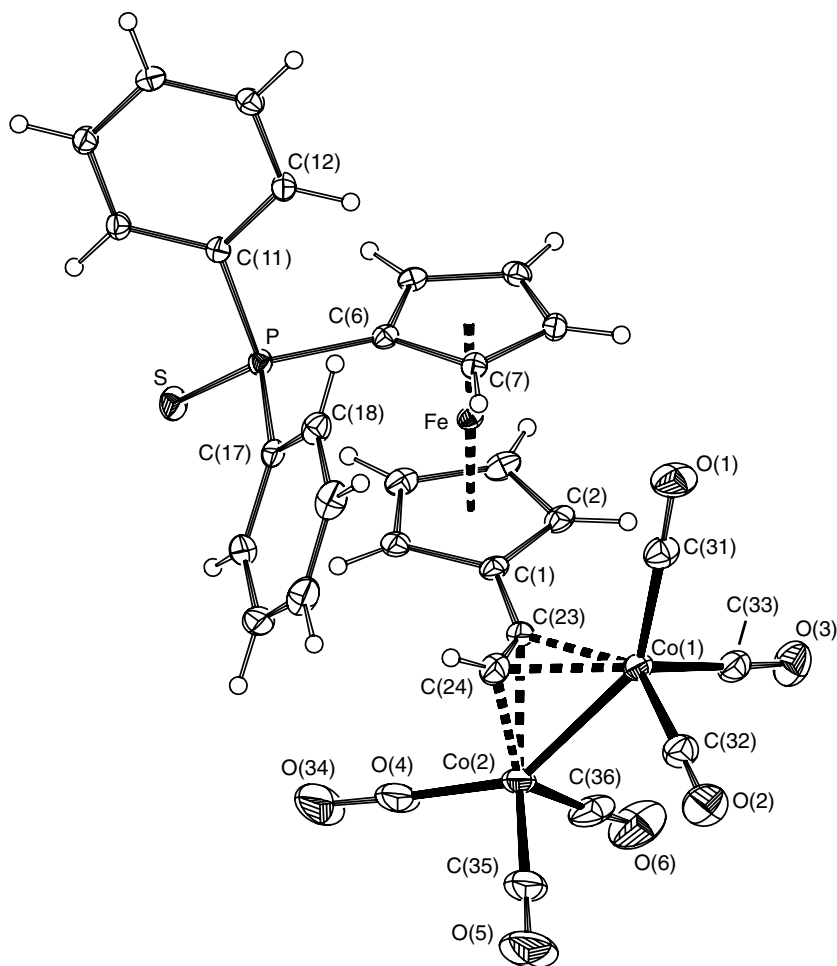
Fig. 5. Molecular structure of **9**. Displacement ellipsoids are scaled to the 30% probability level.

Table 1

Selected distances and angles for **9** (in Å and °)^a

Co(1)–Co(2)	2.4633(6)	C(23)–C(24)	1.332(4)
Co(1)–C(23)	1.956(2)	C(24)–H(24)	0.99(3)
Co(2)–C(23)	1.994(2)	C(1)–C(23)	1.446(3)
Co(1)–C(24)	1.955(3)	P–S	1.9537(9)
Co(2)–C(24)	1.950(3)	P–C ^b	1.794(3)–1.822(3)
Co–C	1.784(5)–1.823(4)	Fe–Cg(1)	1.653(1)
C≡O	1.129(7)–1.141(4)	Fe–Cg(2)	1.648(1)
Co–C≡O	176.7(3)–178.3(3)	∠Cp1,Cp2	3.8(1)
Co(1)–Co(2)–C(23)	50.72(7)	Co(2)–Co(1)–C(23)	52.11(7)
C(23)–Co(1)–C(24)	39.8(1)	C(23)–Co(2)–C(24)	39.5(1)
Co(1)–Co(2)–C(24)	50.98(8)	Co(2)–Co(1)–C(24)	50.79(9)
Co(1)–C(23)–Co(2)	77.17(9)	Co(1)–C(24)–Co(2)	78.2(1)
Co(1)–C(23)–C(24)	70.1(2)	Co(2)–C(24)–C(23)	72.1(2)
Co(1)–C(24)–C(23)	70.1(2)	Co(2)–C(23)–C(24)	68.5(2)
C(1)–C(23)–C(24)	145.5(3)	S–P–C(6,11,17)	112.23(8)–115.44(8)
C(23)–C(24)–H(24)	144(2)	C–P–C ^c	103.6(1)–106.26(1)

^a Least-squares planes are defined as for **1**. See caption to Fig. 1.^b The range of P–C(6,11,17) bond lengths.^c The range of C(6)–P–C(11,17) and C(11)–P–C(17) angles.

80.5(2)°, respectively. Likewise, the C(23)–C(24) bond deviates from coplanarity with Cp1, intersecting the cyclopentadienyl plane at an angle of 14.5(2)°. The conformation of the disubstituted ferrocene moiety is close to *syn*-eclipsed

conformation ($\tau = -83.7(2)^\circ$), similar to **1** and the compounds mentioned above. However, even in **9**, there seems to be no steric congestion between the proximal, bulky substituents at the ferrocene skeleton.

3. Conclusions

Compound **1**, a new functionalized organometallic alkyne, was obtained in a good yield by conventional methods from Ph_2PfcCHO . Although its donor properties have been tested thus far only in σ -acetylide complex **8** and π -alkyne-bridged dicobalt carbonyl complex **9**, it is apparent that the presence of a relatively weakly coordinating thiosphosphoryl group (as compared to the corresponding phosphine) enables this compound to coordinate rather as a simple alkyne than a heterobifunctional donor.

4. Experimental

4.1. Materials and methods

Unless noted otherwise, the syntheses were performed under argon atmosphere and with an exclusion of the direct day light. Tetrahydrofuran (THF) was distilled from potassium-benzophenone ketyl. Toluene, diethyl ether and hexane were dried over potassium metal and distilled. Dichloromethane was dried with anhydrous potassium carbonate or distilled from calcium hydride. Other chemicals and solvents were used as received from commercial suppliers (Fluka, Aldrich; solvents from Lachema).

NMR spectra were measured on a Varian UNITY Inova 400 spectrometer (^1H , 399.95; ^{13}C , 100.58; ^{31}P , and 161.90 MHz) at 298 K. Chemical shifts (δ /ppm) are given relative to an internal tetramethylsilane (^1H and ^{13}C) or an external 85% aqueous H_3PO_4 (^{31}P). IR spectra were recorded on an FT IR Nicolet Magna 760 instrument in the range of 400–4000 cm^{-1} . Melting points were determined on a Kofler apparatus and are uncorrected.

4.2. Synthesis of $\text{Ph}_2\text{P}(S)\text{fcCHO}$ (**6**)

A mixture of aldehyde **3** (1.99 g, 5.0 mmol) and sulfur (0.19 g, 6.0 mmol) in toluene (50 ml) was gently refluxed for 1 h. The solids dissolved to give a clear solution, which was filtered while hot and crystallized at -18°C . The crystalline product was filtered off, washed thoroughly with hexane and dried in air. Evaporation of the mother liquor and crystallization from hot toluene followed by isolation as given above gave a second crop of **6**. Combined yield: 1.91 g (89%), red brown flakes.

M.p. $184\text{--}185^\circ\text{C}$ (ethyl acetate–hexane). ^1H NMR (CDCl_3): δ 4.54 (apparent q, 2H), 4.58–4.61 (m, 4H), 4.80 (apparent t, 2H) ($4\times \text{CH}$ of fc); 7.38–7.76 (m, 10H, PPh_2), 9.62 (s, 1H, CHO). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 71.36, 73.24 (d, $J_{\text{PC}} = 10$ Hz), 74.18 (d, $J_{\text{PC}} = 12$ Hz), 75.04 ($4\times \text{CH}$ of fc); ca. 77.49 (d, $^1J_{\text{PC}} \approx 95$ Hz, C–P of fc; the signal is obscured by the solvent resonance), 80.03 (C–CHO, fc), 128.40 (d, $J_{\text{PC}} = 13$ Hz), 131.54 (d, $J_{\text{PC}} = 3$ Hz), 131.56 (d, $J_{\text{PC}} = 10$ Hz) ($3\times \text{CH}$, Ph); 133.85 (d, $^1J_{\text{PC}} = 87$ Hz, C_{ipso} , Ph), 193.55 (CHO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 40.9 (s). EI MS: m/z (relative abundance)

431 (27), 430 (M^+ , 94), 402 ($[\text{M}-\text{CO}]^+$, 25), 338 (22), 337 ($[\text{M}-\text{C}_5\text{H}_4\text{CHO}]^+$, 100), 273 (10), 197 (5), 183 (9), 170 (9), 121 ($[\text{C}_5\text{H}_5\text{Fe}]^+$, 5), 56 (Fe, 8). IR (Nujol): ν/cm^{-1} $\nu(\text{C}=\text{O})$ 1679 (vs), 1661 (s); 1242 (s), 1172 (s), 1104 (s), 1032 (m), 1028 (m), 842 (s), 758 (s), 719 (vs), 696 (s), 657 (vs), 542 (s), 499 (s), 490 (s). Anal. Calc. for $\text{C}_{23}\text{H}_{19}\text{FeOPS}$ (430.29): C, 64.20; H, 4.45. Found: C, 64.03; H, 4.70%.

4.3. Synthesis of $\text{Ph}_2\text{P}(S)\text{fcCH}=\text{CBr}_2$ (**7**)

A solution of tetrabromomethane (3.33 g, 10 mmol in 10 mL of dichloromethane) was introduced slowly to an ice-cooled solution of aldehyde **6** (2.16 g, 5.0 mmol) and triphenylphosphane (5.25 g, 20 mmol) in dry dichloromethane (40 mL) with stirring. After the addition was completed (ca. 3 min), stirring was continued for another 20 min at 0°C . The reaction was terminated by adding a mixture of saturated aqueous NaHCO_3 solution (20 mL) and 30% hydrogen peroxide (3 mL) and stirring for 15 min. The organic layer was separated, washed with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ to remove unreacted hydrogen peroxide, and dried over MgSO_4 . The solution was mixed with alumina (grade for chromatography, Brockmann) and the mixture evaporated under reduced pressure (pre-adsorption). The solid was transferred onto a top of a short alumina column and eluted with diethyl ether (Note. Large amounts of the solvent are necessary for complete elution of the product which is only sparingly soluble in ether; triphenylphosphane oxide co-elutes). The yellow eluate was evaporated to dryness, taken up in chloroform (ca. 50 mL) and the solution evaporated again to leave a dark brown oil, which was immediately crystallized by addition of hot methanol (ca. 30 mL). The mixture was allowed to stand at 0°C overnight, the separated product was filtered off, washed with methanol and dried under vacuum. Yield of **7**: 2.45 g (83%), orange crystalline solid.

M.p. dec. above 155°C . ^1H NMR (CDCl_3): δ 4.31 (apparent t, 2H), 4.43 (apparent q, 2H), 4.54 (apparent q, 2H), 4.65 (apparent t, 2H) ($4\times \text{CH}$ of fc); 6.78 (s, 1H, $\text{CH}=\text{C}$), 7.38–7.77 (m, 10H, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 70.80, 71.33, 73.23 (d, $J_{\text{PC}} = 10$ Hz), 74.10 (d, $J_{\text{PC}} = 13$ Hz) ($4\times \text{CH}$, fc); 76.06 (d, $^1J_{\text{PC}} = 95$ Hz, C–P of fc), 81.01 (C– $\text{CH}=\text{C}$, fc), 85.01 ($=\text{CBr}_2$), 128.28 (d, $J_{\text{PC}} = 13$ Hz), 131.37 (d, $J_{\text{PC}} = 3$ Hz), 131.58 (d, $J_{\text{PC}} = 11$ Hz) ($3\times \text{CH}$, Ph); 134.27 (d, $^1J_{\text{PC}} = 87$ Hz, C_{ipso} , Ph), 134.35 ($=\text{CH}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 41.6 (s). EI MS: m/z (relative abundance) 588 (11), 586 (20) and 584 (11) (M^+); 507 (49) and 505 (48) ($[\text{M}-\text{Br}]^+$); 427 (14), $[\text{M}-2\text{Br}]^+$, 402 ($[\text{M}-\text{CHCBr}_2]^+$), 338 (22), 337 ($[\text{M}-\text{C}_5\text{H}_4\text{CHCBr}_2]^+$, 100), 294 (14), 293 (14), 273 (12), 226 (11), 185 (16), 183 (35), 171 (16), 170 (18), 121 (11), 89 (14), 56 (10). IR (Nujol): ν/cm^{-1} 1735 (m), 1173 (s), 1103 (s), 1036 (m), 841 (m), 825 (s), 760 (m), 715 (vs), 700 (m), 654 (vs), 542 (m), 501 (s), 488 (vs). Anal. Calc. for $\text{C}_{24}\text{H}_{19}\text{Br}_2\text{FePS}$ (589.11): C, 49.18; H, 3.27. Found: C, 48.89; H, 3.15%.

4.4. Synthesis of $\text{Ph}_2\text{P}(\text{S})\text{fcC}\equiv\text{CH}$ (**1**)

Butyl lithium in hexanes (4 mL 2.5 M, 10 mmol) was added to a solution of **7** (2.35 g, 4.0 mmol) in dry THF (40 mL) with stirring and cooling to -78°C . The mixture was stirred for 1 h at -78°C and then for 1 h with the cooling bath removed. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution and diluted with diethyl ether. Organic layer was separated, washed with the NH_4Cl solution and then dried over magnesium sulfate. The solvents were removed under reduced pressure yielding a rusty orange residue, which was extracted with hot ethyl acetate (100 mL). The extract was filtered and diluted with hexane (100 mL). A subsequent crystallization at -18°C gave **1** as orange needles, which were filtered off, washed with hexane and dried under vacuum. The mother liquor was evaporated and the residue crystallized in a similar manner (20 mL of each solvent) providing a second fraction of the product. Combined yield: 1.40 g (82%). The compound thus obtained tends to retain traces of ethyl acetate. The presence of the solvent in the bulk material was shown by IR and NMR spectra.

^1H NMR (CDCl_3): δ 2.62 (s, 1H, $\equiv\text{CH}$), 4.27 (apparent t, 2H), 4.42 (apparent t, 2H), 4.48 (apparent q, 2H), 4.54 (apparent q, 2H) ($4\times \text{CH}$ of fc); 7.38–7.46 (m, 10 H, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 65.38 ($\text{C}\equiv\text{CH}$), 71.37, 73.28, 74.35 (d, $J_{\text{PC}} = 12$ Hz) ($3\times \text{CH}$, fc); 74.45 ($\equiv\text{CH}$), 74.84 (d, $J_{\text{PC}} = 10$ Hz, CH, fc) 76.20 (d, $J_{\text{PC}} = 98$ Hz, C–P of fc), 81.15 ($\text{C}-\text{C}\equiv\text{CH}$, fc), 128.24 (d, $J_{\text{PC}} = 12$ Hz), 131.26 (d, $J_{\text{PC}} = 3$ Hz), 131.60 (d, $J_{\text{PC}} = 11$ Hz) ($3\times \text{CH}$, Ph); 134.29 (d, $J_{\text{PC}} = 87$ Hz, C_{ipso} , Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ +41.7 (s). EI-MS: m/z (relative abundance) 428 (8), 427 (23), 426 (M^+ , 82), 337 ($[\text{Ph}_2\text{P}(\text{S})\text{C}_5\text{H}_4\text{Fe}]^+$, 100), 335 (5), 237 (11), 226 (9), 197 (6), 183 (11), 171 (9), 170 (11), 56 (Fe^+ , 11). IR (Nujol): ν/cm^{-1} alkyne $\nu(\text{CH})$ 3290 (w); *3218 (w), $\nu(\text{C}\equiv\text{C})$ 2105 (w); $^*\nu(\text{C}=\text{O})$ 1733 (m), 1307 (m), 1194 (m), 1169 (s), 1154 (m), 1102 (s), *1035 (s), 1027 (s), 914 (m), 840 (s), 819 (s), 753 (s), 178 (vs), 694 (vs), 656 (vs), 627 (m), 614 (m), 566 (m), 543 (s), 526 (vs), 494 (vs), 482 (s), 448 (m), 435 (m); signals labelled with an asterisk are attributable to the residual ethyl acetate. Anal. Calc. for $\text{C}_{24}\text{H}_{19}\text{FePS} \cdot \frac{1}{3}\text{CH}_3\text{CO}_2\text{Et}$: C, 67.78; H, 4.79. Found: C, 67.80; H, 4.69%. HR MS (EI): Calc. for $\text{C}_{24}\text{H}_{19}^{56}\text{FePS}$: 426.0295, found 426.0311.

4.5. Synthesis of $\text{Hg}\{\text{CCfcP}(\text{S})\text{Ph}_2\}_2$ (**8**)

Mercury(II) chloride (68 mg, 0.25 mmol) and KI (249 mg, 1.5 mmol) were suspended in 5% aqueous KOH (5 mL) and the mixture was stirred until all solids dissolved. Then, a hot solution of **1** (85.5 mg, 0.20 mmol) in ethanol–acetone (1:1, 12 mL) was added, causing an immediate formation of an ochre precipitate. The mixture was stirred at room temperature for 30 min, the precipitated solid was filtered off, dried (at 60°C in air) and extracted

with chloroform (20 mL). The filtered orange extract was allowed to crystallize by diffusion of hexane vapours over several days. The solid product formed was filtered off, washed with hexane and dried under vacuum. Yield of **8**: 76 mg (72%), rusty orange microcrystalline solid. Note. The recrystallized product is only *very* poorly soluble in all common organic solvents (CH_2Cl_2 , CHCl_3 , acetone, methanol, etc.)

^1H NMR (CDCl_3): δ 4.28 (apparent t, 2 H), 4.44–4.48 (m, 4H), 4.55 (apparent q, 2H) ($4\times \text{CH}$ of fc); 7.391–7.76 (m, 10H, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 65.60 ($\text{C}\equiv\text{C}$), 71.35, 73.65, 74.72, 74.83 (d, $J_{\text{PC}} = 3$ Hz) ($4\times \text{CH}$, fc); 103.88, 117.97 ($\text{C}\equiv\text{C}$ and $\text{C}-\text{C}\equiv\text{C}$ of fc), 128.30 (d, $J_{\text{PC}} = 12$ Hz), 131.29 (d, $J_{\text{PC}} = 3$ Hz), 131.72 (d, $J_{\text{PC}} = 11$ Hz) ($3\times \text{CH}$, Ph); 134.45 (d, $J_{\text{PC}} = 87$ Hz, C_{ipso} , Ph); the C–P signal at fc is obscured by the solvent resonance. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ +41.7 (s). FAB MS: m/z 1052 (M^+), 426 ($[\text{Ph}_2\text{P}(\text{S})\text{fcC}\equiv\text{CH}]^+$). IR (Nujol): ν/cm^{-1} $\nu(\text{C}\equiv\text{C})$ 2163 (vw), 2147 (w), 2122 (vw); 1306 (m), 1167 (s), 1101 (s), 1034 (m), 1023 (m), 997 (w), 920 (m), 845 (m), 831 (m), 760 (m), 746 (m), 712 (vs), 694 (s), 649 (vs), 627 (m), 614 (m), 541 (s), 486 (s), 467 (s), 435 (s). Anal. Calc. for $\text{C}_3\text{H}_3\text{Fe}_2\text{HgP}_2\text{S}_2 \cdot 0.3 \text{CHCl}_3$: C, 53.37; H, 3.37. Found: C, 53.39; H, 3.40%.

4.6. Synthesis of $[\text{Co}_2(\text{CO})_6(\mu-\eta^2:\eta^2-\text{I})]$ (**9**)

Dicobalt octacarbonyl (70 mg, 0.20 mmol) and **1** (87 mg, 0.20 mmol) were dissolved in benzene (5 mL) and the reaction mixture was stirred overnight at room temperature. The volume of the reaction solution was reduced under vacuum to ca. 2 mL and the residue transferred onto a top of a chromatographic column filled with silica gel in diethyl ether–hexane (1:2). Eluting with the same solvent mixture provided firstly a minor band containing traces of unreacted alkyne, and then major, brownish band of the product. The latter was collected and evaporated to give **9** as a brown microcrystalline solid showing green-red dichroism (126 mg, 88%).

^1H NMR (CDCl_3): δ 4.31, 4.34 ($2\times$ apparent t, 2H), 4.38, 4.48 ($2\times$ apparent q, 2H) ($4\times \text{CH}$ of fc); 6.03 (s, 1H, $\text{CH}[\text{Co}]$), 7.41–7.77 (m, 10H, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 71.32, 71.89, 73.82 (d, $J_{\text{PC}} = 10$ Hz), 74.46 (d, $J_{\text{PC}} = 12$ Hz) ($4\times \text{CH}$, fc); 75.72 ($\text{CH}[\text{Co}]$), 86.25 ($\text{C}-\text{CC}[\text{Co}]$ of fc), 88.98 ($\text{C}[\text{Co}]$), 128.30 (d, $J_{\text{PC}} = 13$ Hz), 131.31 (d, $J_{\text{PC}} = 3$ Hz), 131.65 (d, $J_{\text{PC}} = 11$ Hz) ($3\times \text{CH}$, Ph); 134.43 (d, $J_{\text{PC}} = 87$ Hz, C_{ipso} , Ph), 199.44 (br, CO); the C–P signal at fc probably coincides with the solvent resonance. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ +41.7 (s). FAB MS: m/z 713 ($[\text{M}+\text{H}]^+$), 657 ($[\text{M}+\text{H}-2\text{CO}]^+$), 628 ($[\text{M}-3\text{CO}]^+$), 572 ($[\text{M}-5\text{CO}]^+$), 544 ($[\text{M}-6\text{CO}]^+$). IR (Nujol): ν/cm^{-1} $\nu(\text{C}\equiv\text{O})$ 2091 (vs), 2055 (vs), 2033 (vs), 2010 (vs), 1996 (vs); 1170 (m), 1099 (m), 1034 (w), 1026 (m), 826 (m), 752 (m), 716 (s), 694 (s), 656 (s), 512 (s), 490 (s), 455 (m). HR MS Calc. for $\text{C}_{30}\text{H}_{20}\text{Co}_2^{56}\text{FeO}_6\text{PS}$ ($[\text{M}+\text{H}]^+$): 712.8732. Found: 712.8752.

Table 2

Crystallographic data, data collection and structure refinement parameters for **1**, **5**, **6**, **7** and **9**

Compound	1	5	6	7	9
Formula	C ₂₄ H ₁₉ FePS	C ₂₂ H ₁₈ BrFeP	C ₂₃ H ₁₉ FeOPS	C ₂₄ H ₁₉ Br ₂ FePS	C ₃₀ H ₁₉ Co ₂ FeO ₆ PS
<i>M</i> (g mol ^{−1})	426.27	449.09	430.26	586.09	712.19
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> (Å)	13.2162(2)	8.7250(2)	13.3420(1)	13.0769(2)	7.5876(2)
<i>b</i> (Å)	17.3084(3)	17.0619(5)	17.4117(2)	9.3115(1)	8.8658(2)
<i>c</i> (Å)	17.2149(3)	13.1367(3)	17.0096(2)	18.2543(3)	22.0057(5)
α (°)					97.941(2)
β (°)	101.901(1)	108.136(2)	102.0403(5)	101.9585(6)	95.305(2)
γ (°)					98.614(1)
<i>V</i> (Å ³)	3853.3(1)	1858.44(8)	3864.52(7)	2174.51(5)	1439.88(6)
<i>Z</i>	8	4	8	4	2
<i>D</i> (g mL ^{−1})	1.470	1.605	1.479	1.790	1.643
μ (Mo K α) (mm ^{−1})	0.980	3.049	0.981	4.547	1.806
<i>T</i> ^a	0.664–0.960	0.526–0.652	— ^c	0.355–0.454	0.664–0.939
Diffns total	66940	34315	54363	29273	27361
Unique/obsd ^b diffns	8778/6886	4264/3236	8868/7073	4967/4639	6615/5162
<i>R</i> _{int} (%) ^c	5.26	5.53	3.60	4.24	4.10
No. of params	487	226	487	262	374
<i>R</i> obsd diffns (%) ^d	3.22	4.07	3.22	3.32	3.53
<i>R</i> , <i>wR</i> all data (%) ^d	4.81, 8.56	6.17, 10.56	4.65, 9.76	3.66, 785	5.52, 8.34
$\Delta\rho$ (e Å ^{−3})	0.42, −0.44	0.66, −0.80	0.39, −0.50	0.46, −0.54	0.42, −0.83
CCDC ref. no.	287289	287286	287287	287288	287290

^a The range of transmission coefficients.^b Diffractions with $I_o > 2\sigma(I_o)$.^c $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum F_o^2$, where $F_o^2(\text{mean})$ is the average intensity for symmetry equivalent diffractions.^d $R = \sum |F_o| - |F_c| / \sum |F_o|$, $wR = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$.^e Not corrected.

4.7. X-ray crystallography

Single crystals suitable for X-ray diffraction analysis were selected directly from the reaction batch (**1**: orange plate, $0.03 \times 0.30 \times 0.50$ mm³) or obtained by recrystallization of the bulk material from diethyl ether–hexane (**5**: orange brown prism, $0.15 \times 0.20 \times 0.25$ mm³), ethylacetate–hexane (**6**: red brown prism, $0.13 \times 0.25 \times 0.40$ mm³; **7**: rusty brown prism, $0.23 \times 0.28 \times 0.28$ mm³) and from toluene–hexane (**9**: brown plate, $0.03 \times 0.15 \times 0.25$ mm³).

Full-set diffraction data ($\pm h \pm k \pm l$, $2\theta \leq 55^\circ$) were collected on a Nonius Kappa CCD diffractometer equipped with Cryostream Cooler (Oxford Cryosystems) at 150(2) K using graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) and analyzed with the HKL program package [22]. If appropriate, the data were corrected for absorption by using an empirical multiscan method (SORTAV routine [23]; **5** and **7**) and gaussian correction procedure (**1** and **9**) included in the diffractometer software.

The structures were solved by direct methods (SIR-97 [24]) and subsequently refined by weighted full-matrix least squares on F^2 (SHELXL-97 [25]). The non-hydrogen atoms were refined with anisotropic displacement parameters. The H(24) atom in **9** was identified on the difference electron density map and its coordinates and isotropic displacement parameter were refined without constraints. All other hydrogen atoms were included in the calculated positions [C–H bond lengths: 0.93 (alkene, alkyne and aro-

matic CH groups, and CHO), 0.97 (methylene) and 0.96 (methyl) Å] and assigned $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. Final geometric calculations were carried out with a recent version of PLATON program [26].

Crystallographic data (excluding structure factors) have been deposited with CCDC (see Table 2 for the deposition numbers). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk, or via the internet at www.ccdc.cam.ac.uk.

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