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ARTICLE

Organo Phosphorus-Sulfur-Nitrogen Heterocycles from Thionation of Schiff Bases

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Dedicated to Thomas Klapötke on the Occasion of his 60th Birthday

Abstract. A series of heteroatom derivatives were prepared from the reactions of amido-Schiff bases as well as simpler imine with 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (**FcLR**). Six related structures were characterized by single-crystal X-ray diffraction.

Introduction

Schiff bases have widespread interest due to their diverse pharmacological activities, their widespread presence in common reagents and intermediates in organic synthesis, and as important ligands in coordination chemistry,[1–6] However, there are still many aspects of their chemistries which remain comparatively unexplored. *Hermann Staudinger* first studied the [2 + 2] cycloadditions with ketenes to give β-lactams in 1907.[7] *Corey* et al. utilized this cycloaddition reaction successfully for the first laboratory synthesis of penicillin in 1950.[8] Since then, only a few studies on cycloaddition to C=N bonds have reported. A methoxy-substituted phosphinidene has been added to 1-azadienes to give 1,4 adducts, five-membered ring 1,2-azaphospholenes in 1986.[9] *Streubel* et al. reported 1,2-addition to a C=N bond to yield azaphosphiridine complex from thermal decomposition of the 2*H*-azaphosphirene complex in the presence of an imine in 1994.[10] Phosphinidene complexes, generated from the corresponding 7-phosphanorbornadienes, react with an excess of imine [Ph–CH=N–Me] leading to the five-membered 1,4,2-diazaphospholanes.[11] Phosphinidene complexes can react also with diimines [PhCH=N–$(CH_2)_n$–N=CHPh, n = 2,3,4] giving bicyclic $(CH_2)_n$ bridged diazaphospholanes.[12]

Recently, we have reported the selenation of Schiff bases by Woollins' reagent leading to a series of phosphorus-selenium heterocycles.[13,14] The chemistry of dithiadiphosphetane disulfides has been the subject of several reviews, articles and communications.[15] In the continuation of our interest in the chemistry of sulfur-phosphorus heterocycles, we report here the reactivity of 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (**FcLR**, a ferrocene analogue of Lawesson's reagent) toward amido-Schiff bases and simple imine, and six single-crystal X-ray structures.

Results and Discussion

Synthesis and Characterization

The reaction of *N*′-4-phenylbut-3-en-2-ylidene)benzohydrazide with **FcLR** in refluxing toluene for 7 h led to the formation of a fused ring phosphorus-sulfur heterocycle **1** and a six-membered ring phosphorus-sulfur heterocycle **2** as a by-product, as shown in Scheme 1. Compound **2** was isolated previously from the thionation of urea with **FcLR**,[16] and two analogous trimers, 2,4,6-triphenyl-1,3,5,2,4,6-trioxatriphosphinane-2,4,6-trioxide and 2,4,6-tri(4-methoxy-phenyl)-1,3,5,2,4,6-trioxatriphosphinane-2,4,6-trioxide, have been reported from the reactions of alcohols or carbonyl compounds with thionation reagents.[17,18] Compounds **1** and **2** shows the anticipated $[M + H]^+$ peak in their mass spectra, satisfactory accurate measurements, and appropriate isotopic distributions. The ^{1}H NMR and ^{13}C NMR spectra of **1** and **2** display all the characteristic peaks of the ferrocene backbones. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows two singlet signals at δ_P 55.3 (small peak) and 53.3 (large peak) ppm with the same coupling constant of $^2J(P,P)$ = 46.3 Hz, indicating two isomers being formed with an intensity ratio of ca. 4 : 1. Meanwhile, the $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits a double doublet with a higher chemical shift of δ_P 75.3 ppm, compared to compound **1**.

The reaction of *N*′-3-(2-methoxyphenyl)allylidene)-4-methylbenzohydrazide with **FcLR** under identical reaction conditions gave rise to a totally different five-membered ring 1,3,4-thiadiazole **3** in 64 % yield, as well as the same byproduct **2**, (Scheme 2). Compound **3** appears to arise from the thionation/

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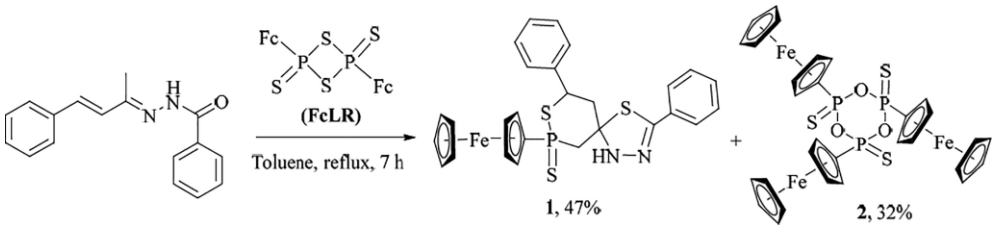
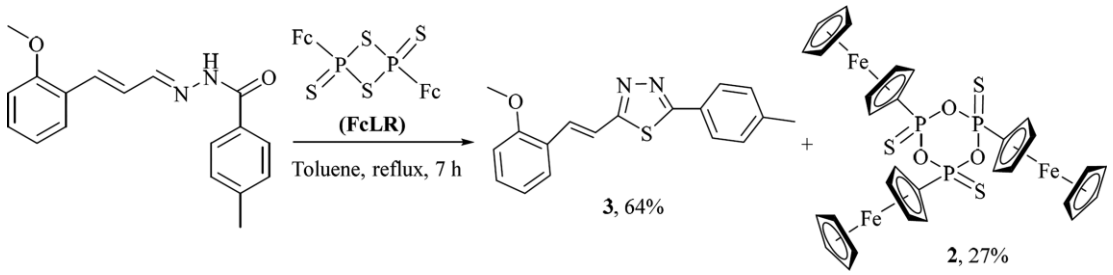
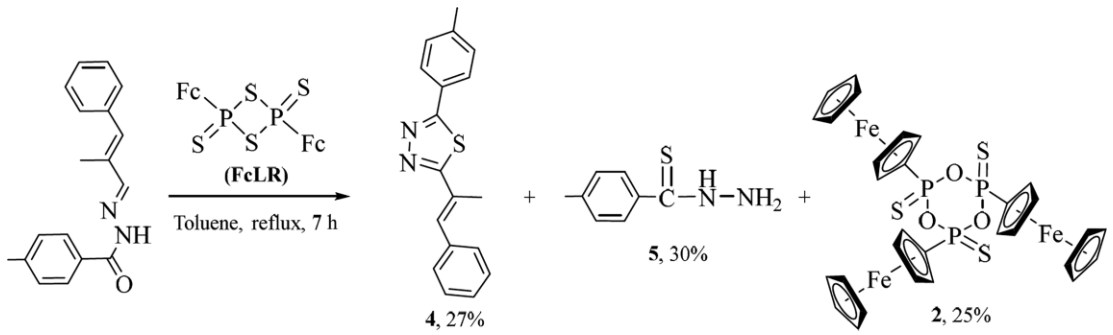


Scheme 1. Thionation of *N*′-4-phenylbut-3-en-2-ylidene)benzohydrazide to heterocycles **1** and **2**.



Scheme 2. Thionation of *N*′-3-(2-methoxyphenyl)allylidene)-4-methylbenzohydrazide to heterocycles **2** and **3**.



Scheme 3. Thionation of 4-methyl-*N*′-(2-methyl-3-phenylallylidene)benzohydrazide to compounds **2**, **4** and **5**.

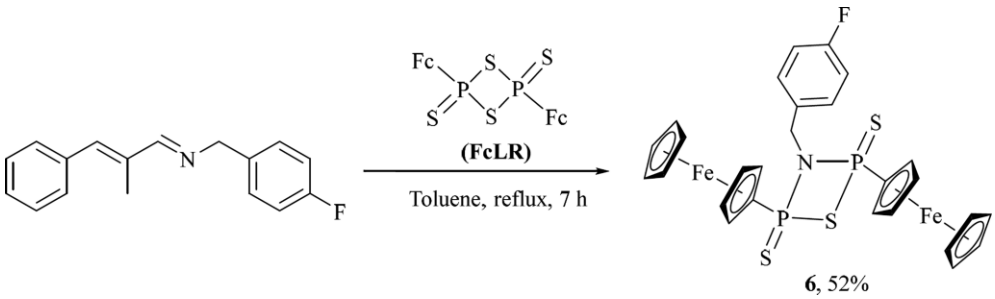
cyclization of *N*′-3-(2-methoxyphenyl)allylidene)-4-methylbenzohydrazide, without the further cycloaddition that results in the formation of **2**. Interestingly, the one of the conjugated double bonds in **3** remains intact, indicating the significantly steric effect from substituent group on the C=N that affects the formation of the terminal product. Commonly, 1,3,4-thiadiazoles can be prepared from thionation cyclization of acylhydrazines including *N*,*N*′-diacylhydrazines and monoacylhydrazines or from cyclization of thiohydrazines including thiosemicarbazides, thiocarbazides, dithiocarbazates, thioacylhy drazinesdrazines, and bithioureas.[19] The method here provides another useful route to synthesize 1,3,4-thiadiazoles from precursor Schiff bases.

A similar 1,3,4-thiadiazole **4** was obtained from the thionation of 4-methyl-*N*′-(2-methyl-3-phenylallylidene)benzohydrazide by **FcLR** under identical conditions, in 27 % yield, accompanied by byproduct **2** in 25 % yield and an additional thioamide **5** in 30 % yield. Like compound **3**, compound **4** appears to result from the thionation/cyclization of the starting amido-Schiff base without further cycloaddition because of the effect of adjacent C=C. Thiohydrazide **5** is an extra product from the thionation containing fragments of the original starting material. Once again, one of the exocyclic conjugated double bonds remains intact in **4** (Scheme 3).

Interestingly, contrast to the above results, the reaction of **FcLR** with the simple Schiff base, *N*-(4-*f*luorobenzyl)-2-methyl-3-phenylprop-2-en-1-imine, under the same reaction conditions led to an unique four-membered P-S-N heterocycle **6** in 52 % yield without any isolable cycloaddition or thionation/cyclization products as shown in Scheme 4. One sulfur atom in the four-membered ring of **FcLR** was replaced by an sp^3 nitrogen atom from the starting Schiff base, leading to a four-membered P-S-N heterocycle **6**. The ^{1}H NMR and ^{13}C NMR spectra display all the characteristic peaks of the ferrocene backbones. No other isomer was found. The ^{31}P{^{1}H} NMR spectrum showed a singlet signal at δ_P 65.5 ppm.

Single Crystal X-ray Structure Analysis

Single crystals of **1**–**6** were grown from slow evaporation of dichloromethane solution of the compound into hexane or slow diffusion hexane into acetonitrile solution of the compound in air at room temperature. The crystallographic data and structure refinement are listed in Tables S1 and S2 (Supporting In-



Scheme 4. Thionation of *N*-(4-fluorobenzyl)-2-methyl-3-phenylprop-2-en-1-imine to the heterocycle **6**.

formation) and the resulting molecular structures are illustrated in Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, and Figure 6. The structures of **1**, **2** and **6** have a single molecule of the compound in their asymmetric units, whereas the structures of **3**, **4** and **5** contain two independent molecules.

The molecular structure of the fused heterocycle **1** is shown in Figure 1. In the solid state, the structure of **1** can be described as spirocyclic, with linked six-membered PSC_4 and five-membered N_2C_3 rings. All three of the pendant groups are oriented in a *cis* fashion and the mean plane of the newly formed PSC_4 ring is nearly perpendicular to the newly formed ring N_2C_3 as measured by a dihedral angle of 76.45°. The five-membered ring and its substituent phenyl ring plane are almost coplanar (dihedral angle of 15.28°), whereas the six-membered ring is nearly perpendicular to its pendant phenyl (dihedral angle of 80.83°). The P=S double bond [1.9514(11) Å] and P–S single bond [2.0795(10) Å] lengths are typical for the P(μ-S)S moity.[20] Two C–S single bond length [1.835(3) and 1.763(3) Å] in the five-membered ring are significantly different to each other, indicative of strain in the unsymmetrical heterocyclic ring. The geometry around P(1) is distorted tetrahedral [S(1)–P(1)–S(2) 114.27(5)°, S(1)–P(1)–C(10) 114.00(10)°].

It can be seen in Figure 2, the structure of **2** shows a slightly puckered six-membered ring comprising alternating P=S groups and O atoms. The trimer contains three Fc–P=S units bridged by oxygen atoms. The structure is quite similar to its phenyl analogue $[PhP(S)O]_3$, which was prepared from the reaction of $PhP(O)Cl_2$ with H_2S and NEt_3.[21] The exocyclic ferrocenyl rings and sulfur atoms peripheral to the ring cavity are oriented *trans* to each other. The P=S bond lengths [1.898(4), 1.890(4) and 1.908(4) Å] are comparable with those [1.894(1)–1.898(1) Å] found in $[PhP(S)O]_3$;[21] however, they are slightly shorter than in the similar organo-phosphorus sulfides [1.93–1.96 Å].[22] The P–O single bond lengths [1.600(7), 1.629(7), 1.615(7), 1.620(7), 1.616(8) and 1.620(7) Å] and O–P–O angles [100.8(4), 100.9(4) and 97.0(4)°] being in chair rings are similar to those [1.613 Å] found in $(PhPOS)_3$.[23–25] The transannular P···P distances [2.953, 2,964, and 3.002 Å] are significantly shorter than that are observed in related P–S containing heterocycles [4.97–6.97 Å].[19] The geometries

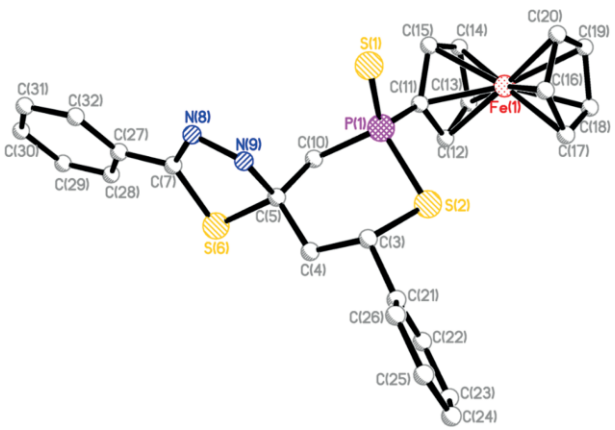


Figure 1. Single crystal X-ray structures of compound **1** (Hydrogen atoms omitted for clarity). Selected bond lengths /Å and angles /° (esds in parentheses): P(1)–S(1) 1.9514(11), P(1)–S(2) 2.0795(10), P(1)–C(10) 1.819(3), C(10)–C(5) 1.538(4), S(2)–C(3) 1.852(3), C(3)–C(4) 1.529(4), C(4)–C(5) 1.531(4), S(6)–C(5) 1.835(3), S(6)–C(7) 1.763(3), C(7)–N(8) 1.282(4), N(8)–N(9) 1.397(3), N(9)–C(5) 1.482(4); S(1)–P(1)–S(2) 114.27(5), S(1)–P(1)–C(10) 114.00(10), P(1)–S(2)–C(3) 97.22(9), S(2)–C(3)–C(4) 112.87(19), C(3)–C(4)–C(5) 117.0(2), C(4)–C(5)–C(10) 114.3(2), C(5)–C(10)–P(1) 115.03(18), C(4)–C(5)–S(6) 107.44(19), C(5)–S(6)–C(7) 88.32(15), S(6)–C(7)–N(8) 115.3(2), C(7)–N(8)–N(9) 111.9(3), N(8)–N(9)–C(5) 112.0(2), S(6)–C(5)–N(9) 101.40(18).

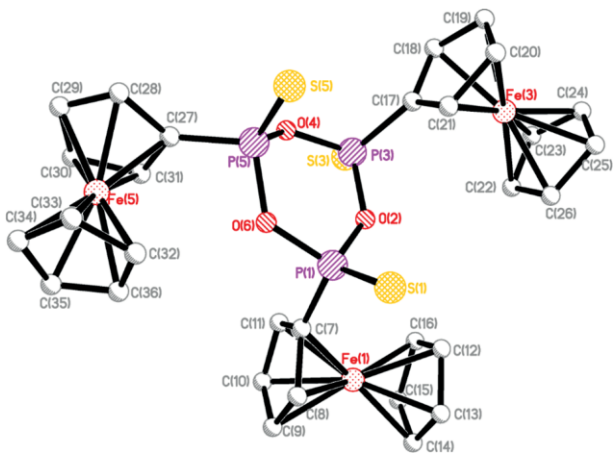


Figure 2. Single crystal X-ray structures of compound **2** (Hydrogen atoms omitted for clarity). Selected bond lengths /Å and angles /° (esds in parentheses): P(1)–S(1) 1.898(4), S(3)–P(3) 1.890(4), S(5)–P(5) 1.908(4), P(1)–O(2) 1.600(7), P(1)–O(6) 1.629(7), P(3)–O(2) 1.615(7), P(3)–O(4) 1.620(7), P(5)–O(6) 1.616(8), P(5)–O(4) 1.620(7), P(1)–C(7) 1.761(12), P(3)–C(17) 1.779(11), P(5)–C(27) 1.744(11); O(2)–P(1)–O(6) 100.8(4), O(2)–P(3)–O(4) 100.9(4), O(4)–P(5)–O(6) 97.0(4), P(1)–O(2)–P(3) 138.0(4), P(3)–O(4)–P(5) 131.2(5), P(5)–O(6)–P(1) 131.1(5), S(1)–P(1)–O(2) 113.9(3), S(1)–P(1)–O(6) 115.0(3), S(3)–P(3)–O(2) 115.3(3), S(3)–P(3)–O(4) 111.8(3), S(5)–P(5)–O(4) 115.1(3), S(5)–P(5)–O(6) 118.8(3).

around P(1) [S(1)–P(1)–O(2): 113.9(3) Å], P(3) [S(3)–P(3)–O(4): 111.8(3) Å] and P(5) [S(5)–P(5)–O(6): 118.8(3) Å] are distorted tetrahedral, indicating the effects of the steric hindrance of three pendant ferrocene groups.

The structures of **3** and **4** as depicted in Figure 3 and Figure 4, consist of similar frameworks of five-membered N_2C_2S rings, each with two pendant functional groups. Interestingly, the N_2C_2S planes are approximately co-planar with substituents (dihedral angles: 20.06° and 6.51°; 7.88° and 15.17° for **3**; 8.25° and 16.92°; 26.44° and 13.84° for **4**). Bond lengths and angles around the N_2C_2S rings fall in the range of those in reported 1,3,4-thiadiazoles, supporting significant ring conjugation in **3** and **4**.[26–28]

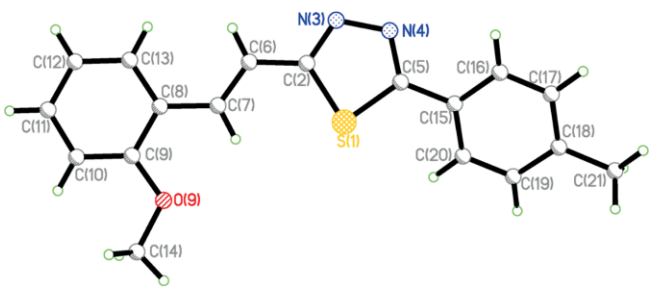


Figure 3. Single crystal X-ray structures of compound **3**. Selected bond lengths /Å and angles /° (esds in parentheses): S(1)–C(2) 1.739(2) [1.735(2)], S(1)–C(5) 1.731(2) [1.734(2)], C(2)–N(3) 1.305(3) [1.307(3)], N(3)–N(4) 1.366(3) [1.372(3)], N(4)–C(5) 1.311(3) [1.306(3)], C(6)–C(7) 1.342(3) [1.374(3)]; C(2)–S(1)–C(5) 87.3(10) [87.51(10)], S(1)–C(2)–N(3) 113.08(17) [113.00(17)], C(2)–N(3)–N(4) 113.21(17) [113.26(17)], N(3)–N(4)–C(5) 113.20(17) [113.02(17)], S(1)–C(5)–N(4) 113.11(17) [113.20(17)].

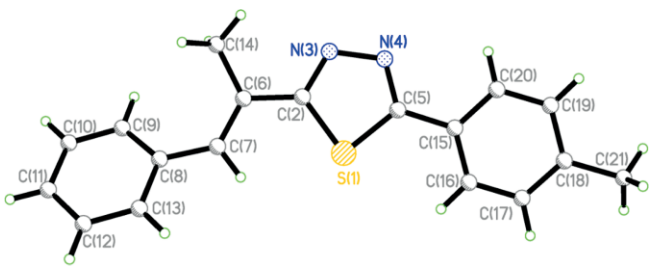


Figure 4. Single crystal X-ray structures of compound **4**. Selected bond lengths /Å and angles /° (esds in parentheses): S(1)–C(2) 1.726(4)[1.736(4)], S(1)–C(5) 1.711(4)[1.724(4)], C(2)–N(3) 1.311(5)[1.321(4)], N(3)–N(4) 1.382(4)[1.371(4)], N(4)–C(5) 1.303(5)[1.293(4)]; C(2)–S(1)–C(5) 87.55(19)[87.25(18)], S(1)–C(2)–N(3) 113.2(3)[112.6(3)], C(2)–N(3)–N(4) 112.7(3)[113.0(3)], N(3)–N(4)–C(5) 112.1(3)[112.8(3)], S(1)–C(5)–N(4) 114.4(3)[114.4(3)].

The structure of **5** reveals the formation of a thiohydrazide from the thionation of Schiff base 4-methyl-*N*′-(2-methyl-3-phenylallylidene)benzohydrazide (Figure 5) though these is some disorder in the structure. This has been modelled as a mixture of –N=NH and –NH–NH_2, which allows for hydrogen-bonding between adjacent molecules, with the hydrogen positions disordered between the two independent molecules. A potential alternative to this that unfortunately could not be successfully crystallographically modeled, which would have involved pyramidalization of the terminal nitrogen, and orientation of the –NH_2 hydrogen atoms out of the molecular plane.

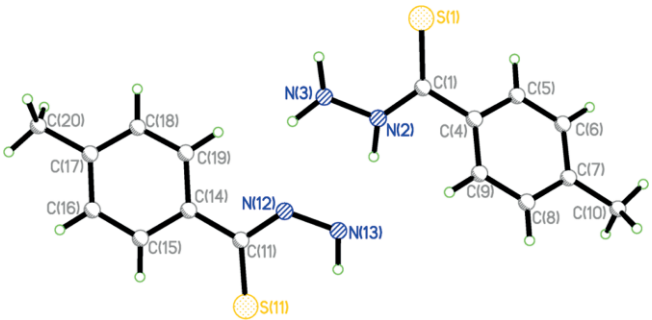


Figure 5. Single crystal X-ray structures of compound **5**. Selected bond lengths (Å) and angles (°) (esds in parentheses): S(1)–C(1) 1.680(10)[1.670(10)], C(1)–N(2) 1.322(12)[1.328(12)], C(1)–C(4) 1.494(13)[1.496(13)], N(2)–N(3) 1.424(11)[1.393(10)]; S(1)–C(1)–N(2) 122.6(8)[120.7(8)], S(1)–C(1)–C(4) 123.3(8)[122.1(8)], C(4)–C(1)–N(2) 113.9(8)[117.1(9)], C(1)–N(2)–N(3) 123.0(8)[126.0(8)].

The X-ray structure of **6** consists of a planar four-membered P(*S*)–N–P(*S*)–S ring with the two pendant ferrocenyl groups being in a *trans* arrangement across the plane of the four-membered ring. The mean plane of the four-membered ring is nearly in perpendicular to the pendant phenyl ring with a dihedral angle of 84.24°. The geometry of P(1) and P(3) is nearly tetrahedral [S(1)–P(1)–S(2) 119.31(7)° and S(2)–P(3)–S(3) 120.13(6)°]. The transannular P···P distance is 2.700 Å, shorter than that [2.91 Å] observed in, the parent Fc-LR; although the phosphorus-sulfur single- and double-bond lengths show good agreement with related structures[29] (Figure 6).

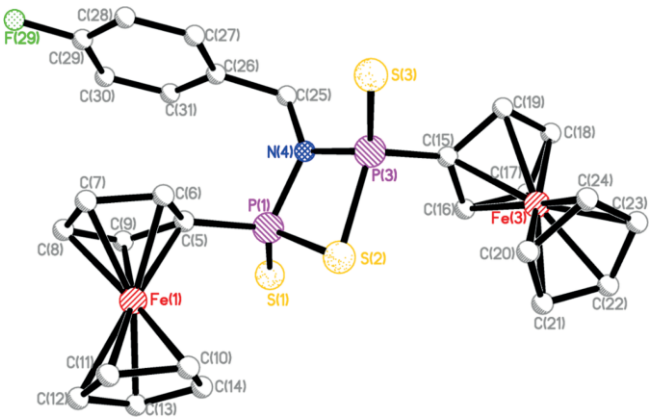


Figure 6. Single crystal X-ray structures of compound **6** (Hydrogen atoms omitted for clarity). Selected bond lengths /Å and angles /° (esds in parentheses): S(1)–P(1) 1.9249(15), S(2)–P(1) 2.1204(15), S(2)–P(3) 2.1207(14), P(3)–S(3) 1.9255(14), P(3)–N(4) 1.683(3), P(1)–N(4) 1.676(3), N(4)–C(25) 1.481(5); S(1)–P(1)–S(2) 119.31(7), S(1)–P(1)–N(4) 117.81(12), P(1)–S(2)–P(2) 79.06(5), S(2)–P(3)–S(3) 120.13(6), S(2)–P(3)–N(4) 86.87(11), P(3)–N(4)–P(1) 106.97(16), P(1)···P(3) 2.6885(14).

Experimental Section

Unless otherwise stated, all reactions were carried out under on oxygen free nitrogen atmosphere using pre-dried solvents and standard

Schlenk techniques, subsequent chromatographic and work up procedures were performed in air. All *N*-substituted benzylidenebenzohydrazides were synthesized by the reaction of benzoic hydrazide with substituted benzaldehydes in presence of a few drops of acetic acid as catalyst.[30] The preparation and spectroscopic characterization of **FcLR** have been reported previously by our group.[29] ^{1}H (400.1 MHz), ^{13}C (100.6 MHz) and ^{31}P{^{1}H} (162.0 MHz) NMR spectra were recorded at 25 °C on a Bruker Advance II 400s. IR spectra were recorded as KBr pellets in the range of 4000–250 cm^{-1} on a Perkin–Elmer 2000 FTIR/Raman spectrometer. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea and the University of St Andrews Mass Spectrometry Service. The bulk purity of new compounds reported here was assessed from solution NMR since we considered that there are no NMR silent impurities. X-ray diffraction data for all structures were collected at 173 K using a Rigaku FR-X Ultrahigh Brilliance Microfocus RA generator/confocal optics and XtaLAB P200 diffractometer system, with Mo-K_α radiation (λ = 0.71075 Å). Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were collected and processed (including correction for Lorentz, polarization and absorption) using CrystalClear.[31] Structures were solved by either direct (SIR2011, SIR2004)[32,33] or dual-space (SHELXT)[34] methods, and refined by full-matrix least-squares against F^2 (SHELXL-2018/3).[35] Non-hydrogen atoms were refined anisotropically, and carbon-bound hydrogen atoms were refined using a riding model. Nitrogen-bound hydrogens were located from the difference Fourier map and refined isotropically subject to a distance restrain, except for the disordered –NH_2 groups in **5**, which were refined using a riding model. All calculations were performed using the CrystalStructure interface.[36]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2005878, CCDC-2005879, CCDC-2005880, CCDC-2005881, CCDC-2005882, and CCDC-2005883 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Synthesis of Compounds 1 and 2: A suspension of *N′*-4-phenylbut-3-en-2-ylidene)benzohydrazide (1.0 mmol) and **FcLR** (0.56 g, 1.0 mmol) in 20 mL of toluene was refluxed for 7 h. After cooling to room temperature and removing toluene in vacuo the residue was purified by silica gel column (eluented by 1 : 2 hexane / dichloromethane) to give the title compounds **1** and **2**.

7-Methyl-3,9-diphenyl-4,8-dithia-1,2-diaza-7-phosphaspiro[4.5]-dec-2-ene 7-sulfide (1): Orange crystals (0.25 g, 47 %). **IR** (selected peaks, KBr): $\tilde{\nu}$ = 1581(m), 1492(s), 1448(s), 1384(m), 1270(s), 1177(s), 1106(m), 1025(s), 971(s), 823(s), 760(vs), 692(vs), 637(s), 582(m), 536(m), 482(s) cm^{-1}. Two diastereomers were found in ca. 1 : 4 intensity ratio based on ^{31}P NMR spectrum. ^{1}H NMR ($CDCl_3$, δ), 8.69 (NH), 7.62–7.59 (m, 4 H, Ar-H), 7.54–7.49 (m, 4 H, Ar-H), 7.46–7.32 (m, 12 H, Ar-H), 5.32 (s, CH_2 from resided solvent CH_2Cl_2), 4.88–4.81 (m, 8 H, Fc-H), 4.62–4.52 (m, 8 H, Fc-H), 4.41 (s, 10 H, Fc-H), 4.39 (s, 10 H, Fc-H), 3.34–3.15 (m, 5 H, CH_2 + CH), 2.95–2.53 (m, 5 H, CH_2 + CH), 2.20 (s, H_2O) ppm. ^{13}C NMR ($CDCl_3$, δ), 145.9 (C=N), 145.2 (Ar-C), 140.3 (Ar-C), 140.2 (Ar-C), 131.3 (Ar-C), 129.9 (Ar-C), 129.6 (Ar-C), 129.2 (Ar-C), 129.1 (Ar-C), 128.5 (Ar-C), 128.3 (Ar-C), 127.7 (Ar-C), 127.6 (Ar-C), 127.0 (Ar-C), 126.9 (Ar-C), 83.7 (Fc-C), 83.6 (Fc-C), 73.9 (Fc-C), 73.7 (Fc-C), 72.6 (Fc-C), 72.4 (Fc-C), 70.4 (Fc-C), 70.2 (Fc-C), 70.1 (Fc-C), 49.0 (CH_2), 48.5 (CH_2), 47.5 (CH_2), 44.7 (CH_2), 31.0 (CH) ppm. ^{31}P NMR ($CDCl_3$, δ), 55.0 (small peak), 53.3 (large peak) ppm. MS (CI^+, *m/z*), 561 $[M + H]^+$. Accurate mass measurement [CI^+, *m/z*]: 561.0337 $[M + H]^+$, calculated mass for $C_{27}H_{25}FeN_2PS_3H$: 561.0340.

2,4,6-Triferrocenyl-1,3,5,2,4,6-trioxatriphosphinane 2,4,6-trisulfide (2). Yellow solid (0.250 g, 32 %). M.p. 97–98 °C. **IR** (selected peaks, KBr): $\tilde{\nu}$ = 1411(m), 1390(m), 1367(m), 1192(s), 1107(m), 1030(m), 940(vs), 892(m), 823(m), 796(m), 756(s), 677(s), 487(m), 468(s) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 5.06–4.94 (m, 4 H, Fc-H), 4.70–4.55 (m, 8 H, Fc-H), 4.45 (s, 5 H, Fc-H), 4.35 (s, 10 H, Fc-H) ppm. **^{13}C NMR** (CD_2Cl_2): δ = 73.6 (Fc-C), 73.4 (Fc-C), 73.1 (Fc-C), 72.9 (Fc-C), 72.8 (Fc-C), 72.1 (Fc-C), 71.0 (Fc-C) ppm. **^{31}P NMR** (CD_2Cl_2): δ = 75.3 [dd, ^{2}J(P,P) = 46.3 Hz and ^{2}J(P,P) = 46.4 Hz] ppm. **MS** (CI^+, *m/z*), 793 $[M + H]^+$. Accurate mass measurement [CI^+, *m/z*]: 792.8463 $[M + H]^+$, calculated mass for $C_{30}H_{27}Fe_3O_2P_3S_3H$: 792.8459.

Synthesis of Compounds 2 and 3: A suspension of *N′*-(3-(2-methoxyphenyl)allylidene)-4-methylbenzohydrazide (0.294 g, 1.0 mmol) and **FcLR** (0.56 g, 1.0 mmol) in 20 mL of toluene was refluxed for 7 h. Upon cooling to room temperature and removing toluene in vacuo the residue was purified by silica gel column (eluented by 1 : 2 hexane / dichloromethane) to give the title compounds **2**, as a yellow solid (0.210 g, 27 %), and **3**.

2-(2-Methoxystyryl)-5-(*p*-tolyl)-1,3,4-thiadiazole (3): Yellow crystals (0.200 g, 64 %). **IR** (selected peaks, KBr): $\tilde{\nu}$ = 1598(m), 1492(s), 1461(s), 1439(s), 1246(s), 1181(m), 1106(m), 1050(m), 1025(s), 909(m), 817(s), 752(s), 731(m), 502(m) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 7.90 (d, *J*(H,H) = 8.2 Hz, 2 H, Ar-H), 7.71–7.55 (m, 3 H, Ar-H), 7.39–7.29 (m, 3 H, Ar-H), 7.05–6.95 (m, 2 H, CH), 3.945 (s, 3 H, OCH_3), 2.46 (s, 3 H, CH_3) ppm. **^{13}C NMR** ($CDCl_3$): δ = 168.2 (CH), 166.8 (CH), 157.6 (Ar-C), 141.5 (Ar-C), 134.3 (Ar-C), 130.7 (Ar-C), 129.8 (Ar-C), 129.7 (Ar-C), 127.9 (Ar-C), 127.8 (Ar-C), 127.6 (Ar-C), 120.6 (Ar-C), 119.1 (Ar-C), 112.1 (Ar-C), 55.6 (OCH_3), 21.5 ppm (CH_3). **MS** (CI^+, *m/z*), 309 $[M + H]^+$. Accurate mass measurement [CI^+, *m/z*]: 309.1065 $[M + H]^+$, calculated mass for $C_{18}H_{16}N_2OSH$: 309.1061.

Synthesis of Compounds 2, 4, and 5: A suspension of 4-methyl-*N′*-(2-methyl-3-phenylallylidene)benzohydrazide (0.278 g, 1.0 mmol) and **FcLR** (0.56 g, 1.0 mmol) in 20 mL of toluene was refluxed for 7 h. Upon cooling to room temperature and removing toluene in vacuo the residue was purified by silica gel column (eluented by 1 : 2 hexane / dichloromethane) to give the title compounds **2** as a yellow solid (0.200 g, 25 %), **4** and **5**.

2-(1-Phenylprop-1-en-2-yl)-5-(*p*-tolyl)-1,3,4-thiadiazole (4): Colorless crystals (0.080 g, 27 %). **IR** (selected peaks, KBr): $\tilde{\nu}$ = 1611(m), 1492(m), 1440(vs), 1311(m), 1181(m), 1053(m), 981(m), 818(s), 756(s), 694(s), 606(s), 508(s) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 7.90 (d, *J*(H,H) = 8.2 Hz, 2 H, Ar-H), 7.46 (s, 1 H, CH), 7.45–7.29 (m, 7 H, Ar-H), 2.53 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3) ppm. **^{13}C NMR** ($CDCl_3$): δ = 171.4 (CH), 167.5 (C), 141.5 (Ar-C), 136.0 (Ar-C), 135.1 (Ar-C), 129.8 (Ar-C), 129.5 (Ar-C), 129.2 (Ar-C), 128.9 (Ar-C), 128.7 (Ar-C), 128.5 (Ar-C), 128.0 (Ar-C), 127.9 (Ar-C), 127.6 (Ar-C), 21.6 (CH_3), 16.6 (CH_3) ppm. **MS** (CI^+, *m/z*), 293 $[M + H]^+$. Accurate mass measurement [CI^+, *m/z*]: 293.1110 $[M + H]^+$, calculated mass for $C_{18}H_{16}N_2SH$: 293.1112.

4-Methylbenzothiohydrazide (5): Colorless crystals (0.050 g, 30 %). **IR** (selected peaks, KBr): $\tilde{\nu}$ = 1594(s), 1525(m), 1500(s), 1411(m), 1315(m), 1230(s), 1184(s), 1025(s), 1007(m), 938(m), 822(vs), 723(m), 678(m), 622(m), 492(m) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 9.00 (s, 2 H, NH_2), 7.76 (s, 1 H, NH), 7.64 [d, *J*(H,H) = 8.2 Hz, 2 H, Ar-H], 7.21 [d, *J*(H,H) = 8.2 Hz, 2 H, Ar-H], 2.40 (s, 3 H, CH_3) ppm. **^{13}C NMR** ($CDCl_3$): δ = 195.6 (C = S), 142.0 (Ar-C), 136.3 (Ar-C),

129.8 (Ar-C), 126.8 (Ar-C), 21.5 (CH_3) ppm. **MS** (CI^+, *m/z*), 167 [M + H]$^+$. Accurate mass measurement [CI^+, *m/z*]: 167.0638[M + H]$^+$, calculated mass for $C_8H_{10}N_2SH$: 167.0642.

Synthesis of 3-(4-Fluorobenzyl)-2,4-diferrocenyl-1,3,2,4-thiazadiphosphetidine 2,4-disulfide (6): A suspension of *N*-(4-fluorobenzyl)-2-methyl-3-phenylprop-2-en-1-imine (0.254 g, 1.0 mmol) and **FcLR** (0.56 g, 1.0 mmol) in 20 mL of toluene was refluxed for 7 h. Upon cooling to room temperature and removing toluene in vacuo the residue was purified by silica gel column (eluented by 1:4 hexane / dichloromethane) to give the title compound **6**. Dark yellow solid (0.205 g, 52%). **IR** (selected peaks, KBr): $\tilde{\nu}$ = 1508(m), 1410(m), 1220(m), 1181(s), 1126(m), 1024(m), 1004(s), 837(s), 752(m), 682(s), 483(m), 461(s) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 7.16 (dd, *J*(H,H) = 8.5 Hz, 2 H, Ar-H), 6.72 (t, *J*(H,H) = 8.5 Hz, 2 H, Ar-H), 4.64–4.62 (m, 2 H, Fc-H), 4.72–4.56 (m, 4 H, Fc-H), 4.48–4.46 (m, 2 H, Fc-H), 4.35 (s, 10 H, Fc-H), 4.18–4.13 (m, 2 H, CH_2) ppm. **^{13}C NMR** ($CDCl_3$): δ = 160.8 (Ar-C), 131.1 (d, *J*(P,C) = 8.1 Hz, Ar-C), 130.3 (Ar-C), 114.8 [d, *J*(P,C) = 21.6 Hz, Ar-C], 78.1 [d, *J*(P,C) = 117.7 Hz, Fc-C], 73.7 [d, *J*(P,C) = 15.0 Hz, Fc-C], 72.4 [d, *J*(P,C) = 14.6 Hz, Fc-C], 71.6 [d, *J*(P,C) = 17.0 Hz, Fc-C], 70.4 (Fc-C), 46.1 (CH_2) ppm. **^{31}P NMR** ($CDCl_3$): δ = 65.5 ppm. **MS** (CI^+, *m/z*), 652 [M + H]$^+$. Accurate mass measurement [CI^+, *m/z*]: 651.9314 [M + H]$^+$, calculated mass for $C_{27}H_{24}FFe_2NP_2S_3H$: 651.9307.

Supporting Information (see footnote on the first page of this article): Further details of the refinement and the crystallographic data and ^{1}H and ^{13}C NMR spectra of compounds **1**–**6**.

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