Citation for published version


DOI

https://doi.org/10.1016/S1387-7003(02)00585-3

Link to record in KAR

http://kar.kent.ac.uk/3756/

Document Version

Author's Accepted Manuscript

Copyright & reuse
Content in the Kent Academic Repository is made available for research purposes. Unless otherwise stated all content is protected by copyright and in the absence of an open licence (e.g., Creative Commons), permissions for further reuse of content should be sought from the publisher, author or other copyright holder.

Versions of research
The version in the Kent Academic Repository may differ from the final published version. Users are advised to check http://kar.kent.ac.uk for the status of the paper. Users should always cite the published version of record.

Enquiries
For any further enquiries regarding the licence status of this document, please contact: researchsupport@kent.ac.uk

If you believe this document infringes copyright then please contact the KAR admin team with the take-down information provided at http://kar.kent.ac.uk/contact.html
The Effect of Substitution of a Thioether Donor by a Phosphine Donor in Thiacrown Complexes of Iron

Frank E. Sowrey, a Philip J. Blower, b John C. Jeffery, c Elizabeth J. MacLean, d and Michael J. Went e,a

a School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NR
b Department of Biosciences, University of Kent, Canterbury, Kent, CT2 7NJ
c Department of Inorganic Chemistry, The University, Bristol, BS8 1TS
d CLRC, Daresbury Laboratory, Warrington, Cheshire, WA4 4AD

Abstract

Electrospray mass spectrometry and thermogravimetric analysis reveals that bis(1-phenyl-1-phospha-4,7-dithiacyclononane)iron(II) is more susceptible to ethene loss than bis(1,4,7-trithiacyclononane)iron(II). This is in accord with X-ray crystallographic studies, which show that the C-S bonds are longer in the former complex suggesting an increased population of the C-S $\sigma^* \pi$-acceptor orbitals.

Keywords: Bond cleavage, Thioether, Phosphine, Iron complexes, Macrocycle

In recent years we have been developing the coordination chemistry of small macrocyclic ligands containing thioether and phosphine donors in order to establish whether they could act as a basis for the development of new metal essential or non-essential radiopharmaceuticals [1,2]. Crucial to this endeavour is the formation of robust complexes that will survive in vivo. Investigations of 1,4,7-trithiacyclononane (9S3) complexes demonstrated that, whilst relatively stable complexes are formed, the ligand can be surprisingly susceptible to ethene loss [3-5]. This has been observed both in the isolation of [Re(9S3)(SCH$_2$CH$_2$SCH$_2$CH$_2$S)]$^+$ following the one-electron reduction of [Re(9S3)$_2$]$^{2+}$ [3,5] and in the electrospray mass spectra of [M(9S3)$_2$]$^{2+}$ (M = Tc, Re, Ru, Os) [4].
An investigation into the C-S bond activation process using extended Hückel theory suggested that it is caused by donation of electron density from metal t$_{2g}$ orbitals into C-S σ* orbitals [4].

We have also investigated the coordination chemistry of 1-phenyl-1-phospha-4,7-dithiaclononane (9PS2) [2,6,7]. Our initial premise was that combining the endodontate nine-membered ring conformational properties of 9S3 with the relatively higher binding strength of a phosphine donor would produce complexes that were more robust. This was confirmed in comparative studies of [Mo(9PS2)(CO)$_3$] and [Mo(9S3)(CO)$_3$] [2]. The greater π-acceptor ability often attributed to phosphines, compared with thioethers [8], also suggested that ethene loss would be less likely to occur since the C-S σ* orbitals would be populated to a lesser extent. However, a comparative study of [Fe(9S3)$_2$]$^{2+}$ and [Fe(9PS2)$_2$]$^{2+}$ reported in this communication shows that in respect of these complexes the reverse is true.¹

We had previously observed that [Ru(9S3)$_2$]$^{2+}$ was more stable than [Os(9S3)$_2$]$^{2+}$ with respect to ethene loss under electrospray conditions, and not surprisingly we now find [Fe(9S3)$_2$]$^{2+}$ continues this trend [4]. The region of spectrum where ethene loss peaks occur for [Fe(9S3)$_2$][BF$_4$]$_2$ is shown in Figure 1a. At a cone voltage of 15V no ethene loss was observed and the dominant species was [Fe(9S3)$_2$]$^{2+}$ (m/z =208.0). However, a peak is observed at m/z = 268.9 which can be assigned to [Fe(9S3)SH]$^+$ indicating fragmentation of 9S3 with only a residual sulfide remaining. Evidence for 9S3 loss is provided by a peak at m/z of =255.0 corresponding to [Fe(9S3)F]$^+$. At a cone voltage of 30V a small additional peak is observed due to loss of ethene to give the ion [Fe(9S3)$_2$ - (CH$_2$CH$_2$)]$^{2+}$ (m/z =194.0). This peak increases in relative intensity as the cone voltage is increased to 60V, but is much smaller than the corresponding peaks in the spectra of [Ru(9S3)$_2$]$^{2+}$ and [Os(9S3)$_2$]$^{2+}$.

Recording the mass spectra of [Fe(9PS2)$_2$](BF$_4$)$_2$ under identical conditions demonstrated a marked difference in stability (Figure 1b). At a cone voltage of 15V the dominant species was [Fe(9PS2)$_2$]$^{2+}$ (m/z = 284.0). However, even at this relatively low cone voltage, the complex undergoes significant loss of ethene as shown by the presence of the peaks at 270.0, 256.0 and 242.0 which correspond to [Fe(9PS2)$_2$ - n(C$_2$H$_4$)]$^{2+}$ (n = 1-3) respectively. The spectrum is dominated by ions in which two 9PS2 derived ligands are coordinated to the iron with only a
small peak observed corresponding to \([\text{Fe}(9\text{PS}2)\text{P}]^+\) \((m/z =342.9)\). As the cone voltage increases
the peaks due to fragments which have lost ethene increase in intensity and a further peak at
228.0 corresponding to \([\text{Fe}(9\text{PS}2)_2 - 4(\text{C}_2\text{H}_4)]^{2+}\) can be clearly seen in the spectra at 45V and
60V. The loss of up to four ethene molecules implies that both C-P and C-S bond cleavage must
be occurring. At cone voltages higher than 45V the complex is fragmented to a much greater
extent and at 60V the \([\text{Fe}(9\text{PS}2)_2]^{2+}\) is no longer the major species present having been replaced
by \([\text{Fe}(9\text{PS}2)_2 - (\text{C}_2\text{H}_4)]^{2+}\). Although the 9PS2 appears to be more strongly attached to the
metal centre than 9S3, the \([\text{Fe}(9\text{PS}2)_2]^{2+}\) complex loses ethene much more readily than the
corresponding 9S3 complex.

To further evaluate the relative stability of the two complexes thermogravimetric analysis
was undertaken. The TGA of \([\text{Fe}(9\text{PS}2)_2](\text{BF}_4)_2\) (Figure 2) shows that the sample is unaffected
until approximately 300°C at which point the sample slowly begins to lose mass. Even at 600°C
the total loss of 27% is less than would be expected for the loss of one 9PS2 (35%). The mass
loss is more in accord with the expulsion of ethene molecules. By comparison the TGA of
\([\text{Fe}(9\text{S}3)_2](\text{BF}_4)_2\) again shows that the complex is stable up to 300 °C after which a large (73 %)
mass loss rapidly occurs strongly suggesting that the complex has decomposed with loss of both
ligands. The slight rise in mass on further heating can be assigned to oxidation of the iron. The
TGA results confirm that the presence of the phosphine donor in the macrocycle does indeed
increase the strength of the iron ligand binding, but at the expense of the stability of the
macrocyclic backbone.

In order to establish the reasons for the relative fragility of the backbone C-S bonds in
\([\text{Fe}(9\text{PS}2)_2][\text{BF}_4]_2\) compared with \([\text{Fe}(9\text{S}3)_2][\text{BF}_4]_2\) the crystal structures of both compounds were
determined.\(^2\) \([\text{Fe}(9\text{S}3)_2][\text{BF}_4]_2\) crystallised with two molecules of MeCN in the lattice. The cation,
which is approximately octahedral with a crystallographically imposed inversion centre, is shown
in Figure 3. The Fe-S distances are only approximately the same \([2.2437(7), 2.2562(6),
2.2581(7)Å]\) and there is a significant variation of the C-S distances dependent on whether the
bond lies in the plane of the metal \(t_{2g}\) orbitals, as has been observed previously in a wide range of
9S3 complexes \([4]\). The structure of the \([\text{Fe}(9\text{S}3)_2]^{2+}\) ion has been determined previously as PF\(_6\),
ClO\(_4\), Sb\(_2\)Cl\(_8\)\(^2-\) and FeCl\(_4\)\(^2-\) salts.\(^9-12\) Comparison with the ClO\(_4\)\(^2-\) salt is not appropriate as it was
disordered. The FeCl$_4^{-2}$ salt was observed to have effectively equivalent Fe-S bonds [2.243(1), 2.244(1), 2.249(1) Å] and in the PF$_6^{-}$ and Sb$_2$Cl$_8^{-2}$ salts the in/out of plane correlation is less pronounced than in the BF$_4^{-}$ salt. The structure of [Fe(9PS$_2$)$_2$$]^{2+}$, which is pseudo octahedral with trans disposition of the phosphine functionalities and crystallographically imposed inversion symmetry, is shown in Figure 4. The Fe-S distances are similar [2.2445(7) and 2.2516(7)Å] and their average (2.248Å) is slightly shorter than that found in [Fe(9S$_3$)$_2$][BF$_4$]$_2$ (2.253Å), while the Fe-P distance [2.2244(7)Å] is significantly shorter than the Fe-S distances and is also shorter than the Cambridge Crystallographic Database$^{13}$ average for iron-phosphine bonds (2.25 Å). Both the C-S and C-P intra-ring bond distances correlate with their orientation with respect to the t$_{2g}$ orbitals. The in-plane S(8)-C(9) bond [1.851(3) Å] is especially long and more typical of a Group 7 structure [3,14]. The effect of coordination can be gauged by comparison with the C-S bonds in 9S$_3$ [1.820(5) and 1.823(5)Å] [15] and in c-PhPS(CH$_2$CH$_2$S)$_2$CH$_2$CH$_2$ [range 1.792(9) to 1.815(9)Å (average 1.804Å)] [2]. In the larger fourteen-membered trans-1,8-diphenyl-1,8-diphospha-4,12-dithia-cyclotetradecane (trans-14P$_2$S$_2$) the C-S bonds are significantly shorter [1.733(7) and 1.759(8) Å] possibly reflecting the strain in the smaller nine-membered rings [16].

Comparisons for the P-C bond lengths [1.843(3) and 1.822(3)Å] with those expected in an uncoordinated nine-membered ring are more difficult to establish. To date crystalline 9PS$_2$ has not been obtained. c-PhPS(CH$_2$CH$_2$S)$_2$CH$_2$CH$_2$ containing a pentavalent phosphorus has P-C bond lengths of 1.831(7) and 1.828(9)Å [2]. The less strained trans-14P$_2$S$_2$ has comparatively long P-C bonds 1.854(7) and 1.837(7) Å [16]. In the eleven-membered rings 2,6,10-triphenyl-2,6,10-triphosphabicyclo(9.4.0)pentadeca-11(1),12,14-triene and 6-phenyl-6-phospha-2,10-dithiabicyclo(9.4.0)pentadeca-11(1),12,14-triene [17] the P-C bonds lengths are in range 1.834(8) - 1.862(8) and in the twelve-membered 1,5,9-triphospha-1,5,9-tris(2-propyl)cyclododecane the range is 1.831(5) to 1.862(5) [18]. It can be concluded that in [Fe(9PS$_2$)$_2$$]^{2+}$ the C-S bonds are significantly lengthened while P-C bonds are relatively unchanged compared with uncoordinated systems.

Whilst complexes formed from 9PS$_2$ may be more inert with respect to ligand substitution than analogous 9S$_3$ complexes, the results described in this paper demonstrate that in iron(II) complexes the 9PS$_2$ ligand is more susceptible to decomposition via ethene loss. The
mass spectrometry, thermogravimetric and structural data indicate that replacement of a thioether
by a phosphine weakens the remaining C-S bonds. The implication is that in the 9PS2 complex
the C-S σ* orbitals are accepting more electron density than the analogous 9S3 complex, hence
the C-S bonds are longer and weaker in [Fe(PS2)₂]^{2+} compared with [Fe(9S3)₂]^{2+} resulting in
more facile ethene loss. Calculational studies are planned to compare the π-acceptor abilities of
these two ligands.

Footnotes

1 Complexes [Fe(9S3)₂][BF₄]₂ and [Fe(9PS2)₂][BF₄]₂ were prepared by literature methods.¹⁹,⁷

2 Crystallographic Data for [Fe(9S3)₂][BF₄]₂(MeCN)₂: C₁₆H₃₀B₂F₈FeN₂S₆, monoclinic, space
group P2(1)/c a =10.8033(15), b =15.129(2), c =8.3709(11) Å, β =105.263(2), U = 1319.9(3) Å³,
T = 293 K, Z =2 μ = 1.114 mm⁻¹, Reflections collected 8286, Independent reflections 3020 (R_{int}
= 0.0768) The final wR₂ was 0.1180 (all data). X-ray measurements were made using a Bruker
SMART CCD area-detector diffractometer with Mo-Kα radiation (λ = 0.71073 Å) [20].

Intensities were integrated [21] from several series of exposures, each exposure covering 0.3° in
ω, and the total data set being a hemisphere. Absorption corrections were applied, based on
multiple and symmetry-equivalent measurements [22]. The structure was solved by direct
methods and refined by least squares on weighted F² values for all reflections [23]. All non-
hydrogen atoms were assigned anisotropic displacement parameters and refined without
positional constraints. Hydrogen atoms were constrained to ideal geometries and refined with
fixed isotropic displacement parameters. The structure of the dicationic metal complex has
crystallographically imposed inversion symmetry. Thus the asymmetric unit contains half a
molecule of the Fe cation, a single BF₄ anion and one molecule of MeCN. Complex neutral-atom
scattering factors were used [24].

Crystallographic Data for [Fe(9PS2)₂][BF₄]₂. C₂₄H₃₄B₂F₈FeO₂P₂S₄, M = 778.19, triclinic, space
group P-1, a =8.5574(12), b =9.9103(14), c =10.7513(15) Å, α =104.837(3), β =112.378(3), γ
=101.472(3)°, U = 768.91(19) Å³, T = 150 K, Z =1, μ = 0.940 mm⁻¹, Reflections collected 7671,
Independent reflections 4031 (R_{int} = 0.0343) The final wR₂ was 0.1294 (all data). The data was
collected using the microcrystal diffraction facility on station 9.8 of the Synchrotron Radiation
Source, CLRC Daresbury Laboratory [25,26]. The data was collected on a Bruker AXS SMART
CCD area-detector diffractometer. The crystal, which had been grown by slow evaporation from
acetonitrile, was mounted on the end of a two-stage glass fibre with perfluoropolyether oil, and cooled by a nitrogen-gas stream [27]. The wavelength was calibrated by measurement of the unit cell parameters of a standard crystal of known structure. Data collection nominally covered a sphere of reciprocal space by three series of ω-rotation exposure frames with different crystal orientation φ angles. Reflection intensities were integrated using standard procedures [28], allowing for the plane-polarised nature of the primary synchrotron beam. Corrections were applied semiempirically for absorption and incident beam decay [29]. Unit cell parameters were refined from the observed ω angles of all strong reflections in the complete data sets [30]. The structure was solved by routine automatic direct methods and refined by least-squares refinement of all unique measured F² values [31].

**Supplementary data:** Full tables of atomic parameters, bond lengths and angles are deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

**Acknowledgments.** We thank the EPSRC for funding. We acknowledge the provision of time on DARTS, the UK national synchrotron radiation service at the CLRC Daresbury Laboratory, through funding by the EPSRC. We also acknowledge use of the University of Kent, Department of Biosciences, Welcome Trust Protein Science Facility and thank Dr Peter Slater, University of Surrey, for TGA measurements.

**References**


[22] G. M. Sheldrick. SADABS: A program for absorption correction with the Siemens SMART system; University of Göttingen: Germany, 1996.


Legends for figures

Fig 1 Ethene loss regions of electrospray mass spectra recorded at cone voltages 15 to 60V with a Finnigan MAT LCQ ion trap mass spectrometer. Samples were prepared by dissolution of ~1mg of sample in 1ml acetonitrile, this solution was further diluted by a factor of 10 and 20µl injected directly into the ionisation chamber. (a) [Fe(9S3)2][BF4]2  (b) [Fe(9PS2)2][BF4]2

Fig 2 TGA measurements of [Fe(9S3)2][BF4]2 and [Fe(9PS2)2][BF4]2 run at 5°C/min up to 600°C in air using a Stanton Redcroft STA780 thermal analyser.

Fig 3 Molecular structure of [Fe(9S3)2]2⁺ showing the atom labelling system. Atoms are represented as 50% probability ellipsoids. Selected bond lengths (Å): Fe(1)-S(1) 2.2437(7), Fe(1)-S(3) 2.2562(6), Fe(1)-S(2) 2.2581(7), In plane bonds: S(1)-C(6) 1.835(3), S(2)-C(2) 1.831(3), S(3)-C(4) 1.828(3), C(1)-C(2) 1.515(4), C(3)-C(4) 1.522(4), C(5)-C(6) 1.523(4), Out of plane bonds: S(1)-C(1) 1.819(3), S(2)-C(3) 1.818(3), S(3)-C(5) 1.810(3); Selected bond angles (º): S(1)-Fe(1)-S(3) 90.22(2), S(1)-Fe(1)-S(2) 89.78(2), S(3)-Fe(1)-S(2) 89.90(2), S(3)-Fe(1)-S(2) 90.52(2), S(1)-Fe(1)-S(2) 90.70(2), S(1)-Fe(1)-S(2) 90.10(2), S(3)-Fe(1)-S(2) 89.36(2)

Fig 4 Molecular structure of [Fe(9PS2)2]2⁺ showing the atom labelling system. Atoms are represented as 50% probability ellipsoids. Selected bond lengths (Å): Fe(1) - P(2) 2.2244(7), Fe(1) - S(5) 2.2445(7), Fe(1) - S(8) 2.2516(7), P(2) - C(11) 1.802(3), C(3) - C(4) 1.531(4), C(6) - C(7) 1.504(4), C(9) - C(10) 1.516(4), In plane bonds: P(2) - C(3) 1.843(3), S(5) - C(6) 1.832(3), S(8) - C(9) 1.851(3), Out of plane bonds: P(2) - C(10) 1.822(3), S(5) - C(4) 1.825(3), S(8) - C(7) 1.823(3); Selected bond angles (º): P(2) - Fe(1) - S(5) 92.00(2), P(2) - Fe(1) - S(5) 88.00(2), P(2) - Fe(1) - S(8) 86.58(2), P(2) - Fe(1) - S(8) 93.42(2), S(5) - Fe(1) - S(8) 90.77(2), S(5) - Fe(1) - S(8) 89.23(2)
Fig 2

[Graph showing mass loss vs. temperature for two compounds.

- [Fe(9PS2)2][BF4]2
- [Fe(9S3)2][BF4]2]