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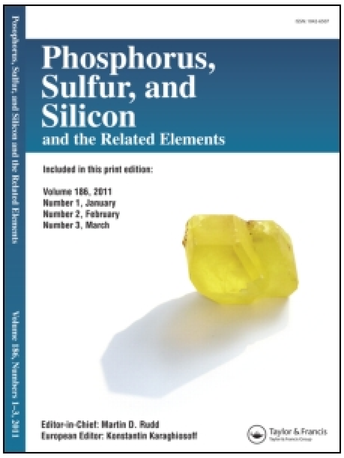

Phosphorus, Sulfur, and Silicon and the Related Elements

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MONO-, BIS- AND TRIS-METALLATED PHOSPHORUS COMPOUNDS

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Abstract Some new organometallated phosphorus compounds can be derived from the isolobal analogy. With $CpFe(CO)_2$ = Fp = ferrio substituent as the coordinating complex fragment on the central phosphorus atom, the syntheses, reactivities and structures of mono-, di- and triferriophosphines, -phosphonium salts and -chalcogeno- or -alkylidenephosphoranes are reported.

INTRODUCTION

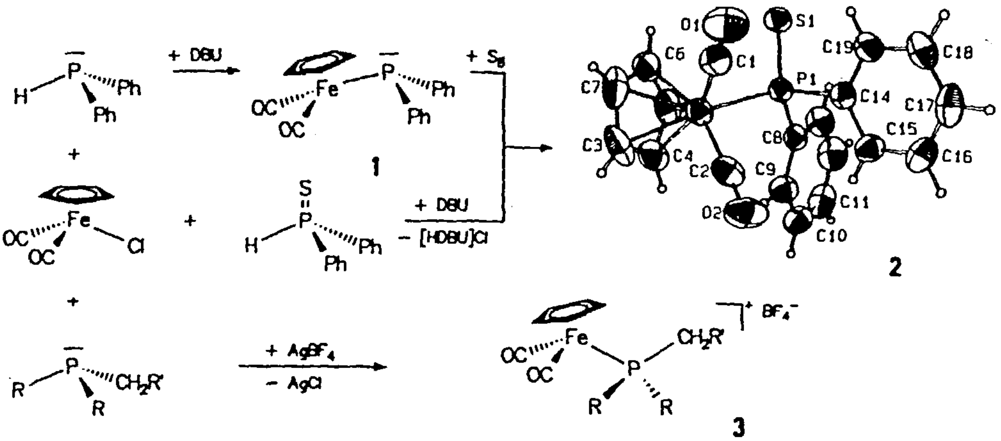
We are interested in the chemistry of organometallated phosphorus compounds which are isolobal to organic phosphorus compounds like phosphines, phosphonium salts and chalcogeno- or alkylidenephosphoranes. Previously we reported on some of our results which focused on open and closed diferriophosphonium salts and diferriothioxophosphoranes [1-7]

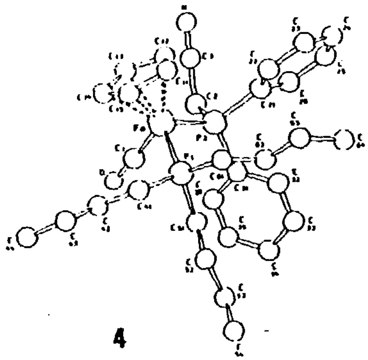
RESULTS AND DISCUSSION

The monoferrio derivatives of phosphorus **1** - **3** are obtained from the reactions of $CpFe(CO)_2Cl$ with PPh_2H, $PPh_2(H)S$ or PPh_2R' as shown in scheme 1.

The α-deprotonation of **3** does not succeed because of a competing base reaction. The ${}^nBu_3P$-modified monoferriophosphonium salt **4**, however, can be deprotonated to give the corresponding alkylideneferriodiphenylphosphoranes **6** which are isolobal to the phosphorus ylides of the Wittig-type (scheme 2). And, indeed, they react with benzaldehyde to give alkenes [8].

The diferriodiphenylphosphonium salt **7** arises from the reaction of $CpFe(CO)_2Cl$ with either **1** (1:1 molar) or with Ph_2PSiMe_3 (2:1 molar) shown in scheme 3. The *open* cation of **7** undergoes a photolytically induced CO elimination to give the *closed* diferriodiphenylphosphonium cation **7'**. Using the bissilylated phosphine


+ DBU
+ S_8
+ DBU
− [HDBU]Cl
+ $AgBF_4$
− AgCl
BF_4^-
1
2
3
O1
S1
C6
C1
P1
C19
C18
C7
C14
C17
C15
C3
C8
C4
C2
C9
C16
O2
C11
C10



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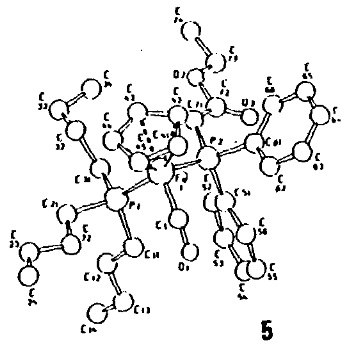

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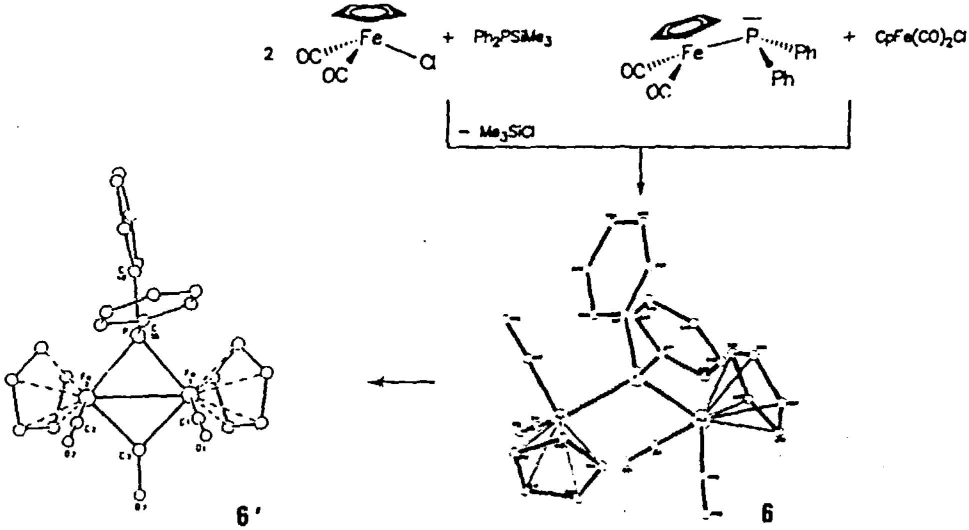
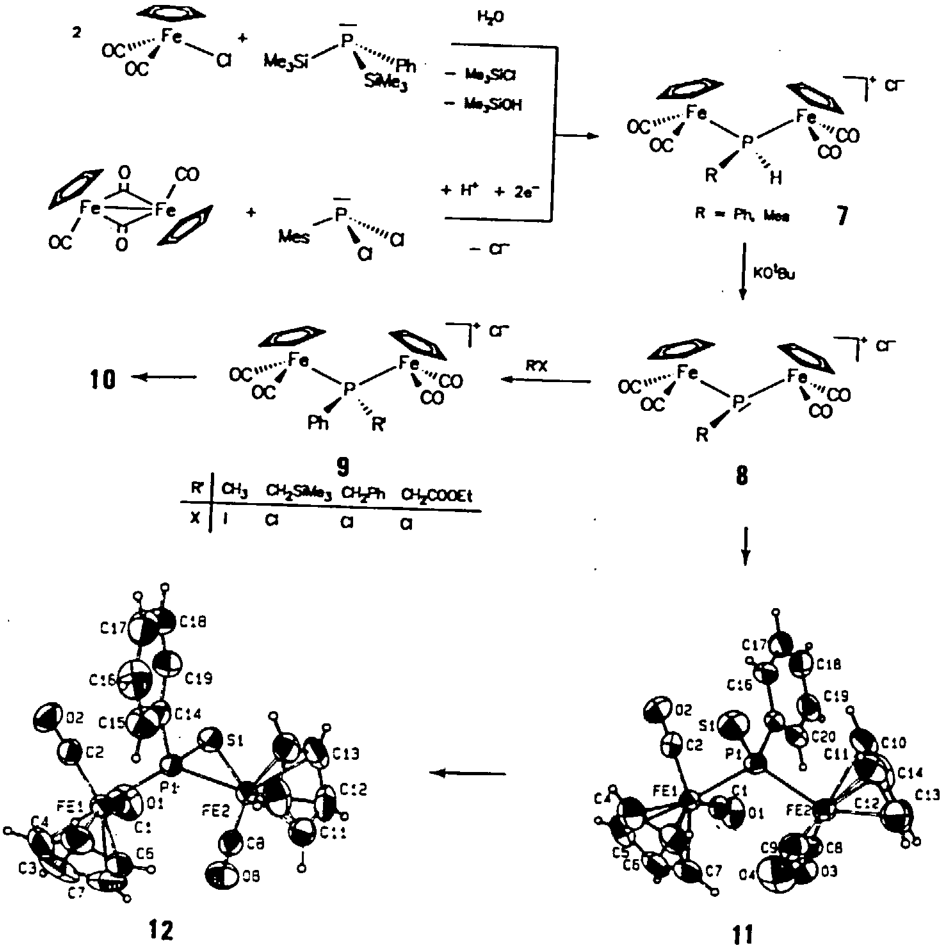
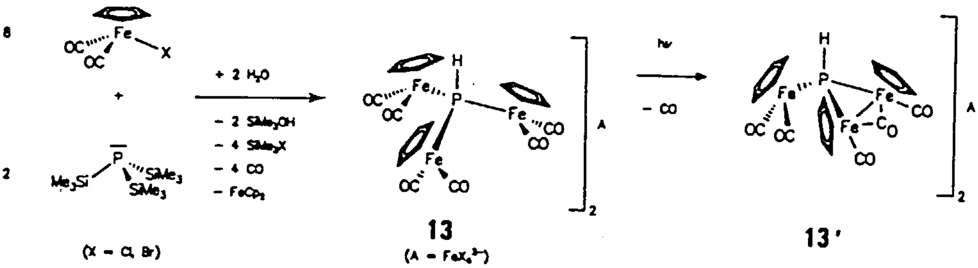
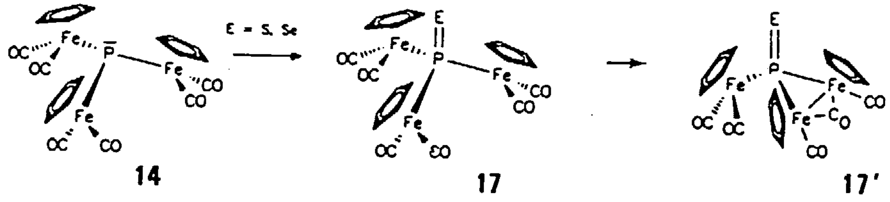

2
+ Ph_2PSiMe_3
+ $CpFe(CO)_2Cl$
− Me_3SiCl
6'
6



R'	CH3	CH2SiMe3	CH2Ph	CH2COOEt
X	I	Cl	Cl	Cl





$PhP(SiMe_3)_2$ we obtain the PH-functionalized diferriophosphonium salt **8** which after deprotonation to the diferriophosphine **9** is realkylated to form the mixed diorganyldiferriophosphonium salts **10** (scheme 4). **10** can also be deprotonated in the α-position to give the alkylidenediferriophosphorane or, more accurately, the μ_2-phosphaalkene complex **11**, because it loses Fp_2.

The diferriophosphine **9** is very easily oxidized to give the corresponding *open* diferriochalcogenophosphorane **12**, where R-P=S acts as a 2 e donor to two 17 e complex fragments. The photolytic decarbonylation of **12** leads, after migration of the resulting $CpFeCO$ fragment to the P=S bond, to the heterocyclopropane sytem **13** (scheme 5) where R-P=S now acts as a 4 e donor.

The trismetallated PH-functionalized triferriophosphonium salt **14** is obtained by the 8 : 2 stoichiometric reaction of $CpFe(CO)_2Cl$ and $P(SiMe_3)_3$ in the presence of water. The X-ray structure analysis shows that the FeP_3-skeleton in **14** is nearly flattened. The open form of **14** loses one CO-ligand to give the closed triferriophosphonium cation **14'** (scheme 6).

Both compounds **14**, **14'** can be deprotonated to give the open and closed triferriophosphines **15**, **15'** which can be transformed by quaternization to the corresponding PR- and PCl-triferriophosphonium salts **16**, **16'** or by oxidation to the chalcogenotriferriophosphoranes **17**, **17'** (scheme 7).

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