Pergamon

Tetrahedron 58 (2002) 9785–9792

TETRAHEDRON

Synthesis of poly-ferrocene heterocycles by cycloaddition of mono- or bis(ferrocenecarbonyl)acetylenes and bis[1,2]dithiolo[1,4]thiazinethiones

Susana Barriga,[a] Carlos F. Marcos,[b] Olivier Riant[c] and Tomás Torroba[a,*]

[a]*Departamento de Química, Facultad de Ciencias, Universidad de Burgos, 09001 Burgos, Spain*
[b]*Departamento de Química Orgánica, Facultad de Veterinaria, Universidad de Extremadura, 10071 Cáceres, Spain*
[c]*Département de Chimie, Université Catholique de Louvain, 1348 Louvain la Neuve, Belgium*

Received 15 August 2002; revised 16 September 2002; accepted 10 October 2002

Abstract—Cycloaddition of a bis[1,2]dithiolo[1,4]thiazine ketothione and mono- or bis(ferrocenecarbonyl)acetylenes under catalysis by scandium triflate gave mono- and bis-ferrocenecarbonyl-1,3-dithiolylidene[1,2]dithiolo[1,4]thiazines. Cycloaddition of a bis-dithiolothiazine dithione and bis-ferrocenylbutynedione gave 3,5-di(bis-ferrocenecarbonyl-1,3-dithiolylidene)[1,4]thiazine, a structure related to extended tetrathiafulvalenes

1. Introduction

Fifty years after the discovery of ferrocene, its golden anniversary has shown a continuously growing rich chemistry.[1] Effectively, ferrocene is now currently employed as a crucial component for redox-active chemical sensors for voltammetric detection of cations[2] as well as anions,[3] and metal-containing signalling probes for the detection of estrogen receptors,[4] barbiturates,[5] dinucleosides,[6] and DNA hybridisation events,[7] thus opening the way to DNA and gene sensors.[8] Classical areas of ferrocene chemistry, such as asymmetric catalysis,[9] or ferrocene materials (liquid crystals,[10] conductive,[11] magnetic,[12] and optical[13] devices) nowadays coexist with emergent areas such as electron transfer devices[14] and ferrocene dendrimers.[15] Many of these areas depend on the development of new synthetic methods designed for ferrocene derivatives, especially those regarding bis-ferrocenes[16] and poly-ferrocenes.[17] We have prepared planar chiral bis- and poly-ferrocene derivatives,[18] suitable for the construction of new materials, from enantiopure 1,2-disubstituted ferrocenes.[19] On the other hand, searching for new stable heterocycles, we have prepared some new bis[1,2]dithiolo-[1,4]thiazines,[20] bis[1,2]dithiolopyrroles,[21] a [1,2]dithiolo-[1,4]thiazine,[22] bis[1,2]dithiolylamines[23] and 1,2-dithiolodisulfides,[24] all in one-pot multicomponent reactions, and studied their exceptional reactivity as dipolarophiles or 1,3-dipolar reagents.[25] Cycloadditions are the pathway of choice for the construction of complex ferrocene-containing heterocycles, providing that suitable ferrocene dipolarophiles are developed. In this paper we report the preparation of some achiral and chiral mono and bis(ferrocenecarbonyl)-acetylenes **3a–c** and **7a** and **b**, their reactions with the bis[1,2]dithiolo[1,4]thiazine ketothione **4** and dithione **8**, and the electrochemical study of the most interesting derivatives.

2. Results and discussion

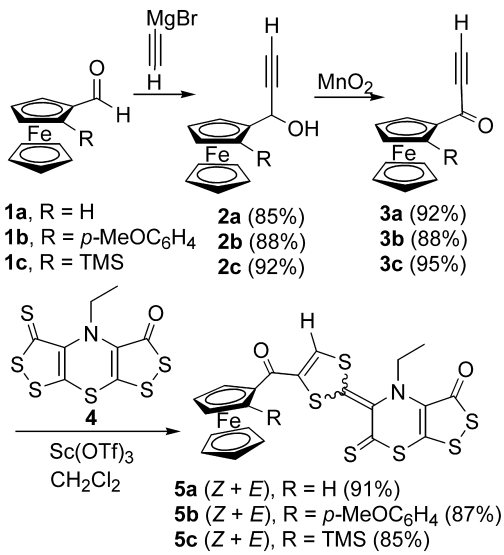
Activated alkynes bearing a single ferrocene group were synthesized from the corresponding ferrocenecarboxaldehyde **1a** or the chiral 2-substituted ferrocenecarboxaldehydes **1b** and **c**.[18b,19b] Thus, **1a–c** were treated with ethynylmagnesium bromide to obtain the corresponding propargylic alcohols **2a–c** that were successively oxidized with magnesium oxide to give 1-ferrocenylprop-2-yn-1-one **3a**, (R_{Fc})-1-[α-(*p*-methoxyphenyl)ferrocenyl]prop-2-yn-1-one **3b**, and (S_{Fc})-1-[α-(trimethylsilyl)ferrocenyl]prop-2-yn-1-one **3c** (Scheme 1). Compound **3a** was previously obtained by a somewhat complex and low-yielding methodology,[26] but the present method is easier and more general.

Cycloaddition of 1-ferrocenylprop-2-yn-1-one **3a** (1 equiv.) and the bisdithiolothiazine ketothione **4**[20a,b] (1 equiv.) in the presence of scandium triflate, [$Sc(OTf)_3$] (50 mol%), a typical catalyst for cycloadditions,[27] in dichloromethane at room temperature for 10 min, gave, after column chromatography, **5a** (*Z*+*E*) (91%), red solid mp 114–115°C (Scheme 1). Mass spectroscopy and HRMS showed that

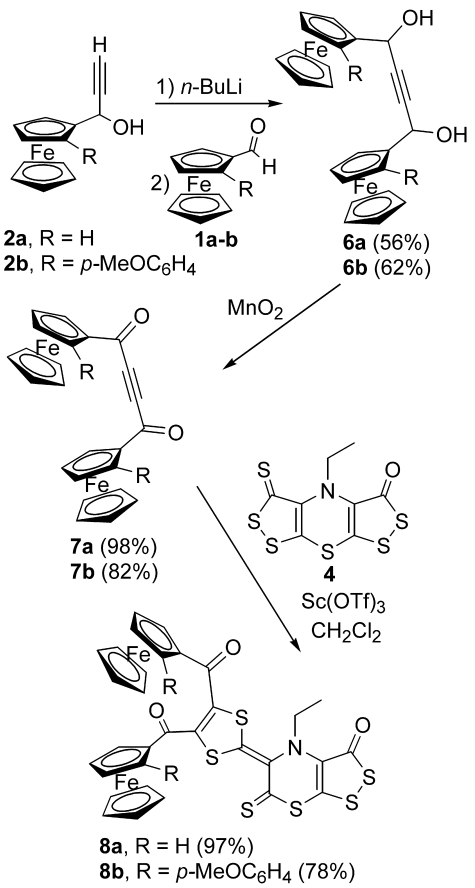
Keywords: ferrocene; heterocycle; dithiole; thiazine; extended TTF; cyclic voltammetry.

* Corresponding author. Tel.: +34-947-258088; fax: +34-947-258087; e-mail: ttorroba@ubu.es

0040–4020/02/$ - see front matter
PII: S0040-4020(02)01295-4



Scheme 1. Synthesis and cycloadditions of ferrocenylpropynones.



Scheme 2. Synthesis and cycloadditions of bisferrocenecarbonylacetylenes.

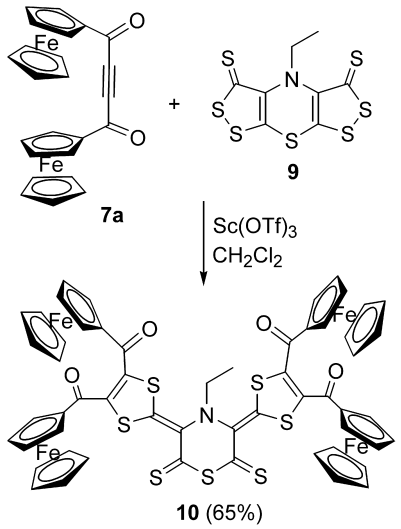
5a was the 1:1 adduct with the molecular formula $C_{21}H_{15}FeNO_2S_6$. Its ^{1}H NMR showed two vinylic proton signals with a relative intensity of 2:1, the ferrocene proton signals, a complex methylene group (two multiplets), and a broad methyl group. Its ^{13}C NMR showed two thione group signals with a relative intensity of 2:1, two pairs of carbonyl group signals, each pair of signals with relative intensities of 2:1, 11 sp^2-tertiary carbon signals with the form of paired high+short signals, eight aromatic carbon signals, two methylene groups, and two methyl groups, all consistent with a 2:1 mixture of geometric isomers with the structure **5a**. In similar conditions, **4** (1 equiv.) reacted with **3b** (1 equiv.), or **3c** (1 equiv.), in the presence of $Sc(OTf)_3$ (50 mol%) in dichloromethane at room temperature for 10 min, to give the corresponding 1:1 cycloadducts **5b** (*Z*+*E*), or **5c** (*Z*+*E*), that were characterized by spectroscopy (Scheme 1). The presence of the chiral ferrocene group in **5b**,**c** is evidenced by the complexity of their NMR spectra. The 1,3-dithiole proton appeared in fact as four signals of different intensities due to the existence of two geometric isomers and two dynamic diastereomers. These are produced by the simultaneous presence of chiral ferrocene and asymmetric nitrogen under restricted inversion.

To avoid the generation of geometric isomers, we then synthesized symmetric acetylenes bearing two ferrocene groups. Thus, the propargylic alcohols **2a** and **2b** were subjected to reaction with *n*-butyllithium and then with the ferrocenecarboxaldehydes **1a** and **1b**, respectively, to give the corresponding diols **6a** and **6b** in moderate yields (56–62%). These diols were successively oxidized with magnesium oxide to give the 1,4-bisferrocenylbut-2-yn-1,4-dione **7a**, and the optically pure (R_{Fc}, $R_{Fc'}$)-1,4-bis[α-(*p*-methoxyphenyl)ferrocenyl]but-2-yn-1,4-dione **7b** in good yields (82–98%) (Scheme 2).

Cycloaddition of **7a** (1 equiv.) or **7b** (1 equiv.) and the bisdithiolothiazine ketothione **4** (1 equiv.) in the presence of $Sc(OTf)_3$ (50 mol%) in dichloromethane at room temperature for 15 min, gave, after column chromatography, **8a** (97%), red solid mp >300°C, and **8b** (78%), red solid mp 103–104°C, respectively (Scheme 2).

Again the presence of dynamic stereoisomers caused by the restricted inversion of nitrogen was evidenced in the ^{1}H NMR spectra by the signals corresponding to the diastereotopic methylene protons, that, for **8a**, produced two groups of six signals (two quartets) separated by 100 Hz, each group corresponding to one proton. In the case of **8b**, the ^{1}H NMR spectrum showed four groups of peaks, each one integrating for 0.5 hydrogen atoms, separated by 156 and 160 Hz, respectively. Analogously, the cycloaddition of **7a** (2 equiv.) and the bisdithiolothiazine dithione **9**[20a,b] (1 equiv.) in the presence of $Sc(OTf)_3$ (50 mol%) in dichloromethane at room temperature for 15 min, gave, after column chromatography, **10** (65%), red solid mp 152–153°C (Scheme 3).

The symmetry of **10** is evidenced by the simplicity of its ^{1}H and ^{13}C NMR spectra, as compared with previous examples. The structure of **10** was confirmed by HRMS (FAB+) to be the 2:1 adduct of **7a** and **9**, that included four ferrocene groups on the periphery of two 1,3-dithiole rings conjugated through a thiazine ring. This compound **10** brings together electron-acceptor and electron-donor groups in a structure that is also related to extended tetrathiafulvalenes.[28] Ferrocene–dithiole and ferrocene–TTF hybrid electron donors have been synthesised[29] as well as ferrocene–acceptor diads[30] in search for new materials. Cycloadducts



Scheme 3. Cycloaddition of a bis-dithiolothiazine dithione.

5a–c, **8a**,**b**, and **10** combine both features and are the first examples of a new class of poly-ferrocene heterocycles.

2.1. Electrochemical study

We performed cyclic voltammetry experiments of 5×10^{-4} M solutions of **8a** and **10** in dichloromethane at 20°C, using Bu_4NPF_6 as supporting electrolyte in an approximate 0.1 M concentration, a platinum ball as working electrode, platinum wire as an auxiliary electrode and saturated calomelanes as reference electrode. The cyclic voltammograms were measured at different scanning velocities, showing that the process for **8a** was always reversible. The relation between the intensity of the oxidation wave and the reduction wave was constant at 50, 100, 200 and 500 mV/s. The intensity was proportional to the square root of the scan speed. Fig. 1 shows the voltammogram of **8a** measured at 100 mV/s. The half-wave potential was found at E_0=0.78 V.

Similarly, we measured cyclic voltammograms for **10** at different scanning velocities, showing that the process was always irreversible, with a large difference between the intensities in the oxidation and the reduction areas. The intensity observed in the reduction area was proportional to the scan speed, being higher at lower velocities. Fig. 2 shows the cyclic voltammogram of **10** measured at

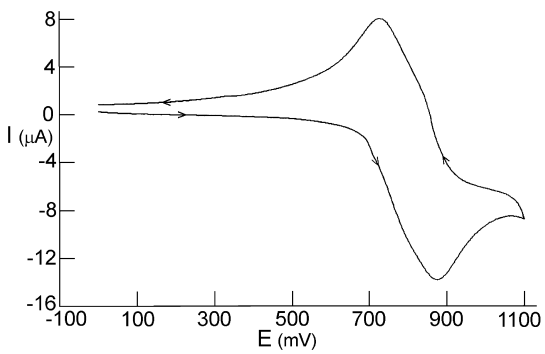


Figure 1. Cyclic voltammogram of **8a** measured in CH_2Cl_2 at room temperature.

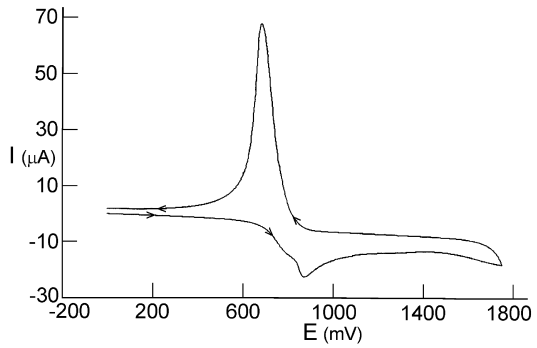


Figure 2. Cyclic voltammogram of **10** registered in CH_2Cl_2 at room temperature.

100 mV/s. The oxidation peak potential appeared at E_p^{ox}=0.84 V.

3. Conclusion

We have shown that 1,3-dipolar cycloadditions of polycylic 1,2-dithiol-3-thiones and mono- or diferrocenecarbonyl acetylenes constitute a rapid way to make polyheterocyclic systems bonded to one to four ferrocene groups that are not easily available by other routes. The new heterocyclic systems, obtained by this methodology, showed chiral conformers in ^{1}H NMR at room temperature that gave rise, when planary chiral ferrocene derivatives were used, to complex NMR spectra. The electrochemical behaviour, studied by cyclic voltammetry, showed, in one case, a reversible process in which the ferrocene groups do not electronically communicate. The sum of electron acceptors and donors in the structures confers to these compounds a promising future as new organic materials.

4. Experimental

4.1. General

Bis[1,2]dithiolo[1,4]thiazine ketothione **4** and dithione **9** were prepared as described.[20a,b] (R_{Fc})-α-(*p*-methoxyphenyl)ferrocenecarboxaldehyde **1b**, and (S_{Fc})-α-(trimethylsilyl)ferrocenecarboxaldehyde **1c** were prepared as described.[18b,19b] Dichloromethane was distilled from phosphorus pentoxide, THF was distilled from sodium, using benzophenone as indicator. Melting points were not corrected. CH_2 and CH groups were identified by DEPT experiments on representative examples. Flash column chromatography was carried out on silica gel C60 (Merck).

4.2. General procedure for the synthesis of ferrocenylpropynols 2a–c

Ethynylmagnesium bromide (8.33 mL, 0.45 M in THF, 3.75 mmol) was added to a solution of ferrocenecarboxaldehyde **1a–c** (2.50 mmol) in THF (5 mL) and the resulting solution was stirred at room temperature for 1 h. An aqueous saturated solution of NH_4Cl (5 mL) was then added to the latter solution, the organic layer was separated and the aqueous layer extracted with diethyl ether (3×10 mL). The combined organic extracts were dried

(Na_2SO_4), the solvent was removed by rotary evaporation, and the resulting residue was purified by flash chromatography (cyclohexane–diethyl ether 4:1).

4.2.1. 1-Ferrocenylprop-2-yn-1-ol (2a). Yellow solid (510 mg, 85%), mp 82–83°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.18–5.16 (m, 1H, CHOH), 4.39–4.35 (m, 2H, 2×CH aromatic), 4.23 (s, 5H, 5×CH aromatic), 4.21–4.20 (m, 2H, 2×CH aromatic), 2.62–2.61 (m, 1H, C≡CH), and 2.51–2.48 (m, 1H, OH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 89.14 (C aromatic), 83.51 (*C*≡CH), 72.66 (C≡*C*H), 68.78, 68.35, 68.13, and 66.40 (4×*C*H aromatic), and 60.61 (*C*HOH); IR (KBr, cm^{-1}) ν 3289 (OH), 3266 (OH), 1389, 1294, 1227, 1105, 1044, 1015, 997, 988, 810, 508, 489; MS (EI) *m/z* 240 (M^+, 85), 214 (M−26, 15), 186 (Fc^+, 20), 138 (100), 121 ($CpFe^+$, 25), 56 (Fe^+, 20). HRMS, M^+=240.0216 $C_{13}H_{12}FeO$ requires 240.0238.

4.2.2. (R_{Fc})-1-[α-(*p*-Methoxyphenyl)ferrocenyl]-2-propyn-1-ol (2b). Yellow sticky solid (761 mg, 88%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.53 (d, *J*=8.8 Hz, 2H, 2×CH aromatic), 6.89 (d, *J*=8.8 Hz, 2H, 2×CH aromatic), 5.28 (s, br, 1H, CHOH), 4.56–4.54 (m, 1H, CH aromatic), 4.49–4.47 (m, 1H, CH aromatic), 4.30–4.28 (m, 1H, CH aromatic), 4.23 (s, 5H, 5×CH aromatic), 3.83 (s, 3H, CH_3), and 2.60–2.56 (m, 2H, C≡CH and OH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 158.34 (C aromatic), 130.09 (*C*H aromatic), 129.12 (C aromatic), 113.49 (*C*H aromatic), 89.14 (C aromatic), 87.27 (C aromatic), 83.76 (*C*≡CH), 73.17 (C≡*C*H), 70.18, 69.86, 67.10, and 66.98 (4×*C*H aromatic), 58.98 (*C*HOH), and 55.19 (CH_3); IR (KBr, cm^{-1}) ν 3282 (OH), 2956, 2925, 2851, 2836, 1610, 1522, 1453, 1438, 1248 (C–O), 1179, 1031, 831; MS (EI) *m/z* 346 (M^+, 69), 320 (M−26, 52), 292 (10), 208 (75), 149 (100), 121 ($CpFe^+$, 20). HRMS, M^+=346.0681 $C_{20}H_{18}FeO_2$ requires 346.0656.

4.2.3. (S_{Fc})-1-[α-(Trimethylsilyl)ferrocenyl]prop-2-yn-1-ol (2c). Yellow sticky solid (718 mg, 92%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.14–5.10 (m, 1H, CHOH), 4.63–4.61 (m, 1H, CH aromatic), 4.37–4.35 (m, 1H, CH aromatic), 4.23 (s, 5H, 5×CH aromatic), 4.17–4.15 (m, 1H, CH aromatic), 2.54–2.51 (m, 1H, C≡CH), 2.33–2.31 (m, 1H, OH), and 0.28 (s, 9H, 3×CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 96.30 (C aromatic), 83.91 (*C*≡CH), 74.88 (C≡*C*H), 72.92 (*C*H aromatic), 70.45 (C aromatic), 70.04, 69.30, 68.66 (3×*C*H aromatic), 60.00 (*C*HOH), and 0.33 (*C*H_3). IR (KBr, cm^{-1}) ν 3285 (OH), 2942, 1374, 1245, 1230, 1096, 1020; MS (EI) *m/z* 312 (M^+, 25), 297 (M−15, 15), 286 (M−26, 8), 239 (M−73, 13), 186 (Fc^+, 20), 121 ($CpFe^+$, 15), 56 (Fe^+, 14). HRMS, M^+_{found}=312.0689 $C_{16}H_{20}FeOSi$ requires 312.0633.

4.3. General procedure for the synthesis of ferrocenylpropynones 3a–c

Manganese (IV) oxide (2.61 g, 30.0 mmol) was added to a stirred solution of ferrocenylpropynol **2a–c** (1.00 mmol) in CH_2Cl_2 (6 mL) and the resulting solution was stirred at room temperature for 15 min. Then the reaction mixture was filtered through celite and washed with CH_2Cl_2 until the filtered solvent was colourless.

4.3.1. 1-Ferrocenyl-2-propyn-1-one (3a). Purified by flash chromatography (cyclohexane–diethyl ether 4:1); red solid (219 mg, 92%), mp 77–78°C (cyclohexane–diethyl ether) (lit.[26c] 75–77°C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.93–4.91 (m, 2H, 2×CH aromatic), 4.62–4.60 (m, 2H, 2×CH aromatic), 4.25 (s, 5H, 5×CH aromatic), and 3.29 (m, 1H, C≡CH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 180.12 (*C*=O), 81.31 (C≡*C*H), 79.62 (*C*≡CH), 77.14 (C aromatic), 73.53, 73.43, and 70.47 (3×*C*H aromatic); IR (KBr, cm^{-1}) ν 1618 (C=O), 1446, 1273, 1115, 824, 508, 489, 470; MS (EI) *m/z* 238 (M^+, 100), 210 (25), 184 (13), 121 ($CpFe^+$, 10), 56 (Fe^+, 30). HRMS, M^+_{found}=238.0061 $C_{13}H_{10}FeO$ requires 238.0081.

4.3.2. (R_{Fc})-1-[α-(*p*-Methoxyphenyl)ferrocenyl]prop-2-yn-1-one (3b). Purified by flash chromatography (cyclohexane–diethyl ether 4:1); red solid (303 mg, 88%), mp 149–150°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.52 (d, *J*=8.6 Hz, 2H, 2×CH aromatic), 6.86 (d, *J*=8.6 Hz, 2H, 2×CH aromatic), 5.08–5.05 (m, 1H, CH aromatic), 4.82–4.78 (m, 1H, CH aromatic), 4.68–4.66 (m, 1H, CH aromatic), 4.27 (s, 5H, 5×CH aromatic), 3.83 (s, 3H, CH_3), and 3.18 (s, 1H, C≡CH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 180.02 (*C*=O), 158.72 (C aromatic), 131.15 (*C*H aromatic), 127.98 (C aromatic), 113.49 (*C*H aromatic), 91.12 (C≡*C*H), 82.10 (*C*≡CH), 76.02 (C aromatic), 73.68, 71.98, and 71.68 (3×*C*H aromatic), and 55.20 (CH_3); IR (KBr, cm^{-1}) ν 3250, 1629 (C=O), 1520, 1247, 1233, 1183, 1029; MS (EI) *m/z* 344 (M^+, 100), 320 (10), 198 (50), 183 (20), 121 ($CpFe^+$, 25), 56 (Fe^+, 13). HRMS, M^+_{found}= 344.0490 $C_{20}H_{16}FeO_2$ requires 344.0500.

4.3.3. (*S*)-1-[2-(Trimethylsilyl)-1-ferrocenyl]-2-propyn-1-one (3c). Purified by flash chromatography (cyclohexane–diethyl ether 9:1); red solid (295 mg, 95%), mp 136–137°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.15–5.13 (m, 1H, CH aromatic), 4.73–4.70 (m, 1H, CH aromatic), 4.60–4.57 (m, 1H, CH aromatic), 4.27 (s, 5H, 5×CH aromatic), 3.24–3.21 (m, 1H, C≡CH), and 0.29 (s, 9H, 3×CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 181.04 (*C*=O), 83.91 (C≡*C*H), 81.76 (*C*≡CH), 80.41, 76.51, 74.86, and 70.46 (4×*C*H aromatic), and −0.08 (*C*H_3); IR (KBr, cm^{-1}) ν 1632 (C=O), 1407, 1105, 1044, 1015, 997, 988, 810 (Si–C), 508, 489; MS (EI) *m/z* 311 (M+1, 16), 310 (M^+, 72), 295 (M−15, 100), 267 (M−73, 9), 121 ($CpFe^+$, 22), 56 (Fe^+, 15). HRMS, M^+_{found}= 310.0512 $C_{16}H_{18}FeOSi$ requires 310.0476.

4.4. General procedure for the cycloaddition of ferrocenylpropynones 3a–c with 4-ethyl-3-oxobis[1,2]dithiolo-[3,4-*b*:4′,3′-*e*][1,4]thiazine-5-thione 4

Ferrocenylpropynone **3a–c** (0.187 mmol) was added to a solution of 4-ethyl-3-oxobis[1,2]dithiolo[3,4-*b*:4′,3′-*e*]-[1,4]thiazine-5-thione **4** (50 mg, 0.155 mmol) and $Sc(OTf)_3$ (38 mg, 0.077 mmol) in dichloromethane (2 mL) and the resulting solution was stirred at room temperature for 10 min. The solvent was removed by rotary evaporation.

4.4.1. (*Z*+*E*) 3-Oxo-4-ethyl-5-(4-ferrocenecarbonyl-1,3-dithiol-2-ylidene)[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione (5a). Purified by flash chromatography (cyclohexane–diethyl ether 4:1) (*Z*+*E*) isomers, red solid (79 mg,

91%), mp 114–115°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (s, 0.6H, (*E*)C=C*H*), 7.86 (s, 0.4H, (*Z*)C=C*H*), 4.96 (s, 1H, CH aromatic), 4.93 (s, 1H, CH aromatic), 4.91 (s, 2H, 2×CH aromatic), 4.70 (s, 5H, 5×CH aromatic), 3.63–3.52 (m, 1H, 1/2CH_2), 3.36–3.26 (m, 1H, 1/2CH_2), 1.27–1.24 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.02 (*C*=S), 190.05 (*C*=S), 187.25, 186.81, 184.88, and 184.58 (4×*C*=O), 166.14, 165.68, 154.18, 153.22, 141.23, 140.71, 132.26, 131.90, 131.81, 129.98, and 129.81 (11×sp^2 *tertiary* C), 73.66, 73.57, 73.54, 71.12, 70.81, 70.77, 70.68, and 70.56 (8×*C*H aromatic), 48.08 (CH_2), 47.43 (CH_2), 13.52 (CH_3), and 13.42 (CH_3); IR (KBr, cm^{-1}) ν 1652, 1645, 1622 and 1616 (C=O), 1346, 1284 (C=S), 1119; MS (FAB+) *m/z* 561 (M^+, 25), 532 (M−29, 16). HRMS (FAB+), M^+_{found}= 560.8777 $C_{21}H_{15}FeNO_2S_6$ requires 560.87765.

4.4.2. (*Z*+*E*) (R_{Fc})-3-Oxo-4-ethyl-5-{4-[α-(*p*-methoxyphenyl)ferrocenecarbonyl]-1,3-dithiol-2-ylidene}[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione (5b). Purified by flash chromatography (cyclohexane–diethyl ether 4:1); red solid (90 mg, 87%), mp 133–134°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (s, 1H, C=C*H*), 7.70 (s, 1H, C=C*H*), 7.62 (s, 1H, C=C*H*), 7.56 (s, 1H, C=C*H*), 7.41–7.30 (m, 4H, 4×CH aromatic), 6.83–6.72 (m, 4H, 4×CH aromatic), 4.80 (s, 4H, 4×CH aromatic), 4.64 (s, 2H, 2×CH aromatic), 4.34 (s, 2H, 2×CH aromatic), 4.30 (s, 2H, 2×CH aromatic), 4.28 (s, 6H, 6×CH aromatic), 3.80 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 3.56–3.46 (m, 2H, CH_2), 3.26–3.18 (m, 2H, CH_2), and 1.37–1.21 (m, 6H, 2×CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.17, and 189.86 (2×*C*=S), 188.58, 188.50, 184.81, and 184.45 (4×*C*=O), 165.76, 165.70, 158.66, 158.57, 154.14, 153.07, 142.16, 141.93, 141.70, and 141.66 (10×sp^2 *tertiary* C), 132.17, and 132.11 (2×C=*C*H), 132.04 and 131.80 (2×*C* aromatic), 130.80, 130.75, 128.19, 128.16, 113.33, and 113.25 (6×*C*H aromatic), 90.95 and 90.68 (2×*C* aromatic), 74.29, 73.99, 73.82, 73.66, 72.09, 72.06, 71.93, 71.87, 71.83, 71.57, 70.79, 70.71, and 70.60 (13×*C*H aromatic), 55.20 (CH_3), 48.06 and 47.32 (2×CH_2), 13.45 and 13.30 (2×CH_3); IR (KBr, cm^{-1}) ν 1667 (C=O), 1651 (C=O), 1633 (C=O), 1616 (C=O), 1519, 1403, 1342, 1246 (C=S), 1097, 826; MS (FAB+) *m/z* 668 (M+1, 3). HRMS (FAB+), $(M+1)_{found}$=667.8992 $C_{28}H_{22}FeNO_3S_6^+$ requires 667.9273.

4.4.3. (*Z*+*E*) (S_{Fc})-3-Oxo-4-ethyl-5-{4-(α-trimethylsilylferrocenecarbonyl)-1,3-dithiol-2-ylidene}[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione (5c). Purified by flash chromatography (cyclohexane–diethyl ether 9:1); red solid (84 mg, 85%), mp 105–106°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (s, 1H, C=C*H*), 8.10 (s, 1H, C=C*H*), 7.96 (s, 1H, C=C*H*), 7.88 (s, 1H, C=C*H*), 4.99 (s, 2H, 2×CH aromatic), 4.78 (s, 2H, 2×CH aromatic), 4.66 (s, 2H, 2×CH aromatic), 4.36 (s, 5H, 5×CH aromatic), 4.36 (s, 5H, 5×CH aromatic), 3.62–3.51 (m, 2H, CH_2), 3.38–3.24 (m, 2H, CH_2), 0.98–0.87 (m, 6H, 2×CH_3), 0.32 (s, 9H, Si(CH_3)$_3$), and 0.19 (Si(*C*H$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.09, and 189.83 (2×*C*=S), 188.32, 188.22, 184.97, and 184.78 (4×*C*=O), 166.51, 166.24, 165.92, 154.38, 154.23, 153.28, 141.50, 141.35, and 141.02 (9×sp^2 *tertiary* C), 132.35, and 132.30 (2×C=*C*H), 131.98, 131.85, 130.88, 130.22, 129.84, and 128.78 (6×*C*H aromatic), 82.41 and 82.28 (2×*C* aromatic), 79.95, 79.85, 75.02, 70.66, 70.56 (5×*C*H aromatic), 47.51 and 47.44 (2×CH_2), 14.10 and 14.03 (2×CH_3), 0.98 and 0.19 (2×SiCH_3); IR (KBr, cm^{-1}) ν 1667 (C=O), 1652 (C=O), 1633 (C=O), 1622 (C=O), 1616, 1408, 1346, 1311, 1246 (C=S), 1143, 1118, 1107, 1046, 837, 822 (Si–C); MS (FAB+) *m/z* 633 (M^+, 10), 604 (M^+−29, 10), 601 (M^+−32, 5), 285 (23), 149 (87). HRMS (FAB+), $(M+2)_{found}$= 634.9476 $C_{24}H_{25}FeNO_2S_6Si^{+2}$ requires 634.9328.

4.5. General procedure for the synthesis of bis-ferrocenylbutynediols 6a and b

n-Butyllithium (1.54 mL 1.42 M in hexanes, 2.20 mmol) was added to a stirred solution of ferrocenylpropynol **2a** and **b** (1.00 mmol) in THF (5 mL) at −78°C and the resulting solution was stirred for 15 min. Then ferrocenecarboxaldehyde **1a** and **b** (1.00 mmol) was added and the resulting solution was left to reach room temperature and stirred for additional 30 min. An aqueous saturated solution of NH_4Cl (5 mL) was then added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3×10 mL) and the combined organic extracts were dried (Na_2SO_4), the solvent was removed by rotary evaporation, and the resulting residue was purified by flash chromatography (cyclohexane–diethyl ether 1:1).

4.5.1. 1,4-Bis(ferrocenyl)but-2-yn-1,4-diol (6a). Yellow solid (254 mg, 56%), mp 128–129°C (cyclohexane–diethyl ether). ^{1}H NMR (CD_3COCD_3, 400 MHz) δ 5.38–5.36 (m, 2H, 2×CH), 4.55–4.53, 6.38 (m, 2H, 2×CH aromatic), 4.48–4.46 (m, 2H, 2×CH aromatic), 4.36–4.35 (m, 2H, 2×CH aromatic), 4.24 (s, 10H, 10×CH aromatic), and 4.18–4.16 (m, 4H, 2×CH aromatic and 2×OH); ^{13}C NMR (CD_3COCD_3, 100 MHz) δ 86.38 (*C*≡*C*), 70.79 (aromatic C), 70.68, 69.73, 69.46, and 68.78 (4×*C*H aromatic), and 62.31 (*C*H); IR (KBr, cm^{-1}) ν 3095 (OH), 1291, 1234, 1125, 1105, 1039, 1022, 998, 972, 821, 505, 486; MS (EI) *m/z* 454 (M^+, 100), 436 (M−17, 11), 420 (M−34, 16), 316 (87), 214 (20), 186 (Fc^+, 35), 121 ($CpFe^+$, 40), 56 (Fe^+, 27). HRMS, M^+_{found}=454.0297 $C_{24}H_{22}Fe_2O_2$ requires 454.0319.

4.5.2. (R_{Fc},$R_{Fc'}$)-1,4-Bis[α-(*p*-methoxyphenyl)ferrocenyl]-but-2-yn-1,4-diol (6b). Yellow solid (414 mg, 62%), mp 71–72°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.48 (d, *J*=8.8 Hz, 4H, 4×CH aromatic), 6.83 (d, *J*=8.8 Hz, 4H, 4×CH aromatic), 5.29–5.27 (m, 2H, 2×*C*H), 4.43–4.40 (m, 2H, 2×CH aromatic), 4.25–4.24 (m, 2H, 2×CH aromatic), 4.23–4.21 (m, 2H, 2×CH aromatic), 4.17 (s, 10H, 10×CH aromatic), and 3.81 (s, 3H, 2×CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 158.28 (*C* aromatic), 130.24 (*C*H aromatic), 129.39 (*C* aromatic), 113.42 (*C*H aromatic), 88.75 (*C*≡*C*), 87.20 and 85.25 (2×*C* aromatic), 70.28, 69.92, 67.62, and 66.82 (2×*C*H aromatic), 59.50 (*C*H), and 55.22 (CH_3); IR (KBr, cm^{-1}) ν 3427 (OH), 2923, 1522, 1247, 1033, 831; MS (FAB+) *m/z* 667 (M+1, 6). HRMS (FAB+), M^+_{found}=667.1277 $C_{38}H_{35}Fe_2O_4$ requires 667.1234.

4.6. General procedure for the synthesis of bis-ferrocenylbutynediones 7a and b

Manganese (IV) oxide (2.61 g, 30.00 mmol) was added to a stirred solution of the bisferrocenylbutynediol **6a** and **b**

(0.50 mmol) in CH_2Cl_2 (5 mL) and the resulting solution was stirred at room temperature for 15 min. Then the reaction mixture was filtered through celite and washed with CH_2Cl_2 until the filtered solvent was colourless. Then the solvent was removed by rotary evaporation, and the resulting residue was purified by flash chromatography (cyclohexane–diethyl ether 4:1).

4.6.1. 1,4-Bis(ferrocenyl)but-2-yn-1,4-dione (7a). Purple solid (220 mg, 98%), mp 161–162°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.00 (dd, J=3.8, 1.9 Hz, 4H, 4×CH aromatic), 4.71 (dd, J=3.8, 1.9 Hz, 4H, 4×CH aromatic), and 4.34 (s, 10H, 10×CH aromatic); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 179.56 (*C*=O), 83.68 (*C*≡*C*), 79.72 (aromatic C), 79.72, 70.80, and 70.58 (3×*C*H aromatic); IR (KBr, cm^{-1}) ν 1618 (C=O), 1446, 1273, 1115, 824, 508, 489, 470; MS (EI) *m*/*z* 450 (M^+, 100), 186 (Fc^+, 20), 149 (60), 121 ($CpFe^+$, 25). HRMS, M^+_{found}= 450.0008 $C_{24}H_{18}Fe_2O_2$ requires 450.0006.

4.6.2. (R_{Fc},$R_{Fc'}$)-1,4-Bis[α-(*p*-methoxyphenyl)ferrocenyl]-but-2-yn-1,4-dione (7b). Purple solid (271 mg, 82%), mp 65–66°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.55 (d, J=8.8 Hz, 4H, 4×CH aromatic), 6.88 (d, J=8.8 Hz, 4H, 4×CH aromatic), 5.04–5.02 (m, 2H, 2×CH aromatic), 4.86–4.85 (m, 2H, 2×CH aromatic), 4.72–4.70 (m, 2H, 2×CH aromatic), 4.30 (s, 10H, 10×CH aromatic), and 3.82 (s, 6H, 2×CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 179.39 (*C*=O), 158.82 (*C* aromatic), 131.12 (*C*H aromatic), 127.69 (*C* aromatic), 113.05 (*C*H aromatic), 91.24 (*C* aromatic), 84.76 (*C*≡*C*), 76.35 (*C*H aromatic), 76.03 (*C* aromatic), 73.61, and 72.15 (2×*C*H aromatic), and 55.23 (*C*H_3); IR (KBr, cm^{-1}) ν 2924, 1630 (C=O), 1609 (C=O), 1521, 1245 (ArC–O–C), 1107, 826; MS (FAB+) *m*/*z* 663 (M+1, 10). HRMS (FAB+), $(M+1)_{found}$= 663.0866 $C_{38}H_{31}Fe_2O_4$ requires 663.0921.

4.7. General procedure for the cycloaddition of bis-ferrocenylbutynediones 7a and b with 4-ethyl-3-oxo-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-5-thione 4

Bisferrocenylbutynedione **7a** and **b** (0.150 mmol) was added to a solution of 4-ethyl-3-oxo-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-5-thione (40 mg, 0.124 mmol) and $Sc(OTf)_3$ (30 mg, 0.060 mmol) in dichloromethane (2 mL) and the resulting solution was stirred at room temperature for 10 min. The solvent was removed by rotary evaporation.

4.7.1. 3-Oxo-4-ethyl-5-{4,5-bis(ferrocenecarbonyl)-1,3-dithiol-2-ylidene}[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione (8a). Purified by flash chromatography (cyclohexane–diethyl ether 1:1); red solid (93 mg, 0.120 mmol, 97%), mp >300°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.90–4.88 (m, 1H, CH aromatic), 4.87–4.85 (m, 1H, CH aromatic), 4.72–4.59 (m, 6H, 6×CH aromatic), 4.37 (s, 5H, 5×CH aromatic), 4.35 (s, 5H, 5×CH aromatic), 3.64 (six signals, dq, J=14.4, 7.2 Hz, 1H, 1/2CH_2), 3.39 (six signals, dq, J=14.4, 7.2 Hz, 1H, 1/2CH_2), and 1.32 (t, J=7.2 Hz, 3H, CH_3); the low solubility of **8a** in common solvents precluded the acquisition of its ^{13}C NMR spectrum; IR (KBr, cm^{-1}) ν 1664 (C=O), 1612 (C=O), 1348, 1272 (C=S), 1085, 1049, 489; MS (FAB+) *m*/*z* 774 (M+1, 3), 663 (2), 633 (1), 577 (20), 95 (38), 81 (45), 69 (75), 55 (100). HRMS (FAB+), $(M+1)_{found}$=773.8791 $C_{32}H_{24}Fe_2NO_3S_6$ requires 773.8779.

4.7.2. (R_{Fc},$R_{Fc'}$)-3-Oxo-4-ethyl-5-{4,5-bis[α-(*p*-methoxyphenyl)ferrocenecarbonyl]-1,3-dithiol-2-ylidene}[1,2]-dithiolo[3,4-*b*][1,4]thiazine-6-thione (8b). Purified by flash chromatography (cyclohexane–diethyl ether 7:3); red solid (95 mg, 78%), mp 103–104°C (cyclohexane–diethyl ether). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48–7.13 (m, 4H, 4×CH aromatic), 6.72–6.64 (m, 3H, 3×CH aromatic), 6.44 (d, J=8.4 Hz, 1H, CH aromatic), 5.05–5.03 (m, 1H, CH aromatic), 4.92–4.89 (m, 1H, CH aromatic), 4.79–4.65 (m, 4H, 4×CH aromatic), 4.50 (s, 3H, 3×CH aromatic), 4.46 (s, 3H, 3×CH aromatic), 4.40 (s, 2H, 2×CH aromatic), 4.37 (s, 2H, 2×CH aromatic), 3.72 (s, 3H, CH_3), 3.68 (s, 1H, CH_3), 3.54 (s, 2H, CH_3), 3.40 (six signals, dq, J=14.0, 7.0 Hz, 1/2H, 1/4CH_2), 3.39 (six signals, dq, J=14.0, 7.0 Hz, 1/2H, 1/4CH_2), 3.00 (six signals, dq, J=14.0, 7.0 Hz, 1H, 1/2CH_2), and 1.15 (t, J=7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.68 (*C*=S), 189.63, 188.01, and 184.66 (3×*C*=O), 163.98, 158.72, 158.59, 158.54, 141.12, 140.53, 132.26, 131.50, 131.41, 131.24, 131.07, 130.23, 128.072, 127.94, 127.69, 126.89, 113.01, 112.86, 112.83, 112.59, 93.75, 93.61, 93.03, 92.54, 77.16, 76.36, 76.31, 76.15, 76.11, 72.08, 71.96, 71.92, 71.60, 71.52, 71.48, 71.42, 70.51, and 70.34 (38×sp^2 *tertiary* C, C and *C*H aromatic), 55.22, 55.14, 55.12, and 55.10 (4×*C*H_3), 47.68 (*C*H_2), 13.42, and 13.34 (2×*C*H_3); IR (KBr, cm^{-1}) ν 2955, 2924, 2852, 1667 (C=O), 1632 (C=O), 1520, 1405, 1342, 1244 (C=S), 1036, 828; MS (FAB+) *m*/*z* 985 (M^+, 15), 95 (45), 81 (50), 69 (85), 55 (100). HRMS (FAB+), M^+_{found}=984.9563 $C_{46}H_{35}Fe_2NO_5S_6$ requires 984.9538.

4.7.3. 4-Ethyl-3,5-di{4,5-bis(ferrocenecarbonyl)-1,3-dithiol-2-ylidene}[1,4]thiazine-2,6-dithione (10). 1,4-Bis-ferrocenylbut-2-yn-1,4-dione **7a** (83 mg, 0.184 mmol) was added to a solution of 4-ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*]-[1,4]thiazine-3,5-dithione **9** (25 mg, 0.074 mmol) and $Sc(OTf)_3$ (18 mg, 0.037 mmol) in dichloromethane (2 mL) and the resulting solution was stirred at room temperature for 30 min. The solvent was removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (cyclohexane–ethyl acetate 4:1) to give **10**, red solid (59 mg, 0.048 mmol, 65%), mp 152–153°C (cyclohexane–ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.88–4.61 (m, 16H, 16×CH aromatic), 4.37 (s, 10H, 10×CH aromatic), 4.25 (s, 10H, 10×CH aromatic), 3.60 (q, J=7.1 Hz, 2H, CH_2), and 1.46 (t, J=7.1 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.36 (*C*=S), 188.97, and 188.84 (2×*C*=O), 162.57, 139.08, 138.71, and 133.73 (4×sp^2 *tertiary* C), 78.00, and 77.73 (C aromatic), 74.05, 73.91, 73.82, 70.83, 70.75, 70.70, 70.62, 70.56, and 70.43 (9×*C*H aromatic), 49.69 (*C*H_2), and 13.97 (*C*H_3); IR (KBr, cm^{-1}) ν 2922, 2851, 1630 (C=O), 1441, 1270 (C=S), 1081, 486; MS (FAB+) *m*/*z* 1239 (M^+, 6), 663 (7), 186 (Fc^+, 6), 121 ($CpFe^+$, 15), 95 (38), 81 (50), 69 (80), 55 (100). HRMS (FAB+), $(M+1)_{found}$=1239.8517 $C_{56}H_{42}Fe_4NO_4S_7^+$ requires 1239.8556.

Acknowledgements

We thank Dr Gabriel García-Herbosa, Departamento de

Química, Universidad de Burgos, for assistance in the electrochemical study. We gratefully acknowledge financial support from the Spanish Institutions: Dirección General de Investigación (Project ref. BQU2001-0258 and grant no. FP97-08858491), Junta de Castilla y León, Consejería de Educación y Cultura, y Fondo Social Europeo (Project ref. BU07/00B) and Junta de Extremadura, Consejería de Educación y Juventud, y Fondo Social Europeo (Project ref. IPR00C043).

References

1. (a) Adams, R. D. *J. Organomet. Chem.* **2001**, *637–639*, 1. For a general review see: (b) Togni, A.; Hayashi, T. *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*. VCH-Wiley: Weinheim-New York, 1995.
2. Recent examples are: (a) Sancenon, F.; Benito, A.; Hernández, F. J.; Lloris, J. M.; Martínez-Manez, R.; Pardo, T.; Soto, J. *Eur. J. Inorg. Chem.* **2002**, 866–875. (b) Sutcliffe, O. B.; Chesney, A.; Bryce, M. R. *J. Organomet. Chem.* **2001**, *637–639*, 134–138. (c) Hall, C. D.; Kirkovits, G. J.; Djedovic, N. K.; Truong, T. K. U.; Tucker, J. R. H. *Pure Appl. Chem.* **1998**, *70*, 2359–2363. For a review, see: (d) Beer, P. D.; Gale, P. A.; Chen, G. Z. *Coord. Chem. Rev.* **1999**, *186*, 3–36.
3. Recent examples are: (a) Gale, P. A.; Hurthouse, M. B.; Light, M. E.; Sessler, J. L.; Warriner, C. N.; Zimmerman, R. S. *Tetrahedron Lett.* **2001**, *42*, 6759–6762. (b) Scherer, M.; Sessler, J. L.; Gebauer, A.; Lynch, V. *Chem. Commun.* **1998**, 85–86. For reviews, see: (c) Beer, P. D.; Cadman, J. *Coord. Chem. Rev.* **2000**, *205*, 131–155. (d) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71–80.
4. Osella, D.; Nervi, C.; Galeotti, F.; Cavigiolio, G.; Vessieres, A.; Jaouen, G. *Helv. Chim. Acta* **2001**, *84*, 3289–3298.
5. (a) Collinson, S. R.; Gelbrich, T.; Hurstouse, M. B.; Tucker, J. H. R. *Chem. Commun.* **2001**, 555–556. (b) See also: Collinson, M. B.; Tucker, J. H. R. *Chem. Soc. Rev.* **2002**, *31*, 147–156.
6. (a) Takase, M.; Inouye, M. *Chem. Commun.* **2001**, 2432–2433. (b) Inouye, M.; Takase, M. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 1746–1748.
7. Yu, C. J.; Wan, Y. J.; Yowanto, H.; Li, J.; Tao, C. L.; James, M. D.; Tan, C. L.; Blackburn, G. F.; Meade, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 11155–11161.
8. (a) Nakayama, M.; Ihara, T.; Nakano, K.; Maeda, M. *Talanta* **2002**, *56*, 857–866. (b) Ihara, T.; Nakayama, M.; Murata, M.; Nakano, K.; Maeda, M. *Chem. Commun.* **1997**, 1609–1610.
9. Recent examples are: (a) Fukuzawa, S.; Fujimoto, K.; Komuro, Y.; Matsuzawa, H. *Org. Lett.* **2002**, *4*, 707–709. (b) You, S. L.; Zhu, X. Z.; Luo, Y. M.; Hou, X. L.; Dai, L. X. *J. Am. Chem. Soc.* **2001**, *123*, 7471–7472. (c) Deng, W. P.; You, S. L.; Hou, X. L.; Dai, L. X.; Yu, Y. H.; Xia, W.; Sun, J. *J. Am. Chem. Soc.* **2001**, *123*, 6508–6519. (d) Sirol, S.; Courmarcel, J.; Mostefai, N.; Riant, O. *Org. Lett.* **2001**, *3*, 4111–4113. (e) Argouarch, G.; Samuel, O.; Riant, O.; Daran, J. C.; Kagan, H. B. *Eur. J. Org. Chem.* **2000**, 2893–2899. For a review, see: (f) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377–2407.
10. Recent examples are: (a) Caramo, M.; Curad, T.; Deschenaux, R.; Even, M.; Marcaccio, M.; Paolucci, F.; Prato, M.; Bofia, S. *J. Mater. Chem.* **2002**, *12*, 829–833. (b) Even, M.; Heinrich, B.; Guillon, D.; Guldi, D. M.; Prato, M.; Deschenaux, R. *Chem. Eur. J.* **2001**, *7*, 2595–2604. (c) Seo, J. S.; Yoo, Y. S.; Choi, M. G. *J. Mater. Chem.* **2001**, *11*, 1332–1338. (d) Nakamura, N.; Maekawahara, H.; Hanasaki, T.; Yamaguchi, T. *Mol. Cryst. Liq. Cryst.* **2000**, *352*, 559–566. (e) Deschenaux, R.; Schweissguth, M.; Vilches, M. T.; Levelut, A. M.; Hautot, D.; Long, G. J.; Luneau, D. *Organometallics* **1999**, *18*, 5553–5559. (f) For a review, see: Imrie, C.; Engelbrecht, P.; Loubser, C.; McCleland, C. W. *Appl. Organomet. Chem.* **2001**, *15*, 1–15.
11. (a) Iyoda, M.; Takano, T.; Otani, N.; Ugawa, K.; Yoshida, M.; Matsuyama, H.; Kuwatani, Y. *Chem. Lett.* **2001**, 1310–1311. (b) Liu, S. G.; Pérez, I.; Martín, N.; Echegoyen, L. *J. Org. Chem.* **2000**, *65*, 9092–9102.
12. Sporer, C.; Ruiz-Molina, D.; Wurst, K.; Kopacka, H.; Veciana, J.; Jaitner, P. *J. Organomet. Chem.* **2001**, *637*, 507–513.
13. Recent examples are: (a) Nemykin, V. N.; Kobayashi, N. *Chem. Commun.* **2001**, 165–166. (b) Stankovic, E.; Toma, S.; Van Boxel, R.; Asselberghs, I.; Persoons, A. *J. Organomet. Chem.* **2001**, *637–639*, 426–434. (c) Moore, A. J.; Chesney, A.; Bryce, M. R.; Batsanov, A. S.; Kelly, J. F.; Howard, J. A. K.; Perepichka, I. F.; Perepichka, D. F.; Meshulam, G.; Berkovic, G.; Kotler, Z.; Mazor, R.; Khodorkovsky, V. *Eur. J. Org. Chem.* **2001**, 2671–2687.
14. Recent examples are: (a) Fukuzumi, S.; Okamoto, K.; Imahori, H. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 620–622. (b) Gan, J.; Tian, H.; Wang, Z. H.; Chen, K. H.; Hill, J.; Lane, P. A.; Rahn, M. D.; Fox, A. M.; Bradley, D. D. C. *J. Organomet. Chem.* **2002**, *645*, 168–175. (c) Plenio, H.; Aberle, C. *Chem. Eur. J.* **2001**, *7*, 4438–4446. (d) Plenio, H.; Aberle, C.; Al Shihadeh, Y.; Lloris, J. M.; Martinez-Manez, R.; Pardo, T.; Soto, J. *Chem. Eur. J.* **2001**, *7*, 2848–2861. (e) Imahori, H.; Guldi, D. M.; Tamaki, K.; Yoshida, Y.; Luo, C. P.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 6617–6628. (f) Imahori, H.; Tamaki, K.; Guldi, D. M.; Luo, C. P.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 2607–2617. For a review, see: (g) Kaifer, A. E. *Acc. Chem. Res.* **1999**, *32*, 62–71.
15. Recent examples are: (a) Stone, D. L.; Smith, D. K.; McGrail, P. T. *J. Am. Chem. Soc.* **2002**, *124*, 856–864. (b) Palomero, J.; Mata, J. A.; González, F.; Peris, E. *New J. Chem.* **2002**, *26*, 291–297. (c) Ashton, P. R.; Balzani, V.; Clemente-León, M.; Colonna, B.; Credi, A.; Jayaraman, N.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. *Chem. Eur. J.* **2002**, *8*, 673–684. (d) Kim, C.; Park, E.; Song, C. K.; Koo, B. W. *Synth. Met.* **2001**, *123*, 493–496. (e) Sengupta, S.; Sadhukhan, S. K. *Organometallics* **2001**, *20*, 1889–1891. (f) Nlate, S.; Ruiz, J.; Blais, J. C.; Astruc, D. *Chem. Commun.* **2000**, 417–418. For a review, see: (g) Cardona, C. M.; Mendoza, S.; Kaifer, A. E. *Chem. Soc. Rev.* **2000**, *29*, 37–42.
16. Recent examples are: (a) Fabian, K. H. H.; Lindner, H.-J.; Nimmerfroh, N.; Hafner, K. *Angew. Chem. Int. Ed.* **2001**, *40*, 3402–3405. (b) Liu, C.-M.; Liang, Y.; Wu, X.; Liu, W.; Ma, Y. *J. Organomet. Chem.* **2001**, *637–639*, 723–726. (c) Wong, W. Y.; Lu, G. L.; Ng, K. F.; Wong, C. K.; Choi, K. H. *J. Organomet. Chem.* **2001**, *637–639*, 159–166.
17. Recent examples are: (a) Thomas, K. R. J.; Lin, J. T. *J. Organomet. Chem.* **2001**, *637–639*, 139–144. (b) Poon, K. W.; Liu, W.; Chan, P. K.; Yang, Q. C.; Chan, T. W. D.; Mak, T. C. W.; Ng, D. K. P. *J. Org. Chem.* **2001**, *66*, 1553–1559.
18. (a) Mamane, V.; Gref, A.; Lefloch, F.; Riant, O. *J. Organomet. Chem.* **2001**, *637–639*, 84–88. (b) Mamane, V.; Riant, O. *Tetrahedron* **2001**, *57*, 2555–2561. (c) Skibniewski, A.; Bluet,

G.; Druze, N.; Riant, O. *Synthesis* **1999**, 459–462. (d) Neo, A. G.; Gref, A.; Riant, O. *Chem. Commun.* **1998**, 2353–2354.
19. (a) Riant, O.; Argouarch, G.; Guillaneux, D.; Samuel, O.; Kagan, H. B. *J. Org. Chem.* **1998**, *63*, 3511–3514. (b) Riant, O.; Samuel, O.; Flessner, T.; Taudien, S.; Kagan, H. B. *J. Org. Chem.* **1997**, *62*, 6733–6745. (c) Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 5835–5836.
20. (a) Marcos, C. F.; Polo, C.; Rakitin, O. A.; Rees, C. W.; Torroba, T. *Angew. Chem. Int. Ed.* **1997**, *36*, 281–283. (b) Rees, C. W.; White, A. J. P.; Williams, D. J.; Rakitin, O. A.; Marcos, C. F.; Polo, C.; Torroba, T. *J. Org. Chem.* **1998**, *63*, 2189–2196. (c) Marcos, C. F.; Rakitin, O. A.; Rees, C. W.; Torroba, T.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 29–30.
21. (a) Marcos, C. F.; Polo, C.; Rakitin, O. A.; Rees, C. W.; Torroba, T. *Chem. Commun.* **1997**, 879–880. (b) Konstantinova, L. S.; Obruchnikova, N. V.; Rakitin, O. A.; Rees, C. W.; Torroba, T. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3421–3427.
22. (a) Marcos, C. F.; Rakitin, O. A.; Rees, C. W.; Souvorova, L. I.; Torroba, T.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 453–454. (b) Rees, C. W.; White, A. J. P.; Williams, D. J.; Rakitin, O. A.; Marcos, C. F.; Torroba, T. *J. Org. Chem.* **1999**, *64*, 5010–5016.
23. Barriga, S.; Konstantinova, L. S.; Marcos, C. F.; Rakitin, O. A.; Rees, C. W.; Torroba, T.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2237–2241.
24. Rees, C. W.; Rakitin, O. A.; Marcos, C. F.; Torroba, T. *J. Org. Chem.* **1999**, *64*, 4376–4380.
25. (a) Barriga, S.; Fuertes, P.; Marcos, C. F.; Miguel, D.; Rakitin, O. A.; Rees, C. W.; Torroba, T. *J. Org. Chem.* **2001**, *66*, 5766–5771. (b) Barriga, S.; Fuertes, P.; Marcos, C. F.; Rakitin, O. A.; Torroba, T. *J. Org. Chem.* **2002**, *67*, 6439–6448.
26. (a) Schloegl, K.; Mohar, A. *Monatsh. Chem.* **1962**, *93*, 861–876. (b) Schloegl, K.; Steyrer, W. *Monatsh. Chem.* **1965**, *96*, 1520–1535. (c) Akiyama, T.; Hattori, T.; Ito, K.; Uryu, T.; Kajitani, M.; Sugimori, A. *Chem. Lett.* **1980**, 361–364.
27. For a review, see: Kobayashi, S. *Eur. J. Org. Chem.* **1999**, 15–27.
28. For a review, see: Segura, J. L.; Martín, N. S. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 1372–1409.
29. (a) Iyoda, M.; Takano, T.; Otani, N.; Ugawa, K.; Yoshida, M.; Matsuyama, H.; Kuwatani, Y. *Chem. Lett.* **2001**, 1310–1311. (b) Liu, S. G.; Pérez, I.; Martín, N.; Echegoyen, L. *J. Org. Chem.* **2000**, *65*, 9092–9102. (c) Herranz, M. A.; Illescas, B.; Martín, N.; Luo, C. P.; Guldi, D. M. *J. Org. Chem.* **2000**, *65*, 5728–5738. (d) Bryce, M. R.; Coffin, M. A.; Skabara, P. J.; Moore, A. J.; Batsanov, A. S.; Howard, J. A. K. *Chem. Eur. J.* **2000**, *6*, 1955–1962. (e) Lee, H. J.; Noh, D. Y.; Underhill, A. E.; Lee, C. S. *J. Mater. Chem.* **1999**, *9*, 2359–2363. (f) Noh, D. Y.; Lee, H. J.; Underhill, A. E. *Synth. Met.* **1999**, *102*, 1698. (g) Zurcher, S.; Petrig, J.; Perseghini, M.; Gramlich, V.; Worle, M.; von Arx, D.; Togni, A. *Helv. Chim. Acta* **1999**, *82*, 1324–1359. (h) Moore, A. J.; Bryce, M. R.; Skabara, P. J.; Batsanov, A. S.; Goldenberg, L. M.; Howard, J. A. K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3443–3449. (i) Hobi, M.; Ruppert, O.; Gramlich, V.; Togni, A. *Organometallics* **1997**, *16*, 1384–1391.
30. (a) Perepichka, D. F.; Perepichka, I. F.; Popov, A. F.; Bryce, M. R.; Batsanov, A. S.; Chesney, A.; Howard, J. A. K.; Sokolov, N. I. *J. Organomet. Chem.* **2001**, *637–639*, 445–462. (b) Green, A.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. *J. Organomet. Chem.* **1999**, *590*, 180–183.