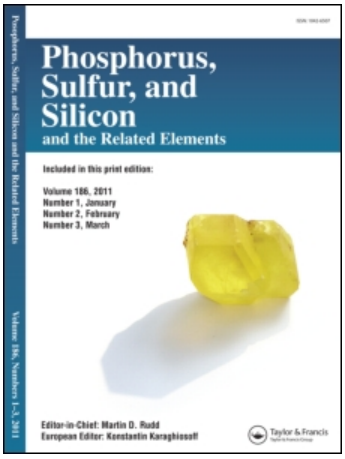


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

1,1'-Diheteroferrocenes of the Group 15 Elements

Arthur J. Ashe III[a]; Saleem Al-Ahmad[a]; Jeff W. Kampf[a]; Steffen Pilotek[a]
[a] Department of Chemistry, The University of Michigan, Ann Arbor, Michigan, USA

To cite this Article Ashe III, Arthur J. , Al-Ahmad, Saleem , Kampf, Jeff W. and Pilotek, Steffen(1994) '1,1'-Diheteroferrocenes of the Group 15 Elements', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 297 — 300
To link to this Article: DOI: 10.1080/10426509408021839
URL: http://dx.doi.org/10.1080/10426509408021839

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 297-300
Reprints available directly from the publisher
Photocopying permitted by license only

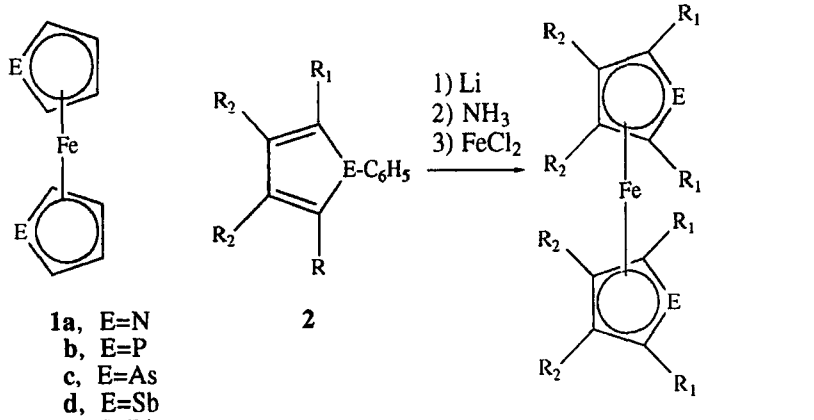
1,1'-DIHETEROFERROCENES OF THE GROUP 15 ELEMENTS

ARTHUR J. ASHE, III*, SALEEM AL-AHMAD, JEFF W. KAMPF AND STEFFEN PILOTEK
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055, USA

Abstract

Polymethyl-1,1'-diheteroferrocenes have been prepared. Their X-ray structures and chemistry are compared.

The 1,1'-diheteroferrocenes of the group 15 elements (**1a-1e**) are of general interest for the study of π-bonding between carbon and the heavier main group elements. Extensive prior work on phosphaferrocenes has demonstrated that **1b** has ferrocene-like properties.[1-3] The recent availability of all of the diheteroferrocenes allows a critical comparison of their properties.[4-10]



1a, E=N
b, E=P
c, E=As
d, E=Sb
e, E=Bi

2

3, R_1 = Me, R_2 = H
4, R_1 = R_2 = Me
5, R_1 = H, R_2 = Me

SCHEME I Preparation of Polymethyl-1,1'-diheteroferrocenes

The heavier 1,1'-diheteroferrocenes (**1b-1e**) are generally available by the reaction of the corresponding 1-phenylheterole (**2**) with lithium metal followed by $FeCl_2$. In this manner the polymethyl-1,1'-diheteroferrocenes (**3**, **4**, **5**) have been prepared in 30-70% yield.

X-ray structures have been obtained for **3c**[5], **3d**[7], **3e**[9], **4c**[7], **4d**[7], and **5b**[1]. Typical structures (**4c** and **4d**) are illustrated in Figure 1, while selected structural data are compared in Table 1. In all cases the compounds show ferrocene-like structures with the Fe atom sandwiched between two symmetrical η^5-heterolyl rings. The C-C bond distances are in the normal range found in metallocenes, while the heteroatom carbon (E-C) bonds are significantly shorter than the sum of the covalent radii, indicating multiple bonding. However the difference between the E-C bond lengths in the diheteroferrocenes and the normal E-C single bond length declines as the atomic number of E increases. Thus multiple bonding seems weaker in the heavier diheteroferrocenes.

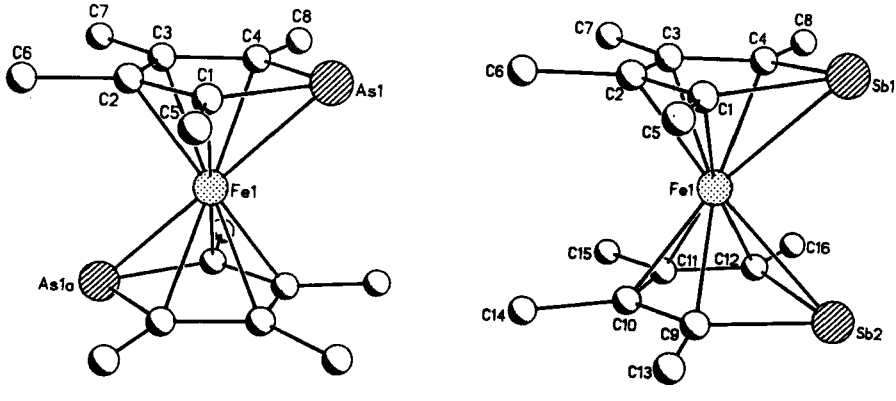
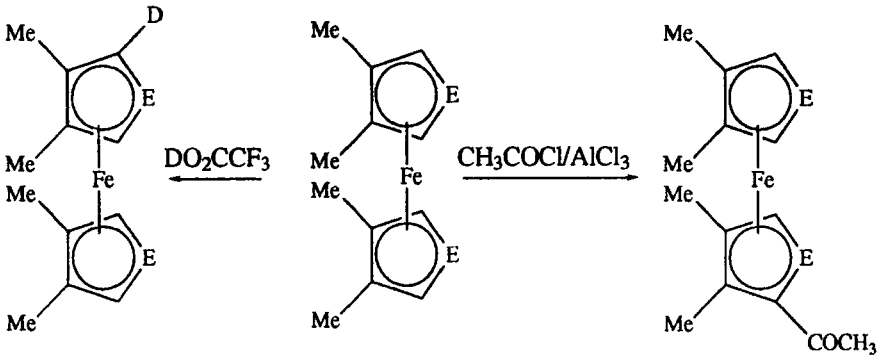


FIGURE 1 The molecule structures of octamethyl-1,1'-diarsaferrocene (**4c**) and octamethyl-1,1'-distibaferrocene (**4d**). The hydrogen atoms have been omitted for clarity.

TABLE I. A Comparison of the C-E Bond Distances in Selected 1,1'-Diheteroferrocenes with the Sum of the Covalent Radii of E and C.

Compound	E	CE Bond Distances	Covalent Radii	Difference	Reference
Ferrocene	CH	1.41 Å	1.54 Å	0.13 Å	–
5b	P	1.76	1.87	0.11	1
3c	As	1.90	1.98	0.08	5
3d	Sb	2.11	2.18	0.07	7
3e	Bi	2.22	2.29	0.07	9

In the solid state distibaferrocenes **3d** and **4d** adopt a cis-eclipsed (C_{2v}) conformation with short (3.68 Å for **3d** and 3.58 Å for **4d**) interannular separations between the Sb atoms. Similarly dibismaferrocene **3e** adopts the same conformation with a Bi...Bi separation of 3.69 Å. Since these distances are significantly shorter than van der Waals separation (4.4 Å for Sb...Sb and 4.6 Å for Bi...Bi), they are indicative of secondary bonding between the heteroatoms. However diarsaferrocene **4c** and diphoshaferrocene **5b** adopt different conformations with larger heteroatom separations. Thus the greater conformational preference of the very heavy diheteroferrocenes for the C_{2v} conformation is consistent with a stronger E...E secondary bonding for Bi and Sb than for As and P.



For **5b**, **5c**, **5d** **5** For **5b**, **5c**

SCHEME 2 Electrophilic Substitution of 1,1'-diheteroferrocenes

1,1'-Diphosphaferrocene **5b**[1] and 1,1'-diarsaferrocene **5c** undergo Friedel-Crafts acetylation at the position α to the heteroatom. 1,1-Distibaferrocene **5d** is the first stibaferrocene with the α-position free. We find that **5d** does not survive Friedel-Craft acetylation conditions but will undergo H/D exchange in dilute trifluoroacetic acid-d. Thus **5d** is the first antimony heterocycle which undergoes electrohilic aromatic substitution. The order of reactivity is found to be **5d>5c>5b**.

ACKNOWLEDGMENT

Support of the National Science Foundation (Grant No. CHE-9224907) is gratefully acknowledged.

REFERENCES

1. G. de Lauzon, B. Deschamps, J. Fischer, F. Mathey and A. Mischler, J. Am. Chem. Soc., 102, 994 (1980).
2. F. Mathey, N. Jour. Chem., 11, 585 (1987).
3. F. Nief, F. Mathey, L. Richard and F. Robert, Organometallics, 7, 921 (1988).
4. G. Thiollet, F. Mathey and R. Poilblanc, Inorg. Chim. Acta, 32, L67 (1979).
5. L. Chiche, J. Galy, G. Thiollet and F. Mathey, Acta Crystallogr., B36, 1344 (1980).
6. A. J. Ashe, III, S. Mahmoud, C. Elschenbroich and M. Wünsch, Angew. Chem., Int. Ed. Engl., 26, 229 (1987).
7. A. J. Ashe, III, J. W. Kampf, S. Pilotek and R. Rousseau, Organometallics, in press.
8. A. J. Ashe, III and T. R. Diephouse, J. Organomet. Chem., 202, C95 (1980).
9. A. J. Ashe, III, T. R. Diephouse, J. W. Kampf and S. M. Al-Taweel, Organometallics, 11, 1491 (1992).
10. A. J. Ashe, III, J. W. Kampf, D. B. Puranik and S. M. Al-Taweel, Organometallics, 11, 2743 (1992).