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Diiron Alkyne Complexes

Construction of a Functionalized Selenophene-Allylidene Ligand via Alkyne Double Action at a Diiron Complex

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Abstract: The diiron μ-vinyliminium compounds $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C^3HC^2HC^1NMe(R)\}]CF_3SO_3$ (R = Me, **2a**; R = Xyl = 2,6-$C_6H_3Me_2$, **2b**; Cp = η^5-C_5H_5) reacted with grey selenium, in the presence of sodium methoxide, to give the corresponding Se-functionalized derivatives $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C^3HC^2(Se)C^1NMe(R)\}]$, **3a**–**b**, in ca. 50 % yields. The monoiron zwitterionic complex $[FeCp(CO)\{SeC^1(NMe_2)C^2HC^3H\}]$, **4**, was obtained as a side-product (31 %) of the reaction leading to **3a**. The treatment of **3b** with S_8/NaOMe afforded the 2-ferrathiophene $[FeCp(CO)\{SC^3HC^2HC^1NMe(Xyl)\}]$, **5**, in 49 % yield. The straightforward reactions of **3a** with a two-fold excess of dialkylacetylenedicarboxylates led to functionalized 3-aminoselenophenes appended to the diiron frame through a bridging allylidene ligand, $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C^7(CO_2R)\text{-}C^6(CO_2R)C^3HC^2SeC^5(CO_2R)C^4(CO_2R)C^1(NMe_2)\}]$ (R = Me, **6a**; R = Et, **6b**; R = *t*Bu, **6c**), in approximately 50 % yields. The synthesis of **6a**–**c** is the result of two distinct modes of reactivity exhibited by the alkyne reactant in one pot, i.e. 1,3-dipolar cycloaddition to C and Se atoms and insertion into Fe-μ-alkylidene. All the products were characterized by means of elemental analysis, IR and multinuclear NMR spectroscopy, and the molecular structure of **6a** was elucidated by a single-crystal X-ray diffraction study.

Introduction

Alkynes are versatile reagents in a multitude of valuable organic transformations,[1] some of them being established even on an industrial scale, such as the Dötz reaction,[2] the alkyne metathesis[3] and the alkyne cyclotrimerization.[4] Alkynes are prone to cyclization reactions, and in particular 1,3-dipolar cycloadditions to various substrates provide straightforward access to a range of heterocyclic structures with possible pharmaceutical applications.[5] The insertion of an alkyne molecule into a metal-carbon bond represents the key step of useful metal-catalysed syntheses,[6] and is a viable procedure to grow organometallic fragments. This kind of reaction has been described with reference to a variety of monometal species and ligands, including alkyls,[7] aryls,[8] vinyls,[9] and alkylidenes.[10] Two adjacent metal centres are able to provide cooperative effects in reactivity, thus favouring the insertion of alkynes into the bond between one metal and a suitable bridging ligand;[11] in this regard, a wide number of reactions have been reported involving, *inter alia*, bridging carbonyl,[12] thiocarbonyl,[13] isocyanide,[14] carbyne,[15] and carbido units.[16]

The insertion of (electron-poor) alkynes into metal-μ-alkylidene bonds aroused attention due to its relevance to the C–C chain growth in the Fischer–Tropsch process,[17] and has been documented with complexes based on the $[M_2Cp_2(CO)_2]$ skeleton (M = Fe, Ru),[18] and Rh–Ru,[19] Rh–Os[20] and Ir–Os systems.[21] In general, a vacant metal site is necessary to allow alkyne entrance through preliminary η^2-coordination; both chemical and photolytic methods may be employed to this purpose,[19,20] except in the rare case that cleavage of the metal–metal linkage is feasible.[21]

The interest of some of us in the construction of functionalized organometallic structures, since almost 20 years ago, has been focused on diiron complexes,[11c,22] which constitute a matter of growing interest for several reasons. First, the dinuclear system offers the opportunity for reactivity patterns which are not available to similar monoiron species, as also mentioned above. In addition, iron as element is substantially nontoxic and earth abundant, and thus an appealing candidate to develop new sustainable metal-directed synthetic routes and metal complexes for medicinal applications.[23]

In the course of our research, we previously described the sequential assembly of small molecular units to afford diiron complexes with a bridging-coordinated Se-functionalized ligand (**A**); this latter is firmly anchored to the [Fe–Fe] frame through a C_3 chain featured by an extensive charge delocalization and described by means of three main resonance forms (see Scheme 1).[24] However, the C^3 carbon clearly manifests alkylidene character, according to X-ray (equidistance between the two iron atoms, as determined for R = Xyl, R′ = Me) and ^{13}C NMR (typical low-field resonance in the range 180–200 ppm) data. Compounds of type **A** exhibit a rich chemistry which is

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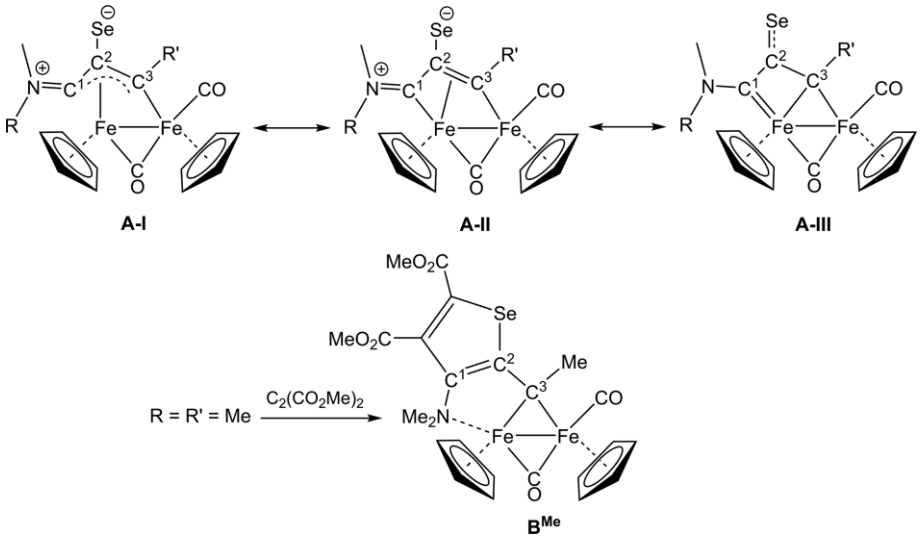

Scheme 1. Resonance forms representing a bridging Se-derivatized C_3 ligand (**A-I**: allylidene; **A-II**: vinyliminium; **A-III**: bis-alkylidene), and alkyne cycloaddition to form a μ-alkylidene-selenophene derivative ($\mathbf{B^{Me}}$).[26] R = Me or Xyl = 2,6-$C_6H_3Me_2$; R′ = alkyl, aryl or CO_2Me.

essentially related to the zwitterionic nature of the bridging ligand.[24b,25] In particular, a peculiar combination of substituents enables 1,3-dipolar cycloaddition by dimethylacetylenedicarboxylate, leading to the selenophene-substituted μ-alkylidene species $\mathbf{B^{Me}}$ (Scheme 1);[26] note that the use of a large excess (up to 10 equiv.) of alkyne does not modify this outcome. In the framework of our recent interest in the development of diiron complexes with bridging C_3 ligands as potential anticancer drugs[27] and on account of the relevance of the selenophene moiety in medicinal chemistry,[28] we came interested in preparing some new simple selenophene derivatives analogous to $\mathbf{B^{Me}}$ for biological studies. Surprisingly, we observed that the Me/H replacement (R′) resulted in a dramatic change of the reactivity of compounds **A** with dialkylacetylenedicarboxylates, activating at the same time two distinct reactivity pathways and thus providing access to a novel class of highly functionalized hydrocarbyl ligands.

Results and Discussion

The previously reported diiron vinyliminium compounds **2a**–**b** were prepared from the respective μ-aminocarbyne precursors, **1a**–**b**, via removal of one carbonyl ligand and subsequent acetylene insertion into iron–carbyne bond, using an optimized procedure (see Scheme 2 and Experimental for details). The reaction of **2a**–**b** with an excess of sodium methoxide, in tetrahydrofuran in the presence of grey selenium, proceeded with dehydrogenative selanylation affording the new selenium-functionalized complexes **3a**–**b**,[24b,25] in approximately 50 % yields (Scheme 2). The methoxide presumably plays the role of a reducing agent towards **2a**–**b**, thus generating neutral radical derivatives undergoing H/Se exchange.[29]

Compound **3b** was isolated after alumina chromatography as a stable solid under N_2 atmosphere, and fully characterized; conversely, **3a** revealed rather unstable especially in solution for prolonged times, hence its characterization relied on elemental analysis, IR and ^{1}H NMR spectroscopy only. The IR spectra of **3a**–**b** in dichloromethane exhibit two bands due to the carbonyl ligands at ca. 1970 and 1790 cm^{-1}, and an additional absorption accounting for the substantial double bond nature of C^1–N (e.g. at 1603 cm^{-1} in the case of **3b**). The NMR spectra of **3a**–**b** (in $CDCl_3$) display diagnostic low field resonances due to the alkylidene {C^3H} unit [e.g. in the case of **3b**: $\delta(^1H)$ = 12.42 ppm, $\delta(^{13}C)$ = 186.7 ppm]. The ^{1}H NMR characterization of **3a** was complicated by the instability of this compound, and broad signals were recognized in this case. Of the two possible isomeric forms expected for **3b** (*E* and *Z*, with reference to the possible orientations of the two different N-substituents), only the *Z* isomer exists in $CDCl_3$ solution.[24b,25] The selenium centre in **3b** manifests itself with a ^{77}Se signal falling at 241.8 ppm. The reaction leading to **3a** is not selective, since a small amount of the monoiron complex **4** was produced, which was recovered in 31 % yield after work-up. Complex **4**, maintaining the C^2–H unit, might be viewed as the result of selenium incorporation along a fragmentation process initiated by electron transfer to **2a**.[30] Compound **4** was identified on the basis of a comparison of its IR and NMR features with those of the strictly analogous species [FeCp(CO){SeC^1(NMe_2)C^2HC^3(Me)}], crystallographically characterized and recently published.[24b] In **4**, the iminium character of the C^1=N bond is evidenced by the inequivalence of the methyl substituents in the ^{1}H NMR spectrum (3.64 and 3.33 ppm, $CDCl_3$ solution). The C^3 carbon exhibits some alkylidene nature [$\delta(^{13}C)$ = 174.1 ppm], while the {C^2H} unit is substantially alkenic [$\delta(^1H)$ = 7.43 ppm, $\delta(^{13}C)$ = 137.5 ppm]. The selenium atom resonates at 210.1 ppm. Although the structure of **4** may be well described as a zwitterionic 2-ferra-5-iminium-selenophene (Scheme 2) in analogy to the crystallographic data of [FeCp(CO){SeC^1(NMe_2)C^2HC^3(Me)}], some delocalization is present within the five-membered cycle and contributions from alternative resonance forms should be envisaged.

Reactions analogous to those yielding **3a**–**b** but employing elemental sulfur did not afford diiron derivatives

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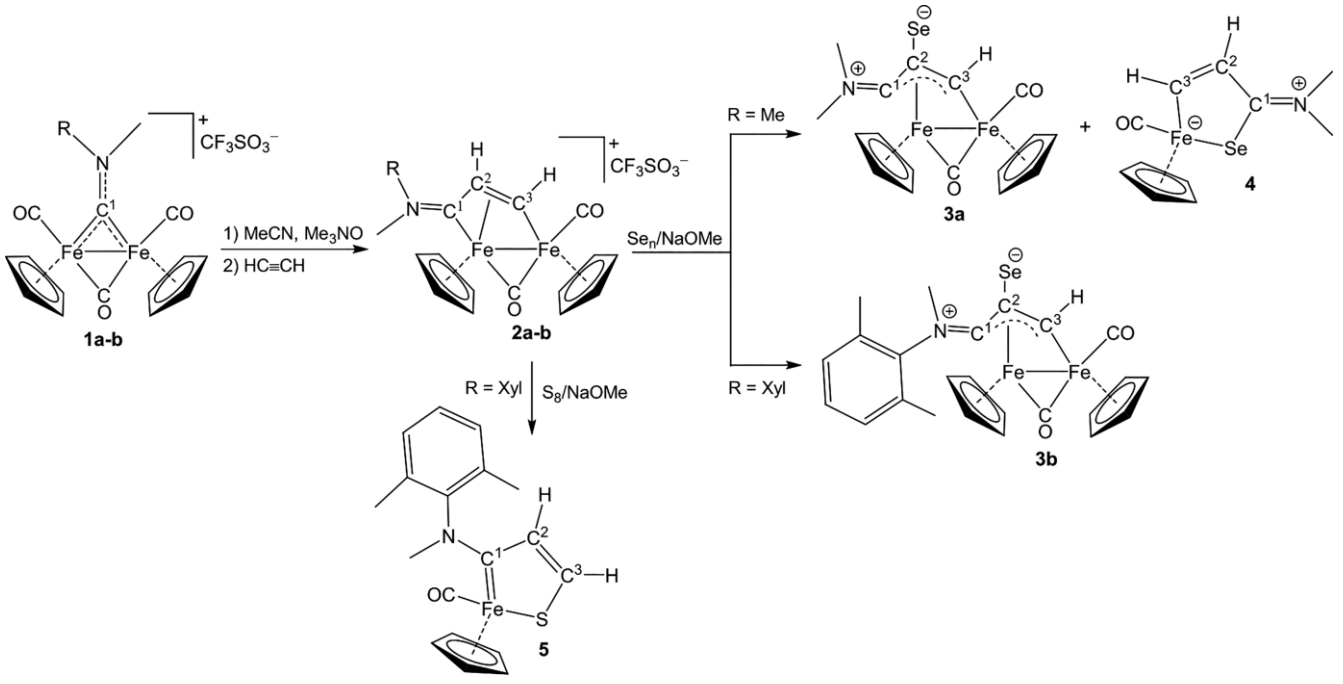


Scheme 2. Synthesis of di- and monoiron complexes via reactions of diiron vinyliminium compounds, **2a**–**b**, with elemental chalcogens and sodium methoxide (R = Me or Xyl = 2,6-$C_6H_3Me_2$).

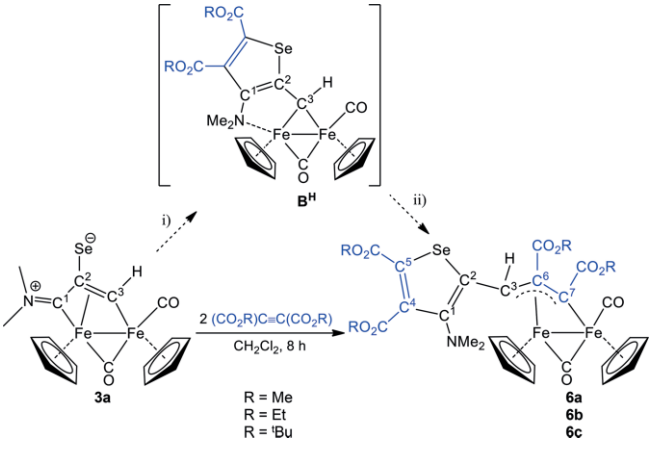
(Scheme 2).[24a] More precisely, a complicated mixture of products was recovered from **3a**, while the reaction involving **2b** resulted in the prevalent formation of **5**. Compound **5**, belonging to a family of strictly similar compounds which was described previously,[24a,31] was isolated in 49 % yield and unambiguously identified by means of a comparative analysis of spectroscopic data. The IR spectrum in CH_2Cl_2 consists of an intense band at 1935 cm^{-1}. The NMR spectra show a single set of resonances, ascribable to the *E* configuration of substituents at the iminium moiety. The C^1 carbon resonates at 253.0 ppm, thus revealing its aminocarbene identity.[32] Typical low field resonances feature also the C^2 and C^3 carbons (132.8 and 182.6 ppm, respectively).[24a]

Similarly to what discussed for **4** and based on the X-ray characterization of [FeCp(CO){$SC^3(Me)C^2HC^1NMe(Xyl)$}], the most representative structure of **5** is a 2-ferra-3-amino-thiophene (Scheme 2), although contributions from other resonance forms are not totally negligible.[24a]

The treatment of a CH_2Cl_2 solution of **3a** with a two-fold molar excess of dialkylacetylenedicarboxylates led to the formation of complexes **6a**–**c**, containing an unprecedented bridging selenophene-modified allylidene ligand (Scheme 3). Compounds **6a**–**c** were isolated in ca. 50 % yields after purification by alumina chromatography.

The structure of **6a** was ascertained by single-crystal X-ray diffraction (Figure 1, Table 1). It consists of a *cis*-[$Fe_2Cp_2(CO)(\mu$-CO)] core, to which is (μ-η^1:η^3)-coordinated an allylidene ligand functionalized with a very rare example of multi-substituted 3-amino-selenophene.[33,34]

It should be noted that allylidene ligands bridging two metal centres in a μ-η^1:η^3 fashion are not uncommon in organometallic chemistry,[35] being previously described also in analogous complexes based on the [$M_2Cp_2(CO)(\mu$-CO)] scaffold (M = Fe[36]



Scheme 3. Synthesis of functionalized selenophene-allylidene diiron complexes, via alkyne 1,3-dipolar annulation (i) and alkyne insertion into Fe-μ-alkylidene bond (ii).

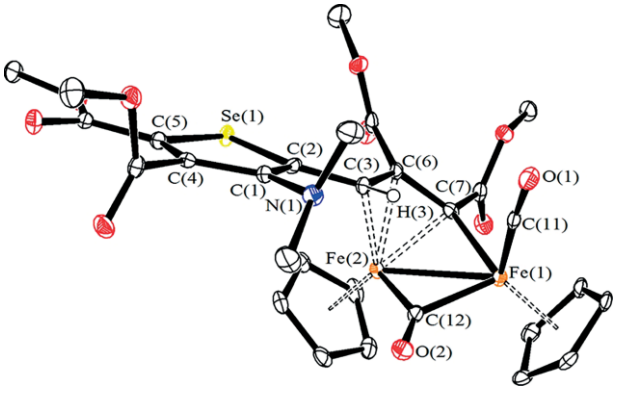


Figure 1. Molecular structure of **6a**. Displacement ellipsoids are at the 30 % probability level. H-atoms, except H(3), have been omitted for clarity.

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Table 1. Selected bond lengths [Å] and angles [°] for **6a**.

Fe(1)–Fe(2)	2.5302(10)	Fe(1)–C(11)	1.750(6)
Fe(1)–C(12)	1.981(5)	Fe(2)–C(12)	1.902(5)
Fe(1)–C(7)	1.948(5)	Fe(2)–C(7)	1.965(5)
Fe(2)–C(6)	2.035(5)	Fe(2)–C(3)	2.061(5)
C(11)–O(1)	1.154(6)	C(12)–O(2)	1.171(6)
C(7)–C(6)	1.438(7)	C(6)–C(3)	1.438(6)
C(3)–C(2)	1.448(6)	C(2)–C(1)	1.385(6)
C(1)–C(4)	1.434(6)	C(4)–C(5)	1.358(7)
Se(1)–C(2)	1.878(5)	Se(1)–C(5)	1.864(4)
C(1)–N(1)	1.419(6)		
Fe(1)–C(11)–O(1)	175.4(4)	Fe(1)–C(12)–Fe(2)	81.31(19)
Fe(1)–C(7)–Fe(2)	80.58(17)	Fe(1)–C(7)–C(6)	124.5(3)
C(7)–C(6)–C(3)	119.2(4)	C(6)–C(3)–C(2)	127.7(4)
C(3)–C(2)–C(1)	122.2(4)	Se(1)–C(2)–C(1)	110.5(3)
C(2)–C(1)–C(4)	114.3(4)	C(1)–C(4)–C(5)	115.9(4)
C(4)–C(5)–Se(1)	111.2(4)	C(2)–Se(1)–C(5)	88.0(2)
C(3)–C(2)–Se(1)	127.1(3)	Sum at N(1)	346.5(7)

or Ru[37]). However, such ligands typically consist of a hydrocarbyl C_3 chain, bearing only a limited degree of functionalization in some cases.[36] In **6a**, Fe(1) is σ-coordinated to C(7) [Fe(1)–C(7) 1.948(5) Å], whereas Fe(2) is coordinated to all three carbon atoms constituting the η³-allylidene unit, i.e. C(3), C(6) and C(7). In agreement with this, C(6)–C(7) [1.438(7) Å] and C(6)–C(3) [1.438(6) Å] distances are almost identical and manifest some π-character. Nonetheless, Fe(2)–C(7) [1.965(5) Å] is slightly shorter than Fe(2)–C(6) [2.035(5) Å] and Fe(2)–C(3) [2.061(5) Å], suggesting also a vinylalkylidene character of the C^3–C^6–C^7 moiety. The μ-CO ligand shows a considerable asymmetry [Fe(1)–C(12) 1.981(5) Å, Fe(2)–C(12) 1.902(5) Å], as a consequence of the more π-acidic terminal CO ligand on Fe(1) with respect to the η³-allylidene ligand on Fe(2). The selenophene ring is perfectly planar [mean deviation from the Se(1)–C(2)–C(1)–C(4)–C(5) least-squares plane 0.0159 Å] and the bonding parameters are comparable to those available for analogous hetero-cyclic systems.[26,34] The C(1)–N(1) distance [1.419(6) Å] is typical for a C(sp^2)–N single bond,[38] as also suggested by the sum of the angles at N(1) [346.5(7)°], which indicates a sp^3 rather than sp^2 hybridization of nitrogen.

The IR spectra of **6a**–**c**, in dichloromethane, share a common pattern consisting of five absorptions, accounting for the terminal and bridging carbonyls, the carboxylato groups and an alkenic function (e.g. for **6a** at 1966, 1799, 1730, 1707 and 1584 cm^{-1}, respectively). The ^1H and ^{13}C NMR spectra of **6a**–**c** (in $CDCl_3$) are in perfect accordance with the X-ray structure of **6a**. They display a single resonance for the amino-group, indicating free rotation around the C^1–N bond. The ^1H resonance of the C^3-bound hydrogen is upfield shifted (e.g. at 0.53 ppm in the case of **6a**), in agreement with what previously recognized for (μ-η¹:η³)-allylidene/vinylalkylidene ligands in analogous diiron and diruthenium complexes.[18d,39] The alkylidene nature of the C^7 carbon is reflected by a diagnostic low field resonance (e.g. at 173.8 ppm for **6a**), while the carbon atoms belonging to the selenophene ring give raise to four signals in the 127–156 ppm range. The ^{77}Se NMR spectra contains a resonance at ca. 560 ppm; for sake of comparison, the selenium atom in unsubstituted selenophene occurs at 613 ppm ($CDCl_3$ solution).[40]

The synthesis of **6a**–**c** might be viewed as the result of a two-step sequence, presumably comprising fast 1,3-dipolar alkyne cycloaddition to the Se and C^1 atoms of **3a**, affording the intermediate selenophene-alkylidene species $\mathbf{B^H}$, followed by slower alkyne insertion into the Fe-μ-alkylidene bond (Scheme 3, steps i and ii). As a matter of fact, the cycloaddition of $C_2(CO_2Me)_2$ to **A** affording $\mathbf{B^{Me}}$ (compare Scheme 1 and Scheme 3) and analogous reactions are almost instantaneous.[26] In contrast to the literature, the alkyne insertion step does not require any chemical/photolytic process to generate a vacant site at one metal centre; instead, the hemilabile nature of the bridging ligand in $\mathbf{B^H}$ is presumably responsible for the initial η²-coordination of the alkyne moiety, which is expected to precede the insertion.[15c] Consistently, it was found that the iron coordination of the amino pendant group in $\mathbf{B^{Me}}$ can be easily replaced by an isocyanide molecule under mild conditions.[26]

Note that the outcomes of the reactions shown in Scheme 1 and Scheme 3 are strictly related to the bulkiness at the C^3 and N atoms. More precisely, the alkyne insertion is feasible with the {C^3H} alkylidene unit (Scheme 3), but precluded in the presence of a R′ substituent (Scheme 1, R′ = Me, CO_2Me, aryl).[24a] Similarly, the alkyne annulation forming the selenophene ring is not possible when nitrogen is substituted with the xylyl moiety, as previously demonstrated.[24a] Accordingly, **3b** was almost unreactive towards dimethylacetylenedicarboxylate in CH_2Cl_2 solution, and only minor decomposition was detected after 18 hours by IR spectroscopy; also, this evidence corroborates the idea that the alkyne insertion must follow the formation of an intermediate selenophene-alkylidene ligand (structure $\mathbf{B^H}$ in Scheme 3).

Conclusions

The versatile {$Fe_2Cp_2(CO)_2$} skeleton is a convenient tool to assemble small organic/inorganic fragments up to the building of unusual molecular architectures, possibly not available from monometal species or conventional organic synthesis.[11c,41] Herein, we have described that the reaction of a preconstructed bridging hydrocarbyl ligand derivatized with a selenido function undergoes addition of two alkyne molecules producing an expansion of the carbonic chain from C^3 to C^7. The resulting selenophene-functionalized μ-allylidene species is unprecedented in organometallic chemistry and might be alternatively viewed as a rare example of multi-functionalized 3-amino-selenophene ring, which is also connected to the diiron core. Two key features should be remarked, being quite uncommon in the landscape of organometallic chemistry: 1) the alkyne reactant plays two distinct roles at two different, non-contiguous sites of the starting molecule, assisted by the cooperative effects provided by the bimetallic system; 2) the alkyne insertion into the Fe-μ-alkylidene bond occurs smoothly due to the hemilabile character of the reacting ligand, weakly binding one iron centre through a pendant amino group. Conversely, alkyne insertion reactions into metal-bridging alkylidenes in poly-metal systems are generally triggered by a photochemical/chemical stimulus, generating a vacant metal site which is required for alkyne entrance.

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Experimental Section

1. Synthesis and Characterization of Compounds

General Details: Unless otherwise specified, operations were carried out under N_2 atmosphere using standard Schlenk techniques, and isolated products were stored under N_2. Solvents were purchased from Merck and distilled before use under N_2 from appropriate drying agents. Organic reactants (TCI Europe or Merck) were commercial products of the highest purity available. Compounds **1a**–**b** were prepared according to a published procedure.[42] Chromatographic separations were carried out on columns of deactivated alumina (Merck, 4 % *w*/*w* water). Infrared spectra of solutions were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer with a CaF_2 liquid transmission cell (2300–1500 cm^{-1} range), and then processed with Spectragryph software.[43] NMR spectra were recorded at 298 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. Chemical shifts (expressed in parts per million) are referenced to the residual solvent peaks (^1H, ^{13}C),[44] or to external standard (^{77}Se, $SeMe_2$). ^1H and ^{13}C NMR spectra were assigned with the assistance of ^1H-^{13}C (*gs*-HSQC and *gs*-HMBC) correlation experiments.[45] NMR signals due to a second isomeric form (where it has been possible to detect them) are italicized. Elemental analyses were performed on a Vario MICRO cube instrument (Elementar).

$[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C^3HC^2HC^1NMe_2\}]CF_3SO_3$, 2a (Figure 2)[46]

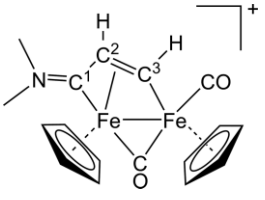

Figure 2. Structure of the cation of **2a**.

Compound **1a** (2.00 g, 3.77 mmol) was dissolved into acetonitrile (30 mL) and treated with Me_3NO (365 mg, 4.86 mmol) in air. The resulting mixture was stirred for 2 hours, and progressive darkening of the solution was observed. The complete conversion of the starting material into the acetonitrile adduct $[Fe_2Cp_2(CO)(\mu\text{-}CO)(NCMe)\{\mu\text{-}CNMe_2\}]CF_3SO_3$ was checked by IR spectroscopy.[47] The volatiles were eliminated under reduced pressure, hence the dark brown residue was dissolved into dichloromethane (ca. 40 mL). A large excess of acetylene, separately produced by dropwise and careful water addition to calcium carbide, was bubbled into the solution for two minutes. The resulting mixture was stirred at room temperature for 72 hours. The final solution was charged on an alumina column. Elution with CH_2Cl_2/THF (1:1 v/v) allowed to separate impurities, then a green-brown fraction was collected using MeOH as eluent. The solvent was evaporated under reduced pressure, then the residue was dissolved in CH_2Cl_2 and this dichloromethane solution was filtered through Celite to remove some NaCl (alumina contaminant). The title product was precipitated upon addition of petroleum ether (ca. 50 mL) to the filtered solution (ca. 20 mL), dried under vacuum and finally stored in air. Yield 1.60 g, 80 %. Anal. calcd. for $C_{18}H_{18}F_3Fe_2NO_5S$: C, 40.86; H, 3.43; N, 2.65; S, 6.06; found C, 40.78; H, 3.51; N, 2.62; S, 6.16. IR (CH_2Cl_2): $\tilde{\nu}$ /cm^{-1} = 1994vs. (CO), 1816s (μ-CO), 1676w (C^2C^1N). ^1H NMR ([D_6]acetone): δ/ppm = 12.38 (br, 1 H, C^3H); 5.52, 5.19 (s, 10 H, Cp); 5.03 (br, 1 H, C^2H); 3.92, 3.33 (NMe_2). $^{13}C\{^1H\}$ NMR ([D_6]acetone): δ/ppm = 256.0 (μ-CO); 226.8 (C^1); 210.2 (CO); 184.8 (C^3); 89.9, 87.1 (Cp); 52.4 (C^2); 50.9, 44.8 (NMe_2).

$[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C^3HC^2HC^1NMe(Xyl)\}]CF_3SO_3$, 2b (Figure 3)[48]

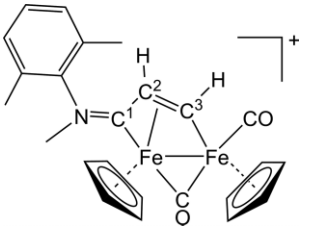

Figure 3. Structure of the cation of **2b**.

The title compound was prepared by using a procedure analogous to that described for **2a**, from **1b** (2.00 g, 3.22 mmol) and acetylene, and stored in air. Brown solid, yield 0.997 g (50 %). Anal. calcd. for $C_{25}H_{24}F_3Fe_2NO_5S$: C, 48.49; H, 3.91; N, 2.26; S, 5.18; found C, 48.22; H, 3.97; N, 2.33; S, 5.09. IR (CH_2Cl_2): $\tilde{\nu}$ /cm^{-1} = 2005vs. (CO), 1820s (μ-CO), 1628m (C^2C^1N). ^1H NMR ($CDCl_3$): δ/ppm = *12.73*, 12.57 (d, 1 H, $^3J_{HH}$ = 7.1 Hz, C^3H); 7.44–6.92 (m, 3 H, C_6H_3); *5.49*, 4.59 (d, 1 H, $^3J_{HH}$ = 7.1 Hz, C^2H); 5.43, *5.36*, *4.74*, 5.16 (s, 10 H, Cp); 4.15, *3.50* (NMe); *2.51*, 2.28, 1.71, *1.93* ($C_6H_3Me_2$). *E*/*Z* ratio = 1.2. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = *253.3*, 253.2 (μ-CO); *233.9*, 232.1 (C^1); 209.7, *208.9* (CO); *189.1*, 188.0 (C^3); 144.7, *141.2* (*ipso*-C_6H_3); 133.6–129.0 (C_6H_3); *90.1*, 89.9, *87.0*, 86.5 (Cp); *53.2*, 52.2 (C^2); *52.1*, 46.1 (NMe); *17.9*, 17.7, *17.5*, 16.9 ($C_6H_3Me_2$).

Synthesis of $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C^3HC^2(Se)C^1NMe_2\}]$, 3a (Figure 4)

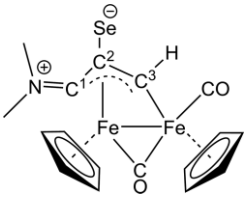

Figure 4. Structure of **3a**.

A stirred mixture of **2a** (200 mg, 0.378 mmol) and grey Se (300 mg, 3.80 mmol) in THF (15 mL) was treated with sodium methoxide (40 mg, 0.74 mmol). The resulting mixture was stirred for 2 hours, until IR analysis evidenced the complete consumption of **2a**. The final mixture was filtered through a celite pad using dichloromethane as eluent. The solvent was removed under reduced pressure from the filtered solution, the residue was repeatedly washed with diethyl ether (4 × 30 mL) and then dried under vacuum. Green solid, yield 92 mg, 53 %. Anal. calcd. for $C_{17}H_{17}Fe_2NO_2Se$: C, 44.58; H, 3.74; N, 3.06; found C, 44.45; H, 3.82; N, 3.12. IR (CH_2Cl_2): $\tilde{\nu}$ /cm^{-1} = 1969vs. (CO), 1790s (μ-CO), 1618m (C^1N). ^1H NMR ($CDCl_3$): δ/ppm = 12.12 (s, 1 H, C^3H); 4.95, 4.66 (s, 10 H, Cp); 3.75, 3.39 (s, 6 H, NMe_2).

$[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C^3HC^2(Se)C^1N(Me)(Xyl)\}]$, 3b (Figure 5)

A stirred mixture of **2b** (100 mg, 0.161 mmol) and grey Se (128 mg, 1.61 mmol) in THF (15 mL) was treated with sodium methoxide (26 mg, 0.48 mmol). The resulting mixture was stirred for 1 hour, until IR analysis evidenced the complete consumption of **2b**. The final mixture was filtered through a celite pad using THF as eluent. The solvent was removed from the filtered solution under reduced

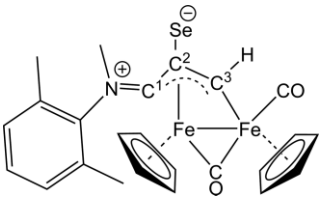

Figure 5. Structure of **3b**.

pressure, the residue was dissolved in CH_2Cl_2 and this solution charged on an alumina column. Elution with CH_2Cl_2 allowed to separate impurities, then a green fraction was collected using THF as eluent. A green solid was isolated upon evaporation of the solvent under vacuum. Yield 48 mg (54 %). Anal. calcd. for $C_{24}H_{23}Fe_2NO_2Se$: C, 52.59; H, 4.23; N, 2.56; found C, 52.38; H, 4.18; N, 2.67. IR (CH_2Cl_2): $\tilde{\nu}$ /cm^{-1} = 1970vs. (CO), 1796s (μ-CO), 1603 (C^1N), 1584w (arom C=C). ^{1}H NMR ($CDCl_3$): δ/ppm = 12.42 (s, 1 H, C^3H); 7.29, 6.97 (m, 3 H, C_6H_3); 5.03, 4.36 (s, 10 H, Cp); 3.59 (s, 3 H, NMe); 2.65, 2.03 (s, 6 H, C_6H_3*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 262.3 (μ-CO); 234.5 (C^1); 211.2 (CO); 186.7 (C^3); 142.2 (*ipso*-C_6H_3); 135.5, 134.3, 129.3, 129.1, 128.9 (C_6H_3); 89.9, 88.5 (Cp); 89.7 (C^2); 47.2 (NMe); 18.1 (C_6H_3*Me*$_2$). ^{77}Se NMR ($CDCl_3$): δ/ppm = 241.8.

Synthesis and isolation of [FeCp(CO){SeC^1(NMe$_2$)C^{2}HC^{3}H}], 4 (Figure 6)

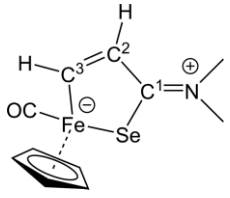

Figure 6. Structure of **4**.

The title compound was obtained as a by-product of the reaction leading to **3a**. The diethyl ether solution collected from the washings (see above) was filtered through an alumina column (diethyl ether as eluent). Thus, a red fraction was obtained, corresponding to **4**. Compound **4** was isolated as an air-stable, red solid upon removal of the solvent under vacuum. Yield 64 mg (31 %). Anal. calcd. for $C_{11}H_{13}FeNOSe$: C, 42.61; H, 4.23; N, 4.52; found C, 42.52; H, 4.30; N, 4.44. IR (CH_2Cl_2): $\tilde{\nu}$ /cm^{-1} = 1930vs. (CO), 1535w (C^3=C^2). ^{1}H NMR ($CDCl_3$): δ/ppm = 8.96 (d, 1 H, $^3J_{HH}$ = 6.3 Hz, C^3H); 7.43 (d, 1 H, $^3J_{HH}$ = 6.3 Hz, C^2H); 4.58 (s, 5 H, Cp); 3.64, 3.33 (s, 6 H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 227.5 (CO); 218.8 (C^1); 174.1 (C^3); 137.5 (C^2); 82.8 (Cp); 43.2 (NMe_2). ^{77}Se NMR ($CDCl_3$): δ/ppm = 210.1.

Synthesis and isolation of [FeCp(CO){SC^{3}HC^{2}HC^{1}NMe(Xyl)}], 5 (Figure 7)

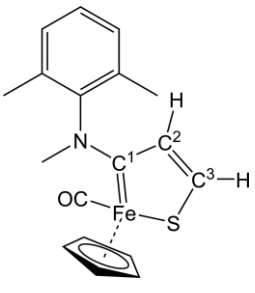

Figure 7. Structure of **5**.

A stirred mixture of **2b** (100 mg, 0.161 mmol) and S_8 (60 mg, 0.23 mmol) in THF (15 mL) was treated with sodium methoxide (26 mg, 0.484 mmol). The resulting mixture was stirred for 30 minutes, until IR analysis evidenced the complete consumption of **2b** and the appearance of an intense band at 1937 cm^{-1} (THF solution). This mixture was filtered through a short alumina pad using THF as eluent, then the volatiles were removed under vacuum from the filtered solution. Subsequent alumina chromatography of the residue led to isolate a red fraction, corresponding to **5**, using heptane/diethyl ether (2:1 v/v) as eluent. Compound **5** was isolated as an air-stable, red solid upon removal of the solvent under vacuum. Yield 28 mg (49 %). Anal. calcd. for $C_{18}H_{19}FeNOS$: C, 61.20; H, 5.42; N, 3.96: S, 9.08; found C, 61.09; H, 5.51; N, 3.92; S, 9.23. IR (CH_2Cl_2): $\tilde{\nu}$ /cm^{-1} = 1935vs. (CO). ^{1}H NMR ($CDCl_3$): δ/ppm = 8.11 (d, $^3J_{HH}$ = 5.6 Hz, 1 H, C^3H); 7.18–7.09 (m, 3 H, C_6H_3); 6.03 (d, $^3J_{HH}$ = 5.6 Hz, 1 H, C^2H); 4.72 (s, 5 H, Cp); 3.68 (s, 3 H, NMe); 2.25, 2.02 (s, 6 H, C_6H_3*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 253.0 (C^1); 217.9 (CO); 182.6 (C^3); 132.8 (C^2); 145.6, 133.4, 133.1, 129.3, 128.9; 127.9 (C_6H_3); 83.1 (Cp); 47.9 (NMe); 17.8, 17.8 (C_6H_3*Me*$_2$).

Synthesis of [Fe$_2$Cp$_2$(CO)(μ-CO){μ-η^1:η^3-C^7(CO$_2$Me)C^6(CO$_2$Me)-C^{3}HC^{2}SeC^5(CO$_2$Me)C^4(CO$_2$Me)C^1(NMe$_2$)}], 6a (Figure 8)

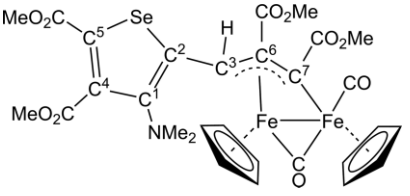

Figure 8. Structure of **6a**.

Addition of dimethylacetylenedicarboxylate (0.12 mL, 0.98 mmol) to a solution of **3a** (150 mg, 0.328 mmol) in THF (15 mL) resulted in fast colour change from green to red, and the resulting solution was stirred for further 8 hours. Afterwards, the volatiles were eliminated under reduced pressure, the residue was dissolved in diethyl ether and this solution charged on an alumina column. The fraction containing the title product was isolated using dichloromethane/diethyl ether (1:1 v/v) as eluent. Removal of the solvent under vacuum afforded a red solid. Yield 150 mg (62 %). Anal. calcd. for $C_{29}H_{29}Fe_2NO_{10}Se$: C, 46.93; H, 3.94; N, 1.89; found C, 46.83; H, 4.00; N, 1.92. IR (CH_2Cl_2): $\tilde{\nu}$ /cm^{-1} = 1966vs. (CO), 1799s (μ-CO), 1730vs. (OC=O), 1707vs-sh (OC=O), 1584w (C=C). ^{1}H NMR ($CDCl_3$): δ/ppm = 4.80, 4.62 (s, 10 H, Cp); 4.05, 3.95, 3.82, 3.81 (s, 12 H, CO_2Me); 2.62 (s, 6 H, NMe_2); 0.53 (s, 1 H, C^3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 262.8 (μ-CO); 213.5 (CO); 179.4, 171.0 (C_6-CO + C_7-CO); 173.8 (C^7); 167.8, 162.6 (C_4-CO + C_5-CO); 155.8 (C^2); 149.2 (C^1); 140.7, 127.4 (C^4 + C^5); 90.5 (C^6); 88.3, 87.0 (Cp); 53.1, 52.8, 52.4, 52.2 (CO_2*Me*); 51.0 (C^3); 43.7 (NMe_2). ^{77}Se NMR ($CDCl_3$): δ/ppm = 557.4.

[Fe$_2$Cp$_2$(CO)(μ-CO){μ-η^1:η^3-C^7(CO$_2$Et)C^6(CO$_2$Et)C^{3}HC^{2}SeC^5-(CO$_2$Et)C^4(CO$_2$Et)C^1(NMe$_2$)}], 6b (Figure 9)

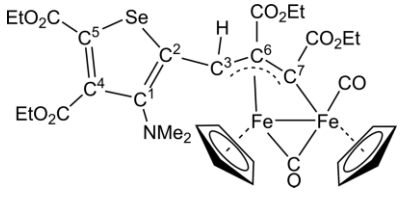

Figure 9. Structure of **6b**.

The title compound was prepared by using the same procedure described for the synthesis of **6a**, from **3a** (130 mg, 0.284 mmol) and diethylacetylenedicarboxylate (0.14 mL, 0.85 mmol). Eluent for

chromatography: diethyl ether. Brown solid, yield 127 mg (56 %). Anal. calcd. for $C_{33}H_{37}Fe_2NO_{10}Se$: C, 49.65; H, 4.67; N, 1.75; found C, 49.60; H, 4.74; N, 1.84. IR (CH_2Cl_2): $\tilde{\nu}$ /cm^{-1} = 1964vs. (CO), 1798s (μ-CO), 1726vs. (OC=O), 1711vs. (OC=O), 1582w (C=C). ^{1}H NMR ($CDCl_3$): δ/ppm = 4.77, 4.60 (s, 10 H, Cp); 4.42–4.18 (m, 8 H, CH_2CH$_3$); 2.61 (s, 6 H, NMe$_2$); 1.57–1.15 (m, 12 H, CH$_2$CH_3); 0.50 (s, 1 H, C^{3}H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ/ppm = 263.4 (μ-CO); 213.9 (CO); 179.3, 170.5 (C$_6$-*C*O + C$_7$-*C*O); 175.0 (C^7); 167.3, 162.3 (C$_4$-*C*O + C$_5$-*C*O); 156.1 (C^2); 149.1 (C^1); 141.2, 128.0 (C^4 + C^5); 91.3 (C^6); 88.7, 87.1 (Cp); 63.3, 62.0, 61.5, 61.1 (*C*H$_2$CH$_3$); 51.3 (C^3); 43.5 (NMe$_2$); 14.9, 14.4, 14.1 (CH$_2$*C*H$_3$). ^{77}Se NMR ($CDCl_3$): δ/ppm = 557.4.

[Fe$_2$Cp$_2$(CO)(μ-CO){μ-η^1:η^3-C^7(CO$_2$*t*Bu)C^6(CO$_2$*t*Bu)-C^{3}HC^{2}SeC^5(CO$_2$*t*Bu)C^4(CO$_2$*t*Bu)C^1(NMe$_2$)}], 6c (Figure 10)

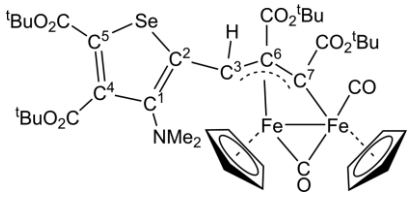

Figure 10. Structure of **6c**.

The title compound was prepared by using the same procedure described for the synthesis of **6a**, from **3a** (104 mg, 0.227 mmol) and di-*tert*-butyl acetylenedicarboxylate (154 mg, 0.681 mmol). Eluent for chromatography: diethyl ether. Brown solid, yield 106 mg (49 %). Anal. calcd. for $C_{44}H_{53}Fe_2NO_{10}Se$: C, 55.83; H, 5.64; N, 1.48; found C, 55.91; H, 5.55; N, 1.41. IR (CH_2Cl_2): $\tilde{\nu}$ /cm^{-1} = 1961vs. (CO), 1793s (μ-CO), 1703vs. (OC=O), 1682vs. (OC=O), 1532w (C=C). ^{1}H NMR ($CDCl_3$): δ/ppm = 4.79, 4.64 (s, 10 H, Cp); 2.56 (s, 6 H, NMe$_2$); 1.76, 1.57, 1.48, 1.42 (s, 36 H, CMe$_3$); 0.21 (s, 1 H, C^{3}H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ/ppm = 265.7 (μ-CO); 214.3 (CO); 179.0, 169.9 (C$_6$-*C*O + C$_7$-*C*O); 176.0 (C^7); 166.2, 161.5 (C$_4$-*C*O + C$_5$-*C*O); 154.9 (C^2); 149.8 (C^1); 142.2, 129.4 (C^4 + C^5); 92.2 (C^6); 88.2, 86.7 (Cp); 83.5, 82.8, 81.8, 81.3 (*C*Me$_3$); 52.6 (C^3); 43.5 (NMe$_2$); 29.1, 28.3, 28.2 (C*Me*$_3$). ^{77}Se NMR ($CDCl_3$): δ/ppm = 555.7.

Table 2. Crystal data and measurement details for **6a**.

	6a
Formula	$C_{29}H_{29}Fe_2NO_{10}Se$
FW	742.19
T, K	100(2)
λ, Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	9.1807(10)
b, Å	9.9630(11)
c, Å	17.678(2)
α,°	101.491(4)
β,°	98.374(4)
γ,°	110.330(4)
Cell Volume, Å^3	1444.6(3)
Z	2
D_c, g cm^{-3}	1.706
μ, mm^{-1}	2.324
F(000)	752
Crystal size, mm	0.19 × 0.16 × 0.13
θ limits,°	2.261–24.997
Reflections collected	31537
Independent reflections	4963 [R_{int} = 0.1379]
Data / restraints /parameters	4963 / 1/397
Goodness on fit on F^2	1.055
R_1 [$I > 2\sigma(I)$]	0.0516
wR_2 (all data)	0.1195
Largest diff. peak and hole, e Å^{-3}	1.099/–0.584

2. X-ray Crystallography

Crystal data and collection details for **6a** are reported in Table 2. Data were recorded on a Bruker APEX II diffractometer equipped with a PHOTON2 detector using Mo-K_α radiation. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[49] Hydrogen atoms were fixed at calculated positions and refined using a riding model, except H(3) which was located in the Fourier map and refined isotropically using the 1.2-fold U_{iso} of the parent C(3) atom. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Deposition Number 1996466 (for **6a**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Supporting Information (see footnote on the first page of this article): NMR spectra of products.

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Keywords: Iron · Alkyne insertion · Cycloaddition · Bridging ligands · Selenophenes

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