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Iminophosphorane-based synthesis of multinuclear ferrocenyl urea, thiourea and guanidine derivatives and exploration of their anion sensing properties

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ABSTRACT

One-flask preparation of bisferrocenyl-substituted urea and thiourea and trisferrocenyl-substituted guanidine have been achieved from the iminophosphorane derived from ferrocenemethyl azide by using aza-Wittig reactions with carbon dioxide and carbon disulfide. Electrochemical studies indicate that there is no electronic communications between the peripheral ferrocene units and only one reversible redox wave is observed, which underwent a remarkable cathodic shift ($\Delta E_{1/2}$=100–170 mV) in the presence of dihydrogenphosphate anion.

1. Introduction

Aza-Wittig methodologies based on the iminophosphorane chemistry have attracted considerable attention recently because of its high potential for the synthesis of nitrogen-containing heterocycles and natural products.[1] In this context, a number of ferrocenyl-substituted azaheterocyles such as: imidazoles,[2] quinolines,[3] oxazoles,[4] thiazolines,[5] thiazoles[6] and nitrogen-rich multinuclear [*m.n*] ferrocenophanes[7] have been prepared, and some of them have proved to be of interest as molecular chemosensors for sensing transition and heavy-metal cations.

Artificial neutral anion receptors became attractive targets of studies because of their analogy to natural systems and because their selectivities were higher than in the case of charged ligands. The redox-active ferrocene moiety has been exploited in the electrochemical sensing of anions, electrochemical ferrocene-based receptors for anions are expected to show cathodic shifts in their redox process when complexed to an anion as they are easier to oxidize or harder to reduce than the free redox-active receptor. In this context, a number of anion receptors have been reported so far, which have various functional groups as anion-binding site. Being neutral these receptors have no inherent electrostatic attraction for anions, which makes the stability constants smaller than those of the analogous cobaltocenium systems. Electrostatic interaction can, however, be switched on by oxidation of the ferrocene group to the ferrocenium ion, and consequently these molecules exhibit interesting electrochemical anion-recognition effects.[8]

Urea is an attractive building block for anion receptors because it contributes two relatively strong hydrogen-bonding sites.[9] The two N–H groups can bind with a single acceptor atom to yield a six-membered chelate ring or with two adjacent oxygen atoms in an oxyanion to yield an eight-membered chelate ring. A variety of urea-based hosts containing one or more urea subunits have been designed and tested for anion recognition and sensing over the past years.[10] New insights into the nature of urea–anion interactions providing structural criteria for the deliberate design of anion selective receptors containing two or more urea binding groups have also been recently reported.[11] There are, however, few examples of urea/ferrocene redox-active anionophores.[12]

Likewise, thiourea subunit is currently used in the design of neutral anion-binding receptors. It provides two hydrogen-bond donor groups that point in the same direction and which are spaced appropriately to interact with a range of anionic substrates.[13] Its synthetic accessibility has allowed its inclusion in a wide variety of anion receptors with much effort still devoted to the synthesis and study of these effective receptor systems.

There is, however, only one example of thiourea/ferrocene redox-active anionophore, although it could not be exploited in the selective electrochemical sensing of anions.[14]

The guanidine function due to its amphoteric nature has a rich history in biological[15] and artificial receptors.[16] The guanidinium group within a variety of molecular architectures forms strong non-covalent interactions with anionic groups through hydrogen bonding and charge pairing interactions. In addition, deprotonated guanidines

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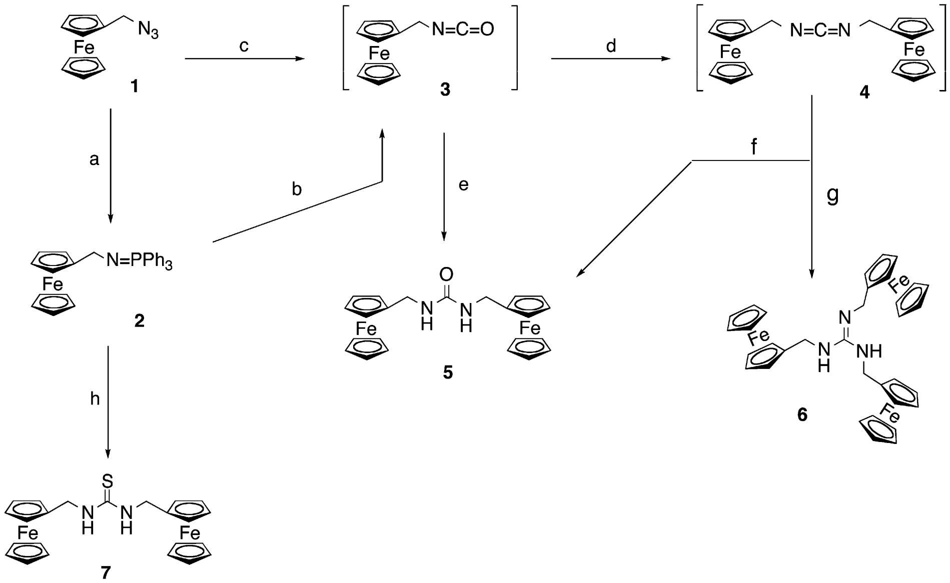

Scheme 1. Reagents and conditions: (a) Ph_3P, Et_2O, rt; (b) CO_2, toluene, rt; (c) PPh_3, CO_2, toluene, 60 °C, N_2; (d) triphenylphosphiniminomethylferrocene or ferrocenemethyl azide, PPh_3, toluene, rt; (e) ferrocenemethyl amine, THF, rt; (f) H_2O, THF, rt; (g) ferrocenemethyl amine, TBAF, THF, rt; (h) ferrocenemethyl amine, CS_2, THF, rt.

(guanidinates) have the potential to develop into valuable ancillary ligands in coordination and organometallic chemistry,[17] although the straightforward coordination of neutral guanidines to metal centres remains comparatively underdeveloped,[18] and metal-guanidinyl complexes are barely known and unexplored.[19]

Ferrocene-based ligands have been found to be useful for incorporating redox functions into supramolecular complexes that bind and allow the electrochemical sensing of cations,[20] anions[21] and neutral molecules[22] by a change in the oxidation potential of the ferrocene. Despite the rich chemistry of guanidines, as the binding site, and ferrocene, as the redox signalling unit, only few examples, however, of guanidinyl–ferrocene derivatives have been described.[23]

Here we present the iminophosphorane-mediated synthesis and anion coordination properties of simple ferrocene-based urea, thiourea and guanidine bearing two or three ferrocene redox units linked through an anion putative binding site either linearly or joined through a star-shape fashion.

2. Results and discussion

2.1. Synthesis

Staüdinger reaction of ferrocenemethyl azide **1**, readily available from trimethylferrocenemethyl ammonium iodide and sodium azide,[24] with triphenylphosphine in diethyl ether at room temperature provided triphenyliminophosphorane **2** as a crystalline solid in 83% yield. Bisferrocenemethyl urea **5** was prepared by one-flask process involving the initial formation of the not isolated ferrocenemethyl isocyanate **3**, from azide **1** by sequential treatment with triphenylphosphine and then carbon dioxide, and subsequent treatment with ferrocenylmethyl amine. Alternatively, when the not isolated isocyanate **3** was treated with iminophosphorane **2** yielded bisferrocenemethyl carbodiimide **4**, which was used without purification for the next step. When carbodiimide **4** was treated with water in tetrahydrofuran solution at room temperature gave bisferrocenemethyl urea **5** in 90% yield, whereas the addition of ferrocenemethyl amine promoted by tetrabutylammonium fluoride (TBAF)[25] yielded trisferrocenemethyl guanidine **6** in 67% yield. Preparation of bisferrocenemethyl thiourea **7** was achieved in 51% yield directly from iminophosphorane **2** by sequential treatment with ferrocenylmethyl amine and then carbon disulfide in tetrahydrofuran at room temperature (Scheme 1).

2.2. Electrochemistry

One interesting attribute of ferrocene derivatives **5**–**7** is the presence of N–H anion-binding sites in proximity of the ferrocene redox-active moieties. The electrochemical properties of receptors **5**–**7** as its own as well as in the presence of variable concentrations of Cl^-, F^-, AcO^-, NO_3^-, HSO_4^- and $H_2PO_4^-$ (in the form of their corresponding tetrabutylammonium salts) as guest anionic species were investigated using cyclic (CV) and differential pulse (DPV) voltammetries. DPV technique has been employed to obtain well-resolved potential information, while the individual redox process is poorly resolved in the CV experiments in which individual $E_{1/2}$ potentials cannot be easily or accurately extracted from these data.

The CV response of **5**–**7** in DMF, also containing 0.1 M $TBAPF_6$ as supporting electrolite, showed only one superimposed single-step oxidation process in the range $E_{1/2}$=0.49–053 V versus decamethylferrocene (DMFc), which implies that the aza-functionalized bridge does not allow the peripheral ferrocenyl subunits to communicate electronically with each other, and they are oxidized independently (Table 1). Preliminary electrochemical anion sensing studies revealed behaviour that was slightly different for each one of the receptors.

On stepwise addition of $H_2PO_4^-$ anion to an electrochemical solution of receptor **5** a strong cathodic shift of the oxidation peak

Table 1
Voltametric and complexation data of ligands **5**–**7** obtained in DMF at 298 K

Receptor[a]	$E_{1/2}$ (V)[b] free	$E_{1/2}$ (V)[b] complex	$\Delta E_{1/2}$ (mV)[c]
5	0.50		
5·F^-		0.46	40
5·AcO^-		0.50	—
5·$H_2PO_4^-$		0.39	110
6	0.49		
6·F^-		0.38	110
6·AcO^-		0.35	140
6·$H_2PO_4^-$		0.32	170
7	0.53		
7·F^-		0.48	50
7·AcO^-		0.46	70
7·$H_2PO_4^-$		0.43	100

[a] Anions added as their tetrabutylammonium salts.
[b] Potential formal is in V versus decamethylferrocene.
[c] Calculated from $\Delta E_{1/2}$=$E_{1/2}$ (free ligand)−$E_{1/2}$ (complexed).

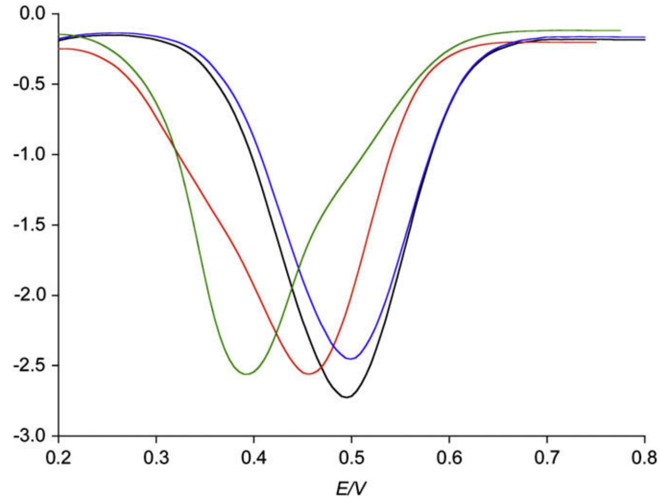

Figure 1. Changes in redox properties of receptor **5** (c=5×10^{-4}) in DMF (black) upon addition of $H_2PO_4^-$ (c=1.25×10^{-2}) (green), AcO^-, (c=1.25×10^{-2}) (blue) and F^- (c=1.25×10^{-2}) (red) anions.

from $E_{1/2}$=0.50 V to $E_{1/2}$=0.39 V ($\Delta E_{1/2}$=110 mV) was observed; maximum perturbation of the DPV was obtained with 2 equiv of added $H_2PO_4^-$ anion. Remarkably, the presence of Cl^-, AcO^-, NO_3^-, HSO_4^- anions had no effect neither on the CV nor DPV, even when present in large excess, only the presence or the F^- anion induced a modest cathodic shift ($\Delta E_{1/2}$=40 mV) (Fig. 1).

A similar study of the anion-recognition properties of receptor **6** has been carried out. The CV response of this trisferrocenyl derivative showed a reversible oxidation process at $E_{1/2}$=0.49 V versus DMFc redox couple. It should be mentioned that electrochemical anion sensing experiments were carried out by DPV. This study revealed a clear electrochemical response on the stepwise addition of F^-, AcO^- and $H_2PO_4^-$ anions, giving rise to cathodic shifts of $\Delta E_{1/2}$ =110 mV for F^-, $\Delta E_{1/2}$=140 mV for AcO^- and $\Delta E_{1/2}$=170 mV for $H_2PO_4^-$ anions, respectively, reflecting a strong binding of the guests upon oxidation of the ferrocene unit (Fig. 2).

Likewise the ferrocene/ferrocenium redox couple or thiourea receptor **7**, $E_{1/2}$=0.53 V versus DMFc, was also cathodically shifted in the same order, although in less extension, in the presence of $H_2PO_4^-$ ($\Delta E_{1/2}$=100 mV), AcO^- ($\Delta E_{1/2}$=70 mV) and F^- ($\Delta E_{1/2}$=50 mV) anions (Fig. 3).

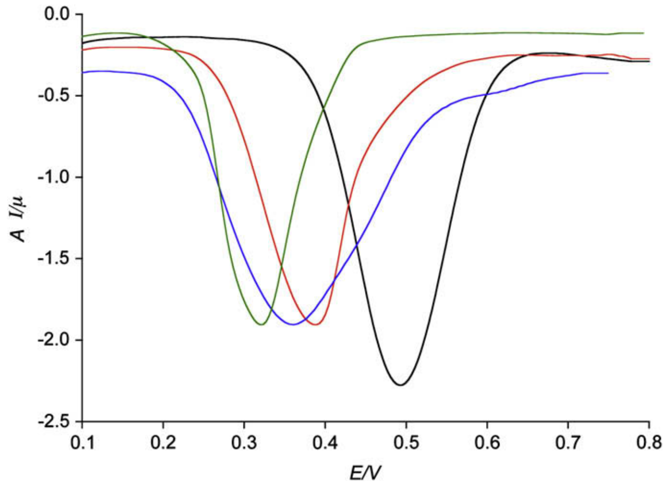

Figure 2. Changes in redox properties of receptor **6** (c=2.5×10^{-4}) in DMF (black) upon addition of $H_2PO_4^-$ (c=10^{-2}) (green), AcO^-, (c=10^{-2}) (blue) and F^- (c=10^{-2}) (red) anions.

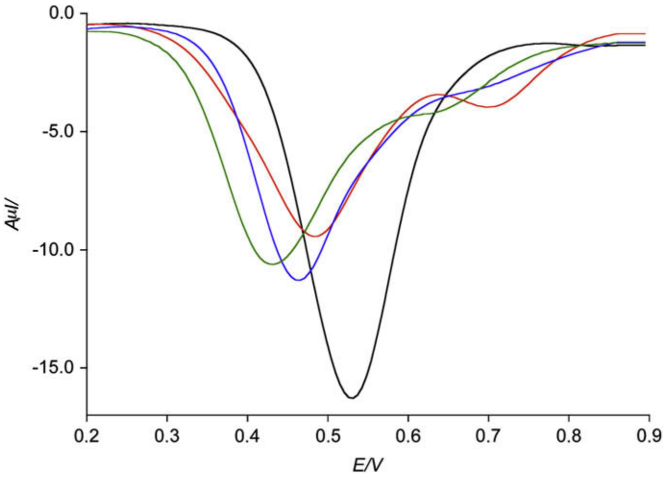

Figure 3. Changes in redox properties of receptor **7** (c=5×10^{-4}) in DMF (black) upon addition of $H_2PO_4^-$ (c=2.5×10^{-2}) (green), AcO^-, (c=2.5×10^{-2}) (blue) and F^- (c=2.5×10^{-2}) (red) anions.

3. Conclusions

Starting from the readily available ferrocenemethyl azide and ferrocenemethyl amine and using aza-Wittig methodologies we have able to prepare poliferrocenyl derivatives in which the metallocene units are linked through urea, thiourea and guanidine bridges. Thus aza-Wittig reaction with carbon dioxide under different conditions provided the key intermediates ferrocenemethyl isocyanate and bis(ferrocenemethyl)carbodiimide, which were converted into the corresponding urea **5** and guanidine **6**, respectively. Thiourea **7** was prepared directly from the iminophosphorane by aza-Wittig type reaction with carbon disulfide. These receptors display electrochemical responses towards dihydrogenphosphate, acetate and fluoride anions, being the tris(ferrocenemethyl)guanidine what showed largest cathodic shifts of the ferrocene oxidation wave. Whereas the urea derivative **5** exhibited a high selectivity for the dihydrogenphosphate anion towards all the tested anions.

4. Experimental section

4.1. General experimental procedures

Melting points were determined on a hot-plate melting point Reichert apparatus and are uncorrected. IR spectra were determined as Nujol emulsions or films in a Nicolet impact 400 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded at 300 and 400 MHz in a Bruker Advance spectrometer. Chemical shifts refer to signals of tetramethylsilane. Carbon atom types (C, CH, CH_2, CH_3) were determined with the DEPT pulse sequence. CV and DPV techniques were performed on a potentiostat/galvanostat controlled by a personal computer and driven by dedicated software with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and an SCE reference electrode. The experiments were carried out with 2.5×10^{-4} M solution of simple in DMF containing 0.1 M solution of $(n\text{-}C_4H_9N)_4PF_6$ as supporting electrolyte. All the potential values reported are relative to the $DMFc^+$/DMFc couple at room temperature. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min and the working electrode was cleaned after each run. The cyclic voltammograms were recorded with a scan rate increasing from 0.05 to 1.00 V s^{-1}, while the DPV were recorded at a scan rate of 4 mV s^{-1} with a pulse height of 10 mV and a step time of 50 ms. Typically, a receptor (2.5×10^{-4} mol) was dissolved in DMF

(5 mL) and TBAHF (base electrolyte) (0.1 mol) added. The guest under investigation was then added as a 0.1 M solution in appropriate solvent using a microsyringe whilst the differential pulse voltammetric properties of the solution were monitored. Decamethylferrocene (DMFc) (−0.07 V vs SCE) was used as an external reference both for potential calibration and for reversibility criteria.

4.2. Triphenylphosphoranylideneaminomethyl ferrocene (2)

A mixture of ferrocenemethyl azide **1** (0.24 g, 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) in diethyl ether (20 mL) was stirred at room temperature for 4 h. The yellow precipitated solid was collected by filtration, washed with cooled diethyl ether (3×2 mL), air-dried and crystallized from dichloromethane/*n*-hexane to give triphenyliminophosphorane **2** as yellow prisms in 83% yield; mp 87 °C. ν_{max} (Nujol)/cm^{-1}: 1585, 1435, 1275, 1207, 1113, 1101, 997, 744, 721 and 696. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.95 (pt, 2H, *J*=1.8 Hz), 3.98 (s, 5H), 4.07 (pt, 2H, *J*=1.8 Hz), 4.13 (d, 2H, *J*=8.5 Hz), 7.47 (m, 9H) and 7.65 (dd, 6H, *J*=8.4 Hz, *J*=11.4 Hz). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 44.6 (CH$_2$, ^2J(P,C)=4.7 Hz), 66.9 (CH), 68.11 (CH), 68.5 (CH), 92.8 (q, ^3J(P,C)=14.7 Hz), 128.1 (CH, ^3J(P,C)=11.4 Hz), 131.0 (CH, ^4J(P,C)=2.0 Hz), 131.9 (q, ^1J(P,C)=95.2 Hz) and 132.5 (CH, ^4J(P,C)=8.9 Hz); δ_P (121.4 MHz, CDCl$_3$): 10.63; MS EI *m*/*z* (%): 476 (M$^+$+1, 13), 475 (M$^+$, 43), 262 (66), 213 (100), 152 (22), 121 (49) and 78 (26). Found: C, 73.36; H, 5.59; N, 2.91. $C_{29}H_{26}FeNP$ (475.36) requires: C, 73.28; H, 5.51; N, 2.95.

4.3. *N*,*N*′-Bisferrocenemethyl urea (5)

4.3.1. *Procedure a*

A solution of ferrocenemethyl azide (0.24 g, 1 mmol) in dry toluene (40 mL) was heated at 60 °C under N$_2$. A constant flow of CO$_2$(g) was passed through the solution at the same temperature for 10 min. Then a solution of triphenylphosphine (0.26 g, 1 mmol) dry toluene (4 mL) was added at 60 °C maintaining the constant flow of CO$_2$(g). The resulting mixture was stirred for 3 h. The reaction course was monitored by IR spectroscopy. The intense band assigned to the azido group (2096 cm^{-1}) was disappeared and the IR spectrum showed an intense band at 2260 cm^{-1}, assigned to the isocyanate functional group. Then a solution of ferrocenemethyl amine (0.21 g, 1 mmol) in dry toluene (4 mL) was added at room temperature under N$_2$. The reaction mixture was kept overnight at room temperature and concentrated to dryness under reduced pressure. The yellow solid was collected by filtration, washed with cooled diethyl ether (3×2 mL), air-dried and crystallized from dichloromethane/*n*-hexane to give urea **5** in 90% yield%; mp 234–235 °C (yellow prisms from dichloromethane/*n*-hexane). ν_{max} (Nujol)/cm^{-1}: 3312, 1733, 1612, 1581, 1255, 1107 and 818. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 3.95 (d, 4H, *J*=4.9 Hz), 4.12 (m, 18H) and 6.05 (t, 2H, *J*=4.9 Hz). ^{13}C NMR (75.4 MHz, DMSO-*d*$_6$): δ 38.4 (CH$_2$), 67.3 (CH), 67.6 (CH), 68.4 (CH), 87.6 (q) and 157.6 (q). MS EI *m*/*z* (%): 457 (M$^+$+1, 38), 456 (M$^+$, 100), 241 (63), 199 (99) and 121 (84). Found: C, 60.69; H, 5.41; N, 6.18. $C_{23}H_{24}Fe_2N_2O$ (456.15) requires: C, 60.56; H, 5.30; N, 6.14.

4.3.2. *Procedure b*

A solution of triphenyliminophosphorane **2** (0.47 g, 1 mmol) in dry toluene (40 mL) was heated at 60 °C under N$_2$. A constant flow of CO$_2$(g) was passed through the solution at the same temperature, until the IR spectrum showed a strong band at 2260 cm^{-1} indicative of the isocyanate formation (about 3 h). Then a solution of ferrocenemethyl azide (0.24 g, 1 mmol) in dry toluene (4 mL) was added at 60 °C under N$_2$, and stirred for 10 min. Afterwards, a solution of triphenylphosphine (0.26 g, 1 mmol) in the same solvent (4 mL) was added and the resulting solution was maintained at the same conditions for 1 h. The reaction mixture was allowed to warm at room temperature and then concentrated to dryness under reduced pressure. The IR spectrum of the reaction crude showed an intense band at 2119 cm^{-1} due to the formed carbodiimide. The crude was extracted with *n*-hexane (3×5 mL) and the combined organic layers were concentrated to dryness under reduced pressure to yield carbodiimide **4** as a yellowish oil. A solution of carbodiimide **4** in wet tetrahydrofuran (10 mL) was stirred at room temperature for 12 h. The reaction mixture was dried over anhydrous magnesium sulfate, filtered off and concentrated to dryness under reduced pressure. The resulting crude was purified by column chromatography (eluent: ethyl acetate/*n*-hexane, 3:1) to give urea **5** as a yellow solid in 93%.

4.4. *N*,*N*,*N*″-Trisferrocenemethyl guanidine (6)

Anhydrous magnesium sulfate (2 g) was added to a solution of carbodiimide **4** (0.24 g, 0.5 mmol) in anhydrous tetrahydrofuran (25 mL) under N$_2$. The suspension was stirred at room temperature for 10 min. Then a solution of ferrocenemethyl amine (0.32 g, 1.5 mmol) in anhydrous tetrahydrofuran (3 mL) was added. The resulting mixture was stirred at room temperature for 10 min and a 1 M solution of TBAF in anhydrous tetrahydrofuran (1.5 mL, 1.5 mmol) was added. The mixture was stirred at room temperature until the intense band (2119 cm^{-1}) due to the carbodiimide group was disappeared (about 12 h). The result mixture was filtered off and the filtrate was poured into Na$_2$HPO$_4$ buffer (pH=7, 10 mL) and extracted with ethyl acetate (3×10 mL). The organic layers were washed with a saturated NaCl solution (2×10 mL) and water (2×10 mL), and concentrated to dryness. The remaining yellow solid was slurried with diethyl ether, filtered, air-dried and recrystallized from methanol to give guanidine **6** as yellow prisms in 67% yield; mp >300 °C decomposes. ν_{max} (Nujol)/cm^{-1}: 3412 (NH), 3283 (NH), 1624, 1168, 1082 and 813. ^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ 2.50 (s, 6H, 3×CH$_2$), 4.16 (m, 27H) and 7.65 (br s, 2H, 2×NH). ^{13}C NMR (75.4 MHz, DMSO-*d*$_6$): 40.3 (CH$_2$), 67.5 (CH), 68.2 (CH), 68.2 (CH), 82.9 (q) and 152.9 (q). MS EI *m*/*z* (%): 653 (M$^+$, 11), 456 (19), 413 (9), 214 (35), 199 (74), 142 (100) and 121 (44). MS (FAB$^+$) *m*/*z* (%): 654 (M$^+$+1, 100), and 653 (M$^+$, 15). Found: C, 62.63; H, 5.49; N, 6.51. $C_{34}H_{35}Fe_3N_3$ (653.21) requires: C, 62.52; H, 5.40; N, 6.43.

4.5. *N*,*N*′-Bisferrocenemethyl thiourea (7)

A solution of triphenyliminophosphorane **2** (0.24 g, 0.5 mmol) and ferrocenemethyl amine (0.21 g, 1 mmol) in tetrahydrofuran (15 mL) was stirred at room temperature for 10 min and carbon disulfide was added (30 μL, 0.5 mmol). The reaction mixture was stirred at room temperature for 1 h and concentrated to dryness under reduced pressure. The resulting crude was purified by column chromatography (eluent: diethyl acetate/*n*-hexane, 1:2). Thiourea **7** was obtained as a yellow solid in 51% yield. mp 138–140 °C. ν_{max} (Nujol)/cm^{-1}: 3390, 3207, 1549, 1518, 1271, 1238, 1103, 1001 and 821. ^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ 4.12 (pt, 4H, *J*=1.7 Hz), 4.19 (s, 10H), 4.19 (d, 4H, *J*=5.4 Hz), 4.24 (pt, 4H, *J*=1.7 Hz) and 7.39 (t, 2H, NH, *J*=5.4 Hz). ^{13}C NMR (75.4 MHz, DMSO-*d*$_6$): δ 40.6 (CH$_2$), 67.0 (CH), 67.6 (CH), 68.0 (CH), 87.5 (q) and 181.8 (q); MS EI *m*/*z* (%): 472 (M$^+$, 44), 438 (87), 413 (49), 282 (67), 257 (38), 240 (88), 200 (95), 162 (100), 121 (57) and 56 (86). Found: C, 58.57; H, 5.17; N, 5.85. $C_{23}H_{24}Fe_2N_2S$ (472.22) requires: C, 58.50; H, 5.12; N, 5.93.

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