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New binucleating ligand with two [P,S] chelation pockets on a single phenyl ring: Syntheses and X-ray structures of 1,4-bis(diphenylphosphino)-2,5-difluoro-3,6-bis(methylthio)benzene and of bimetallic complex $(CO)_3Fe(\mu\text{-}[(PPh_2)(SMe)C_6F_2(SMe)(PPh_2)])Fe(CO)_3$

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Abstract

Double deprotonations of 1,4-dibromo-2,5-difluorobenzene with LDA (2 equiv., $T < -90$ °C) generate a reasonably stable organodilithium intermediate. Quenching this reaction mixture with chlorophosphines $ClPR_2$ produce *p*-bis(phosphino)benzenes $R_2P\text{–}C_6Br_2F_2\text{–}PR_2$ (R = Ph, **4a**; R = ^{i}Pr, **4b**). Facile lithium–bromine exchange occurs upon exposure of **4a** to BuLi (2 equiv., −80 °C), leading to the generation of another organodilithium intermediate. Addition of MeS–SMe (2 equiv.) to such reaction mixtures gives 1,4-bis(diphenylphosphino)-2,5-difluoro-3,6-bis(methylthio)benzene (**2**). Compound **2** is the first example of a neutral binucleating ligand featuring the [P,S] chelating sites on the opposite sides of a single phenyl ring. Compound **4b** does not undergo the analogous transformation when subjected to the same conditions (2BuLi/2MeS–SMe). Addition of **2** to $Fe(CO)_5/2(Me_3NO \cdot 2H_2O)$ reaction mixtures led to the isolation of the bimetallic complex $\{(CO)_3Fe[P,S]\text{–}C_6F_2\text{–}[P,S]Fe(CO)_3\}$ (**3**), ([P,S] represents the chelating pockets formed by adjacent $–PPh_2$ and –SMe groups). All of the new compounds were characterized by spectroscopic and analytical techniques (multinuclear NMR, mass-spectrometry, and/or elemental analysis). In addition, compounds **2** and **3** were characterized via single crystal X-ray diffraction methods.

Keywords: Binucleating; Phosphorus–sulfur ligands; Bimetallic complex; Iron tricarbonyl

1. Introduction

Polydentate ligands containing both phosphorus(III) and sulfur(II) groups in their architectures have been extensively used in coordination chemistry [1]. Derivatives of *o*-phosphinothiophenol (Fig. 1, **1**) are probably the most popular among such [P,S] ligands, as they effectively complex to metal centers via the formation of a five-membered chelate ring [2–5], and are relatively easy to synthesize [6]. Furthermore, the ability to vary the substituents on phosphorus and sulfur allows for facile tuning of the steric and electronic properties of such ligands. Most of the studies involving such [P,S] ligands have been centered on monometallic complexes, and the number of well-defined binucleating [P,S] ligands and their bimetallic complexes is relatively small [7,8]. Recently, we have reported the new syntheses of potentially binucleating ligands – symmetric and unsymmetric 1,2,4,5-tetrakis(phosphino)benzenes [9], where the sequential generation of organodilithium intermediates from 1,4-dibromo-2,5-difluorobenzene followed by $ClPR_2$ quenches (R = Ph, Et, ^{i}Pr) were utilized. Structurally analogous tetrakis(phosphino)- or tetrakis(thio)benzenes with P- or S-donor ligands at the 1,2,4,5 positions have been successfully used as

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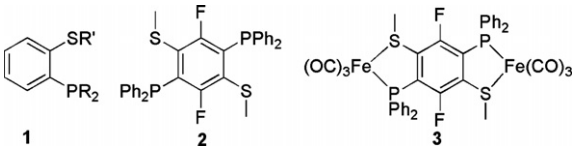


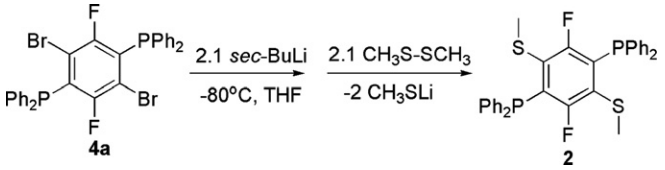
Fig. 1. General representation of *o*-phosphinothiophenols (**1**, R = aryl or alkyl; R' = aryl, alkyl, or a lone pair); structural drawings of 1,4-bis(diphenylphosphino)-2,5-difluoro-3,6-bis(methylthio)benzene (**2**), and its bimetallic complex **3**.

binucleating ligands for the formation of bimetallic complexes [10–12] and of polymetallic aggregates [13–17]. However, no 1,2,4,5-tetrasubstituted benzenes where the chelating sites are defined by mixed P- and S-donor groups have been reported. Herein, we present the syntheses of the first such ligand – 1,4-bis(diphenylphosphino)-2,5-difluoro-3,6-bis-(thiomethyl)benzene (Fig. 1, **2**). Given the potential of [P,S] chelate chemistry [1], such binucleating ligands should be interesting building blocks for the formation of bimetallic complexes and polymetallic arrays, especially since the [N,S] structural analog of **2**, 2,5-diamino-1,4-benzenedithiol has been used for the syntheses of polymeric transition metal complexes [18,19]. Initial coordination studies show that compound **2** acts as an effective binucleating ligand, as ascertained through the formation of the bimetallic bis(iron tricarbonyl) complex (Fig. 1, **3**).

2. Results and discussion

2.1. Syntheses and spectral properties

Organodilithium intermediates have been extensively utilized as dianionic synthons in organic syntheses [20]. Recently, we have shown that organodilithio intermediates can be formed when selected tetrahalobenzenes featuring protons flanked by F/Cl and F/Br atoms are exposed to lithium diisopropylamide (LDA) at low temperatures [9,21]. Quenching such reaction mixtures with chlorophosphines $ClPR_2$ (R = Ph, ^{i}Pr) allowed for the syntheses of 1,4-bis(phosphino)benzenes containing tetrahalogenated central phenyl rings [9,21]. The presence of the heavier halogens (particularly bromine) in the later compounds may be utilized for designing further synthetic steps. For example, we have shown that 1,4-bis(diphenylphosphino)-2,5-dibromo-3,6-difluorobenzene (**4a**) undergoes double lithium–bromine exchange upon reactions with BuLi thus generating another organodilithium intermediate, and quenching the reaction mixtures with chlorophosphines $ClPR_2$ (R = Ph, ^{i}Pr, Et) lead to the syntheses of novel tetrakis(phosphino)difluorobenzenes [9]. Such a synthetic approach (sequential generations of organodilithium intermediates from 1,4-dibromo-2,5-difluorobenzene, followed by electrophile quenches) may potentially be developed into a general synthetic strategy for the construction of other binucleating ligands bearing 1,2,4,5-tetrasubstituted benzene structural frames. We have now focused our initial attention towards developing the corresponding [P,S] ligands. The organodilithium intermediate generated from **4a** via double lithium–halogen exchange readily reacts with dimethyldisulfide, yielding 1,4-bis(diphenylphosphino)-2,5-difluoro-3,6-bis-(methylthio)benzene (**2**) in 58% isolated yield (Eq. (1)). The byproduct of this reaction is CH_3SLi, resulting from a heterolytic disulfide cleavage. This represents a potential problem, as alkali metal organothiolates are known to undergo nucleophilic substitution reactions with fluorines of C_{arom}–F bonds [22,23]. Hence, the reaction sequence depicted in Eq. (1) can potentially proceed further, eventually producing tris(thio) and tetrakis(thio) substituted bis(phosphino)benzenes in the reaction mixture. Although we did not detect the formation of such products under our conditions, alternative sources for the introduction of the thiomethyl groups were also explored. *S*-methyl methanethiosulfonate, $CH_3S–S(=O)_2CH_3$, is particularly attractive for this purpose, as the nucleophilic character of the leaving group (CH_3SO_2Li) should be much less pronounced. However, the substitution of dimethyl disulfide by $CH_3S–S(=O)_2CH_3$ in the reaction sequence depicted in Eq. (1) did not afford expected improvements in the reaction yield. In fact, the opposite was observed: reactions were more difficult to control, and the yields were less reproducible; the reasons behind this were not investigated

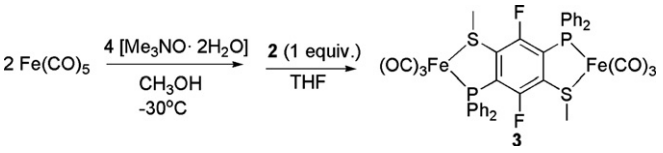


(1)

Spectroscopic characteristics of the main functional groups of **2** (δ 2.17 (s) in ^{1}H NMR for thiomethyl and δ −10.9 (m) in ^{31}P NMR for phosphine) are similar to those reported for other diphenylphosphine derivatives bearing *o*-thiomethylphenyl moieties [2,24]. Thus, it appears that the fluorines on the central phenyl ring in **2** have a negligible effect on the corresponding chemical shift values. Signals in both ^{31}P and ^{19}F NMR spectra of **2** are multiplets, suggesting possible weak ^{31}P–^{19}F interactions, but the coupling is unresolved.

Our attempts to obtain other structural analogs of **2** were less successful. A suitable starting compound, 1,4-bis(diisopropylphosphino)-2,5-dibromo-3,6-difluorobenzene (**4b**) was obtained in good (~70%) yield via the synthetic sequence used for **4a** [9] (dilithiation of 1,4-dibromo-2,5-difluorobenzene followed by ClP^iPr_2 quench). However, substituting **4a** by **4b** in the reaction sequence depicted in Eq. (1) did not produce the expected product, i.e. 1,4-bis(diisopropylphosphino)-2,5-difluoro-3,6-bis-(methylthio) benzene. Substantial amounts of unreacted **4b** were recovered in all experiments, suggesting that Li for Br exchange in **4b** may be restricted or proceeded too slowly under the reaction conditions used.

The binucleating ability of the ligand **2** was ascertained as it ligated two iron tricarbonyl fragments (Eq. (2)). The addition of **2** to a $Fe(CO)_5$/trimethylamine N-oxide [25] mixture resulted in immediate formation of a dark red solution, from which the bimetallic complex **3** was isolated (by crystallization) in moderate 32% yield (Eq. (2)). Monometallic complexes containing metal carbonyl fragments with [P,S] chelation of (2-thiomethylphenyl)diphenylphosphine ligands have been well documented [26–28], but only one complex containing iron tricarbonyl ligated to a neutral [P,S] ligand has been described previously [29]. Compound **3** displays three absorption bands (1996, 1928 (shoulder), and 1905 cm^{-1}) in the carbonyl region of the IR spectrum. Such values are of somewhat (5–15 cm^{-1}) higher energy than the CO absorptions observed for structurally related iron tricarbonyl complexes with chelating diphosphine ligands containing $–PPh_2$ groups [11,30,31]. This shift to higher energy may be caused by the reduced donating abilities of our ligand **2** resulting from the presence of highly electronegative fluorines on the central phenyl ring. Similar changes in the carbonyl frequencies in IR spectra have been observed when $M(CO)_x$ complexes of fluorinated and fluorine-free chelating polyphosphines and polythioethers [10,32] were compared. The ^{31}P NMR spectrum of **3** displays a signal at δ 101.3 (m), and this value is comparable to the chemical shift values observed for iron tricarbonyl complexes with 1,2-bis(diphenylphosphino)benzene (δ 98.7) [33] and 1,2,4,5-tetrakis(diphenylphosphino)benzene (δ 92.8) [11]. The ligation of the $Fe(CO)_3$ fragments to ligand **2** seems to have minimal effect on chemical shift values of fluorine, as the ^{19}F NMR spectrum of complex **3** (δ −92.6) is very close to that of the free ligand (δ −91.8)



(2)

2.2. Structural characterizations of compounds 2 and 3

Compound **2**, the ligand, crystallized around an inversion point with three contiguous carbon atoms on the central phenyl ring and $–PPh_2$, –SMe and F groups attached to each carbon atom (i.e., C1, C2 and C3) comprising the asymmetric unit. This central phenyl ring is almost planar with the P atoms located 0.232(1) Å above and below the plane. There was disorder associated with the position of the –SMe and F fragments as illustrated in Fig. 2 (see Table 1).

The model refined (as detailed in Section 4) consisted of both F and –SMe groups (i.e., F1, S1–C11) constrained together and situated below the central benzene plane as represented on the left (**2-a**) in Fig. 2. If the model refined consisted of atoms F2, C11 and S1, then this would have implied an F2–C11 distance of 2.38(1) Å which was considered as unrealistic. These disordered atoms (i.e., F and S atoms) are situated some 0.5 Å above or below the central plane except for atom F2 which is only 0.257(7) Å. This can be attributed to lesser steric hindrance from the adjacent methyl group C21 as is evident on the representation shown on the right (**2-b**) in Fig. 2. In contrast, F1 is 0.502(8) Å out of the plane and located closer to the $–PPh_2$ group as the C1′–C3–F1 angle of 110.6(4)° suggests. In both of the orientations (**2-a** and **2-b**), the adjacent substituents F, $–SCH_3$ and $–PPh_2$ are located on one side of the phenyl ring, whereas their symmetry equivalents are on the

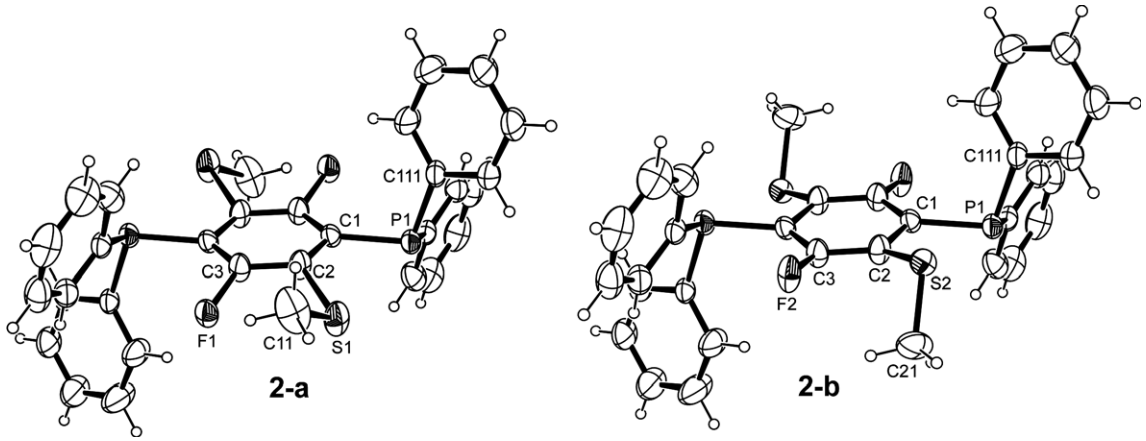


Fig. 2. ORTEP-3 [34] illustration of the 45.6(6)% (**2-a**) and 54.4(6)% (**2-b**) orientation of the F- and MeS-disordered groups in compound **2**. Ellipsoids are drawn at the 30% occupancy level and H atoms are represented by circles of arbitrary radii. Selected bond distances and angles: P1–C1 1.853(3) Å, C2–S1 1.823(4) Å, C2–S2 1.808(3) Å, C3–F1 1.399(7) Å, C3–F2 1.390(6) Å, S1–C11 1.778(11) Å, S2–C21 1.782(8) Å; C11 S1 C2 100.7(4)°, C21 S2 C2 98.0(3)°, C3 C2 S1 116.9(2)°, C3 C2 S2 124.2(2)°.

Table 1
Summary of crystallographic data for **2** and **3**

Compound	**2**	**3**
Formula	$C_{32}H_{26}F_2P_2S_2$	$C_{38}H_{26}F_2Fe_2O_6P_2S_2$
Formula Weight	574.59	854.34
Space group	$P\bar{1}$	$P21/a$
Unit cell dimensions		
a (Å)	9.414(2)	8.397(2)
b (Å)	9.639(2)	26.473(4)
c (Å)	10.125(2)	9.316(1)
α (°)	62.49(1)	90
β (°)	80.98(1)	113.71(1)
γ (°)	61.69(2)	90
V (Å^3)	715.1(3)	1896.1(6)
Z	1	2
ρ_{calc} (g/cm^3)	1.334	1.496
μ (Mo Kα mm^{-1})	0.332	1.014
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
θ Range (°)	2.28–22.46	1.54–24.97
Measured/independent reflections	1860/1402	3320/2291
Final R indices	$R_1 = 0.038$,	$R_1 = 0.045$,
$[I > 2\text{sigma}(I)]$[a]	$wR_2 = 0.090$[b,c]	$wR_2 = 0.096$[d]
R indices (all data)	$R_1 = 0.066$,	$R_1 = 0.088$,
	$wR_2 = 0.102$	$wR_2 = 0.110$
Largest difference in peak and hole	0.294, −0.166	0.335, −0.376
Goodness-of-fit on F^2	1.042	1.017

[a] $R = \Sigma(F_o - F_c)/\Sigma(F_o)$.
[b] $wR = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.
[c] $w = 1/[\sigma^2(F_o^2) + (0.0423 * P)^2 + 0.3539P]$, where $P = (\text{Max}(F_o^2, 0) + 2 * F_o^2)/3$.
[d] $w = 1/[\sigma^2(F_o^2) + (0.0430 * P)^2 + 1.7135P]$.

other side of the same ring (*aaabbb* substitution pattern). The existence of **2** in two orientations is most likely due to the packing effects present in the solid state, as no signal separation corresponding to the presence of **2-a/2-b** in solution was observed by low temperature NMR measurements (^{1}H and ^{31}P, −45 °C, $CDCl_3$). Persulfurated aromatic derivatives have been shown to display varying substitution patterns resulting from different steric orientations of the –SR substituents around the central aromatic core [35], and this has been referred to as a solid state phenomenon, resulting from packing effects.

An ORTEP-3 representation of complex **3** is shown in Fig. 3. The molecule is situated around an inversion point and, as was the case with the ligand **2**, 50% of the molecule comprises the asymmetric unit. The geometry around the Fe was estimated by a τ test, developed to assess the nature of pentacoordinate geometry (trigonal bipyramidal (tbp) vs. square pyramidal) [36]. The parameter τ is expressed as $\tau = (\alpha - \beta)/60$, where α and β are the largest and the second largest angles around the metal center. Therefore, $\tau = 0$ is expected for an ideal square pyramidal geometry, whereas $\tau = 1$ would represent tbp structure. The calculated τ value for the geometry at the iron center in **3** is 0.88, and similar values have been determined for $Fe(CO)_3$ complexes with bidentate chelating bisphosphines [37,38]. Hence, the geometry around the iron centers in **3** can be viewed as slightly

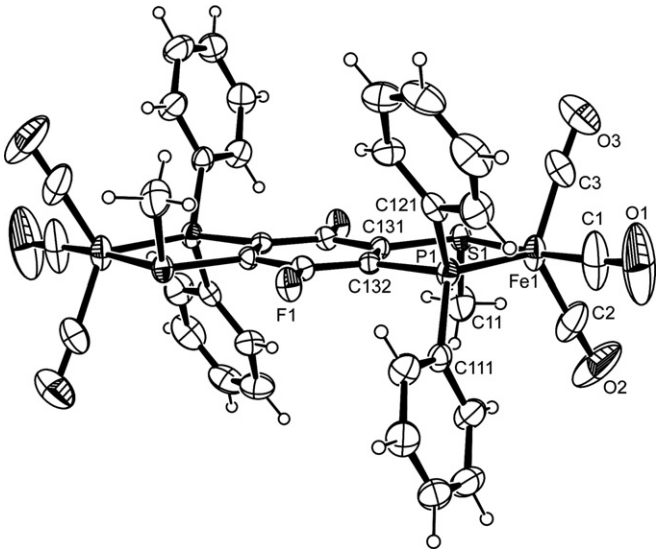


Fig. 3. ORTEP-3 illustration of complex **3**. Ellipsoids are drawn at the 30% occupancy level and H atoms are represented by circles of arbitrary radii. Selected bond distances and angles: Fe1–C1 1.737(6) Å, Fe1–C3 1.770(6) Å, Fe1–P1 2.2066(11) Å, Fe1–S1 2.2578(12) Å, C1–O1 1.146(7) Å, C2–O2 1.152(7) Å, C131–S1 1.791(3) Å, C132–P1 1.852(3) Å; P1 Fe1 S1 88.95(4)°, C131 S1 Fe1 106.63(12)°, C132 P1 Fe1 107.41(11)°, C1 Fe1 S1 176.8(3)°, C3 Fe1 C2 124.2(2)°.

distorted trigonal bipyramidal, with one CO (i.e., C1–O1) and –SMe ligands occupying the axial positions and the remaining two CO's and $-PPh_2$ situated in the equatorial plane. Interestingly, the only other reported $Fe(CO)_3$ complex with a neutral [P,S] ligand, 1-(diphenylphosphino)-1′-(phenylthio)ferrocene, features the iron center in a tbp geometry as well, but with the $-PPh_2$ group in axial and the –SPh in equatorial positions [29]. The different coordination preferences for the ligating groups observed in **3** may be dictated by both steric and electronic effects. The equatorial positions of trigonal bipyramidal complexes containing d^8–d^{10} metal centers are expected to be occupied by acceptor ligands [39]. While the π-acceptor properties of tertiary phosphines such as PPh_3 or even $P(C_6F_5)_3$ are estimated as weak (at best) [40,41], the ligand coordination mode observed in our complex **3** implies that the phosphine moiety of the [P,S] pocket of the ligand **2** is a stronger acceptor that the thioether functionality. However, a significantly bulkier phosphine group may be coordinated in the equatorial position to reduce steric effects.

The S and P atoms in **3** are in the plane of the central phenyl ring of the ligand. Iron atoms in the molecule are positioned above and below this plane, but the displacement is very small (the angle between the planes defined by P1–Fe–S1 and carbon atoms of the central phenyl ring is only 3.2°). Such distortions are more strongly pronounced in the structurally analogous bimetallic complex featuring $Fe(CO)_3$ fragments ligated to 1,2,4,5-tetrakis(diphenylphosphino)-benzene [11]. The Fe–P distance (2.2066(11) Å) in **3** compares well to analogous metal–ligand distances (2.184(1)–2.210(2) Å) determined for phosphine ligands at the equatorial positions in trigonal bipyramidal

{[P,P]FeCO$_3$} complexes ([P,P] represents a chelating bisphosphine) [11,37,38]. Also, the Fe–S bond length (2.2578(12) Å) in **3** is comparable to the Fe–S distance (2.288(2) Å) reported for (*cyclo*-1,3-$C_4H_8S_2$)Fe(CO)$_4$ [42], where the thioether ligates at the axial position of the tbp complex. Carbonyl ligands in **3** are not equivalent in the solid state, but a single peak observed in ^{13}C NMR spectrum (δ 218.4 s, ^{31}P–^{13}C coupling not resolved) suggests a dynamic behavior for the Fe(CO)$_3$ moiety in solution. Such behavior is well documented for iron tricarbonyl complexes with chelating bidentate ligands [32], and possible mechanisms have also been suggested [43].

3. Conclusions

The successful syntheses of the compound **2** suggest that a wide range of new binucleating ligands containing chelating pockets defined by hetero-donor groups can be produced. Such ligands should be useful for the construction of novel bimetallic complexes (e.g. **3**), and for one-dimensional solids.

4. Experimental

4.1. General procedure

All manipulations were carried out using Schlenk techniques or in a dry box under an N_2 atmosphere. Low temperature reactions were performed in Schlenk flasks immersed in an ethanol/liquid N_2 slush, contained in a Dewar flask. Solvents were purified before use by distillation from Na–benzophenone ketyl (ether, THF, hexanes, benzene) or CaH_2 (toluene, isopropanol, dichloromethane) or Na (pyridine) under N_2 atmosphere. Methanol was purified by either distillation from Mg(OCH$_3$)$_2$ or deoxygenated by bubbling nitrogen through it for 1 h. 1,4-Dibromo-2,5-bis(diphenylphosphino)-3,6-difluorobenzene has been prepared utilizing a previously reported synthetic procedure [9]. Commercially available chlorophosphines were purified prior to usage: $ClPPh_2$ was distilled under reduced pressure; ClP^iPr_2 was frozen and degassed while thawing under vacuum (repeated three times). LDA (lithium diisopropylamide) was freshly prepared immediately prior to use according to a published procedure [44]. Dimethyldisulfide was dried over molecular sieves (4 Å), and then frozen and degassed while thawing under vacuum (repeated twice). ^{1}H, ^{31}P, and ^{19}F NMR spectra were recorded on Varian INOVA spectrometer operating at 400, 161, 376 MHz, respectively. Spectra are referenced to tetramethylsilane (^{1}H), 85% H_3PO_4 as an external reference (^{31}P), and $CFCl_3$ as an internal reference in a sealed capillary tube (^{19}F). Low resolution mass spectrometric measurements were performed on Shimadzu QP5050A instrument; high resolution mass spectrometric measurements were performed at Mass Spectrometry Facility of Michigan State University (East Lansing, MI 48824-1319). Infrared spectrometric measurements were performed on either Mattson 3020 FTIR instrument or Perkin–Elmer Spectrum One spectrometer. Elemental analyses were performed at Galbraith Laboratories Inc. (Knoxville, TN 37950-1610).

4.2. Syntheses

4.2.1. 1,4-Bis(diphenylphosphino)-2,5-difluoro-3,6-bis(methylthio)benzene (**2**)

To a stirred solution of 1,4-dibromo-2,5-bis(diphenylphosphino)-3,6-difluorobenzene (2.00 g, 3.12 mmol) in THF (250 mL) at −80 °C was added 2.1 equiv. of *sec*-BuLi as a 1.3 M solution in hexanes. The mixture was stirred at −80 °C for 1 h, and then was slowly treated with a solution of 2.1 equiv. of dimethyldisulfide in THF (10 mL) through a cannula to yield a clear dark brown solution. The mixture was stirred for another hour at −80 °C and then allowed to warm up to room temperature overnight. The resulting solution was filtered, volatiles were removed under vacuo to yield a brown solid. Washing of the latter by hot isopropanol (100 mL) gave **2** as an orange solid. Yield: 1.039 g (58 %). Melting point: 205 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.40 (m, 8H), 7.32 (m, 12H), 2.17 (s, 6H). ^{31}P NMR ($CDCl_3$): δ −10.9 (m). ^{19}F NMR ($CDCl_3$): δ −91.8 (m). HRMS (FAB): Calc. for $C_{32}H_{27}F_2P_2S_2$ 575.0997; found: $m/z = 575.0996$ (MH^+). Crystals suitable for X-ray diffraction experiment were obtained by crystallization of **2** from ether/toluene (1:1) (1 week, −28 °C).

4.2.2. $(CO)_3Fe(\mu-[(PPh_2)(SMe)C_6F_2(SMe)-(PPh_2)])Fe(CO)_3$ (**3**)

A solution of $Me_3NO \cdot 2H_2O$ (0.75 g, 6.75 mmol) in dry methanol (20 mL) was slowly added to a solution of $Fe(CO)_5$ (0.44 mL, 3.37 mmol) in THF (10 mL) kept at −30 °C. A clear brown solution turned dark red upon addition of a solution of **2** (0.968 g, 1.69 mmol) in THF (30 mL). Upon completion of the addition, the reaction mixture was allowed to warm up to room temperature overnight. Volatiles were removed under vacuo to yield a brown solid which was washed with hot toluene (40 mL). Dark brown crystals of **3** were obtained by hexane vapor diffusion into a THF solution (room temperature, 3 days). Yield: 0.464 g (32%). IR (KBr, cm^{-1}; CO; relative intensities given in parentheses): 1996 (0.72), 1928 (0.62, sh), 1905 (1.00). ^{1}H NMR (C_6D_6): δ 7.60 (m, 8H), 6.96 (m, 12H), 2.05 (s, 6H). ^{31}P NMR (C_6D_6): δ 101.3 (m). ^{19}F NMR (C_6D_6): δ −92.6 (m). Anal. Calc. for $C_{38}H_{26}F_2Fe_2O_6P_2S_2$: C, 53.42; H, 3.07. Found: C, 53.18; H, 3.34%.

4.2.3. 1,4-Dibromo-2,5-bis(diisopropylphosphino)-3,6-difluorobenzene (**4b**)

To a stirred cold (−95 °C) solution of 1,4-dibromo-2,5-difluorobenzene (2.00 g, 7.36 mmol) in THF (250 mL) was added (via cannula) freshly prepared LDA (2.0 equiv.) in the same solvent. After 5 min, a solution of 2.3 equiv. of diisopropylchlorophosphine in THF (20 mL) was slowly introduced via a cannula. The mixture was stirred at −95 °C for 1 h and then allowed to warm up to room tem-

perature overnight to give a slightly cloudy yellow mixture. The reaction mixture was filtered and all volatiles were removed under vacuo to yield a light yellow solid, which was purified by washing with hot methanol (70 mL). Yield: 2.575 g (69%). Melting point: 210–211 °C. ^{1}H NMR ($CDCl_3$): δ 2.51 (m, 4H), 1.19 (m, 12H), 0.94 (m, 12H). ^{31}P NMR ($CDCl_3$): δ 27.5 (m). ^{19}F NMR ($CDCl_3$): δ −90.4 (m). HRMS (FAB): calc. for $C_{18}H_{28}F_2P_2Br_2$ 502.0001; found $m/z = 501.9999$ (M^+).

4.3. X-ray crystallography

Suitable crystals of complexes **2** and **3** were selected, coated with epoxy resin and placed on the heads of thin glass fibers, which were anchored in goniometer mounting pins. The individual pin-mounted crystal was then inserted into the goniometer head of the X-ray diffractometer and centered in the beam path. The procedures used to collect the data and refine the structure were as detailed previously for other complexes [9]. The refinement of complex **3** was straightforward as it did not contain disorder. Ligand **2** had crystallized with disorder in the F and MeS groups. This was accounted for by including atoms at the various sites and refining the disordered atoms' occupancies set to one with the F and corresponding S atom above one plane containing identical constrained occupancies. This resulted in a 45.6(6)–54.4(6)% occupancy ratio for S1–C11 and S2–C21 and also for F1 and F2, respectively. This refinement model afforded the lowest figures of merit. Another model (which afforded slightly higher figures of merit), tying the occupancies of trans disposed MeS and F ligands would have implied a very short distance between the methyl ligand and an F atom of 2.383 Å. Finally, suitable convergence of the data was not attained if the symmetry element was removed (i.e., the data refined in the *P*1 space group resulted in correlations of the thermal parameters).

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Appendix A. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, Nos. 607215 and 607216 for compounds **2** and **3** respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; e-mail: http://deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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