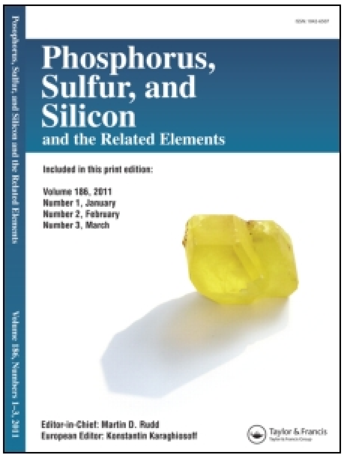

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND DYNAMIC SOLUTION BEHAVIOR OF 2,2',5,5'-TETRAKIS (TRIMETHYLSILYL)-3,3',4,4'-TETRAMETHYL-1,l'-DIPHOSPHAFERROCENE

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To cite this Article Al-taweel, Samir M.(1997) 'SYNTHESIS AND DYNAMIC SOLUTION BEHAVIOR OF 2,2',5,5'-TETRAKIS (TRIMETHYLSILYL)-3,3',4,4'-TETRAMETHYL-1,l'-DIPHOSPHAFERROCENE', Phosphorus, Sulfur, and Silicon and the Related Elements, 130: 1, 203 — 209

To link to this Article: DOI: 10.1080/10426509708033710

URL: http://dx.doi.org/10.1080/10426509708033710

Phosphorus, Sulphur, and Silicon, 1997, Vol. 130, pp. 203–209
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SYNTHESIS AND DYNAMIC SOLUTION BEHAVIOR OF 2,2′,5,5′-TETRAKIS (TRIMETHYLSILYL)-3,3′,4,4′-TETRAMETHYL-1,1′-DIPHOSPHAFERROCENE

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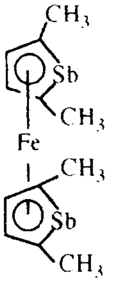
(Received 1 July 1997; Revised 6 September 1997; In final form 6 September 1997)

2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,-1′diphosphaferrocene (5) has been obtained from the reaction of 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylphosphole with lithium followed by $FeCl_2$. In solution, the barrier to ring rotation (ΔG^{**}) of 12.5 kcal/mole can be estimated from variable-temperature ^{1}H-NMR spectroscopy.

Keywords: phosphaferrocene; ring rotation barrier; variable-temperature ^{1}H-NMR

INTRODUCTION

We recently reported the crystal structure of 2,2′,5,5′-tetramethyl-1,1′-distibaferrocene **1**, which adopts a completely eclipsed ferrocenelike conformation with secondary bonding between antimony atoms in the same molecule[1]. The inter-ring Sb...Sb distance is 0.72 Å shorter than van der waals separation, which seems to indicate some sort of secondary bonding between the Sb atoms. Single crystal X-ray diffraction studies show that 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene (**2**) adopts a ferrocene-like conformation with inter-ring Bi...Bi contact, which is 0.91 Å shorter than van der waals separation[2]. Distibaferrocene and dibismaferrocene substituted with sterically demanding groups have been prepared in order to examine this phenomenon[3]. X-ray structure analysis of 2,2′,5,5′-tetrakis (trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-distibaferrocene (**3**) and 2,2′,5,5′-tetrakis(trimethylsilyl)3,3′,4,4′-tetramethyl-1,1′-distibaferrocene (**4**) reveals that there is no Sb...Sb or Bi...Bi inter-ring secondary bonding. It is obvious that the two pairs of eclipsed trimethylsilyl groups, steric repulsion exceeds the Sb...Sb or Bi...Bi bond energy. Since secondary bonding is generally more important for heavier atoms[4, 5] it is of interest to examine the corresponding phosphorus compounds. In order to examine this secondary bonding further, we have prepared a highly substituted diphosphaferrocene (**5**). We report here on the synthesis of 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**5**) and the dynamic behavior of **5** in solution.



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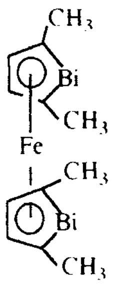

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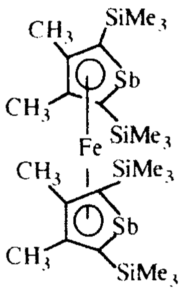

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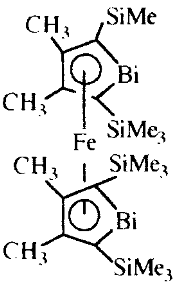

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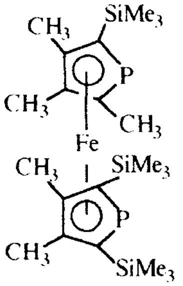

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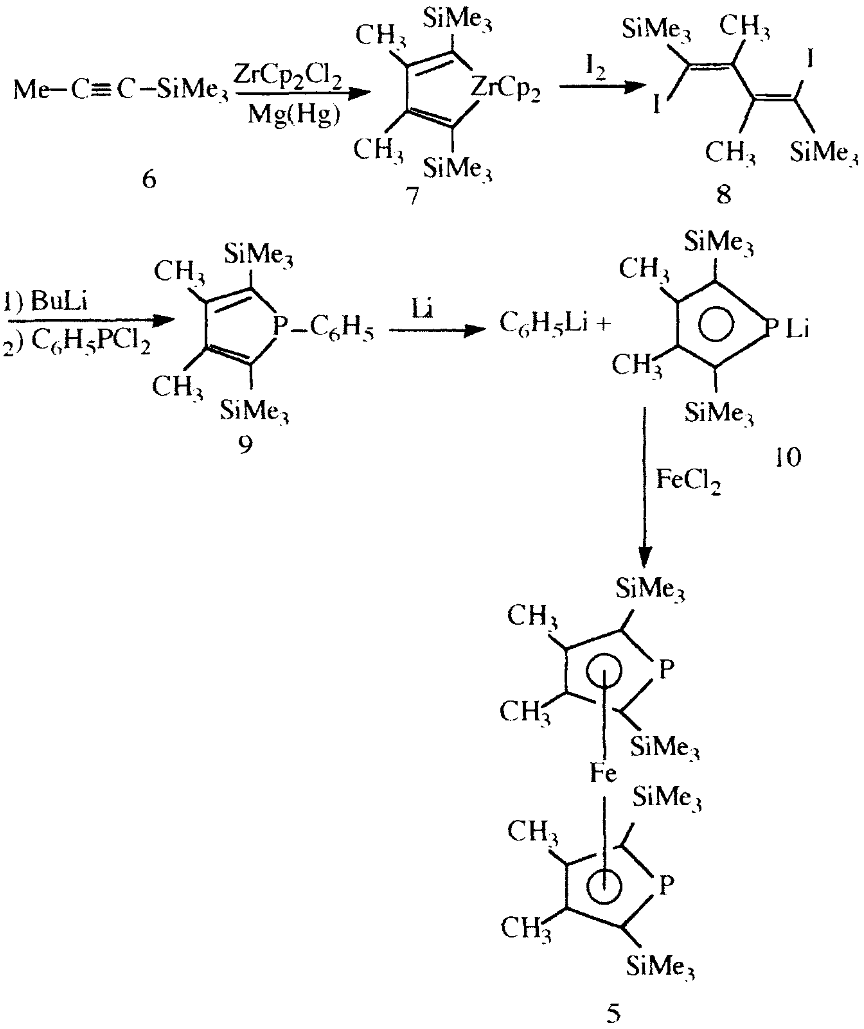
RESULTS AND DISCUSSION

Synthesis

Diphosphaferrocene **5** was prepared by a route similar to that which we reported for dibismaferrocene**4**[2], distibaferrocene **3**[3] and 2,5-bis(trimethylsilyl)-3,4-dimethyl-1-bismaferrocene[6] (See Scheme 1). This sequence is a general method for the synthesis of Group 15 heteroles from disubstituted acetylenes, followed by their conversion to 1,1′-diheteroferrocenes. Thus, 1-(trimethylsilyl)-1-propyne **6** reacts with zirconocene dichloride and magnesium amalgam to give 1,1′-bis(n^5-cyclopentadienyl)zirconacyclopentadiene **7**. Iodonolysis of 1,1′-bis (n^5-cyclopentadienyl) zirconacyclopentadiene **7** gives 86% of white crystalline solid **8**, which on treatment with butyllithium followed by treatment with phenyldichlorophosphine gives an 82% yield of 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethyl phosphole **9**. Phosphole **9** can be reduced by lithium to give the corresponding 2,5-bis(trimethylsilyl)-3,4-dimethylphosphole anion **10** as deep red solution in THF. Subsequent reaction with $FeCl_2$ gives red crystals of diphosphaferrocene **5** in 20% yield.



Scheme 1

^{1}H-NMR Studies

In order to investigate the conformational properties of **5**, we have examined its temperature dependent ^{1}H-NMR spectrum in $CDCl_3$ solution. Energy barriers for several ferrocenes and heteroferrocenes carrying bulky substituents have been evaluated from coalescence studies[3, 7–12]. There is no prior experimental report of rotational barrier of a diphosphaferrocene, although calculations on phosphaferrocenes have been published. The reliability of these calculations for correct estimation of rotational barriers and conformations of transition-metal complexes is well established[13–15].

At 295 K, the ^{1}H-NMR spectrum (360 MHz) of **5** consists of a single Me_3Si resonance (δ = 0.272) and a single ring Me resonance (δ = 2.080) indicating fast ring rotation on the NMR time scale. On cooling to 234 k two distinct Me_3Si signals are observed at δ 0.187 and δ 0.271 and two ring Me signals at δ 2.015 and δ 2.056. Taking the coalescence temperature at 250 K, ΔG^{**} for ring rotation is 12.5 Kcal/mole; calculations are based on equation 1.

$$\Delta G^{**} = 2.3\ RT\ 10.32 + \log \frac{T}{K} \qquad (1)$$

Where T: is the coalescence temperature

K: rate constant of exchange at T

$K = \pi\ \Delta v/\sqrt{2}$

Δv: distance in Hertz between the two peaks at slow exchange.

It is worth mentioning that coalescence of the Me and Me_3Si singlets occured at the same temperature.

The low temperature NMR spectrum indicates that the population of a conformation of C_2 symmetry, in which the equivalency of the two Me_3Si groups as well as the two Me groups on the same ring is broken. This non-equivalency of Me and Me_3Si groups arise from the freezing out the ring rotation to the energetically favored conformation.

The rotational barrier of diphosphaferrocene **5** can be compared with that measured for **3** and **4**, the antimony and bismuth analogues, repectively. The rotation barrier for diphosphaferrocene is slightly lower than that of **3** and **4**, but the difference is not significant. An X-ray crystal structure of **3** showed that it adopted C_2 conformation, most likely diphosphaferrocene **5** also adopts C_2 symmetry in the solid state.

The rotational barrier calculated from variable temperature ^{1}H NMR spectra of 5 can be compared with rotational barrier theoretically calculated for 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene[14, 15], taking into consideration the difference in the substitution pattern. The rotational barrier for 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene was calculated by the use of extended Hückel method. The total energy curve of the system shows a minimum at an angle θ = 140° – 145° (Figure 1a) corresponding to 8.65–8.80 kcal/ mol,

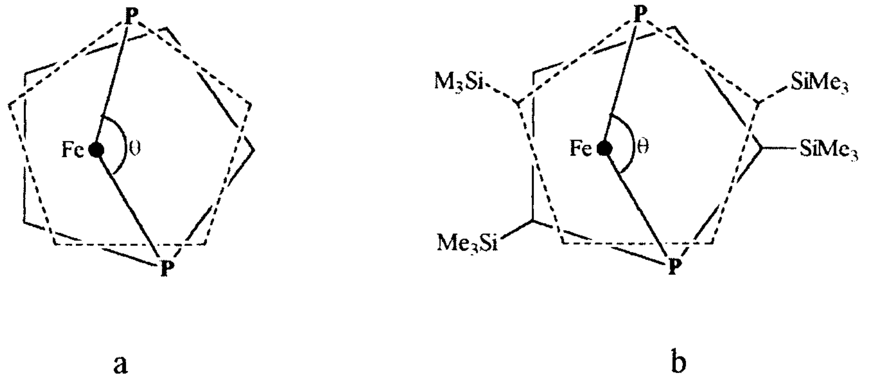


FIGURE 1 Schematic representations of energetically favored conformation of diphosphaferrocene : (a) calculated from extended Hückel method, reference[15], (b) observed for **5** from variable temperature ^{1}H-NMR at temperature below 234K. Methyl groups have been omitted for clarity.

whereangle θ is defined as the dihedral angle between two planes, each bisecting one ring and passing through the metal and the heteroatom.

Variable temperature ^{1}H -NMR spectra show that we were able to "freeze - out" ring rotation on the NMR time scale to the energetically favored conformation as in Figure 1b. Finally, the calculated conformation and the observed conformation 1b are in good agreement with each other as well as with the X-ray structure determination of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene.

It seems that heavier diheteroferrocenes of group 15 elements (Sb,Bi) adopt C_{2v} conformation with strong secondary bonding between the two heteroatoms in the same molecule, while the conformation of diheteroferrocenes for the lighter analogues (P,As) adapt C_2 or C_{2h}, which might be controlled by some kind of metal-ligand orbitals interaction.

EXPERIMENTAL SECTION

General

All reactions were carried out under an atmosphere of nitrogen, Solvents were dried using standard procedures. The exact mass was determined using a VG-70-S spectrometer. NMR spectra were obtained using Brucker WH-360, using $CDCl_3$ as solvent; ^{1}H-NMR spectra were calibrated using signals from the solvents referenced to Me_4Si. Combustion analyses were determined by Galbraith Laboratories, Knoxville, TN.

Phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylphosphole 9

A solution of 2.5 N n-BuLi in hexane (1.78 ml, 4.4 mmol) was added slowly to a solution of (1Z, 3Z)-1,4-bis(trimethylsilyl)-1,4-diiodo-2,3-dimethyl-1,3 butadiene (1.06g, 2.2 mmole) in 40 ml of Et_2O at −65°C with stirring. Stirring was continued at −65°C for 2h, after which the solution was allowed to warm to R.T for 5 min. After being recooled to −65°C, this solution was added to a solution of $PhPCl_2$ (0.38g, 2.2 mmole) in 10 ml of Et_2O at −65°C. The reaction mixture was stirred for 20 min at −65°C and then allowed to warm to 25°C. After solvent was removed under reduced pressure, the residue was extracted with 2 × 50 ml of pentane. Removal of the pentane under reduced pressure affords 0.65 g (89%) of a light yellow solid, m.p 61–62°C. Anal. calcd for $C_{18}H_{29}PSi_2$: C, 65.01; H, 8.79. Found : C, 64.87; H, 8.65. H-NMR ($CDCl_3$, 200 MHz) : δ 0.11 (S, 18H), 2.28 (d, $^4J_{PH}$ = 3.6 Hz, 6H), 7.15–7.35 (m, 5H).

2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′diphosphaferrocene 5

An excess of Li wire cut into pieces approximaely 2 mm in diameter was added with stirring at 25°C to solution of 9 (0.65g, 1.96 mmole) in 15 ml of THF, under nitrogen atmosphere. The initial yellow color changed to dark-red within 40 min. Stirring was continued over night at 25°C, solution was decanted from excess lithium, and the THF solution of lithium 2,5-bis(trimethylsilyl)-3,4-dimethyl-1-phosphacyclopentadienide was added to $FeCl_2$ (0.98 mmole. 0.12g) in 10 ml THF. After warming to 25°C, stirring was continued for 24h. Removal of the solvent under reduced pressure left a dark-red residue which was extracted with pentane (3 × 30ml). Removal of pentane afford red oil, crystallization from MeOH at −5°C afford 0.1g (20%) of red crystal of 5, m. p 150°C.

^{1}H-NMR ($CDCl_3$, 360MHZ) at room temperature for pure product: ∂ 0.272 (S, 18H) 2.080 (S, 12H). Anal: Calcd for $C_{24}H_{48}FeP_2Si_4$: C, 50.86; H,8.54. Found: C, 52.20; H, 8.94 . ;Ms (EI) exact mass:calcd for $C_{24}H_{48}FeP_2Si_4$,m/e 566.1658; found, m/e 566.1671

Acknowledgements

The author is grateful to professor Ashe, A.J., III for his fruitful discussion and for running ^{1}H-NMR spectra.

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