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Preliminary communication

[1]FERROCENOPHANES WITH PHOSPHORUS AND ARSENIC AS THE BRIDGING ATOMS: SYNTHESIS AND SOME REACTIONS. A NEW ROUTE TO FERROCENYLLITHIUM REAGENTS

DIETMAR SEYFERTH* and HOWARD P. WITHERS, Jr.

Department of Chemistry, Masachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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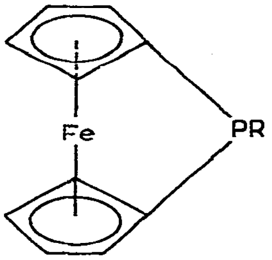
Summary

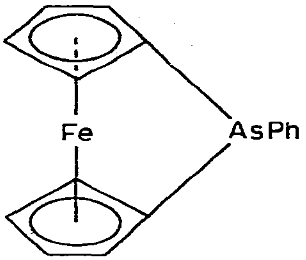
(1,1′-Ferrocenediyl)phenyl-phosphine and -arsine and (1,1′-ferrocenediyl)-methylphosphine have been prepared by the reaction of 1,1′-dilithioferrocene-tetramethylethylenediamine with the respective $RPCl_2$ and $PhAsCl_2$. They react at the Group V bridging atom with sulfur and with reactive metal carbonyl species without disruption of the ferrocenophane system. Organolithium reagents react with these compounds to open the ring and give 1-lithio-1′-phosphino- or arsino-ferrocenes. Some reactions of these new lithium reagents are reported.

Ferrocenophanes have received considerable attention and of some interest have been [1]ferrocenophanes in which the bridging unit is a diorganosilylene moiety [1,2]. Wrighton and his coworkers have used the dichlorosilylene-bridged ferrocenophane to attach ferrocenyl units to high-surface silica and to various electrode surfaces and have shown that the dimethylsilylene-bridged compound undergoes ring-opening on reaction with methanol [3]. It was reasonable to suppose that [1]ferrocenophanes containing bridging atoms other than silicon can be prepared, and we report here concerning our initial studies of [1]ferrocenophanes in which phosphorus (I, II) and arsenic (III) are the atoms which bridge the cyclopentadienyl ligands of the iron atom.

Ferrocenophanes I, II and III were prepared by the addition of the appropriate organodichlorophosphine or phenyldichloroarsine in hexane solution to a suspension of the 1,1′-dilithioferrocene-tetramethylethylenediamine adduct [4] in hexane at −78°C and allowing the reaction mixture to warm slowly to room temperature. In the case of the $PhPCl_2$/1,1′-dilithioferrocene reaction, the (1,1′-ferrocenediyl)phenylphosphine (I) which was produced was isolated in the form of moderately air-sensitive, brick-red nuggets, m.p. 100—102°C, in 53% re-



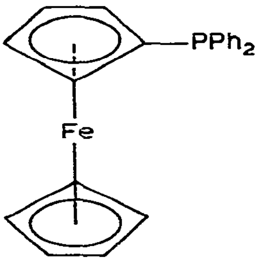
(I, R = Ph;
II, R = CH_3)



(III)

crystallized (from hexane at –30°C) yield. Similarly prepared from methyldichlorophosphine was II, air-sensitive, brick-red flakes, m.p. 70—72°C (dec). A similar reaction with phenyldichloroarsine gave III, red nuggets, m.p. 107.5—109°C, in 34% yield.

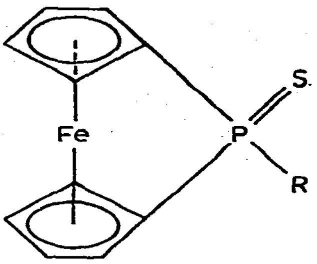
The electronic and ^{13}C nuclear magnetic resonance spectra of these new [1]ferrocenophanes indicate that, as in the silylene-bridged compounds, the cyclopentadienyl rings are tilted. Thus in the electronic spectra (hexane solution) the band which is found at 440 nm in the spectrum of IV was shifted to lower energy: I, 497 nm (ϵ 34.0); II, 498 nm (ϵ 41.0) and III, 494 nm (ϵ 31.2) (ϵ in m^2/mol).



(IV)

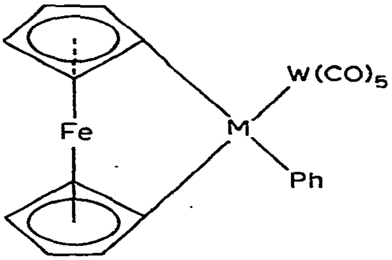
These shifts, which provide a measure of the distortion due to ring tilt, are slightly greater than those reported for the diphenylsilylene-bridged ferrocenophane (483 nm) [1]. Furthermore, this band in the electronic spectra of I, II and III was considerably stronger than the analogous band in the spectrum of IV. The signal due to the carbon atom to which the diphenylphosphino group is attached in the ^{13}C FT NMR spectrum (C_6D_6) of IV is found at δ (C) 76.65 ppm as a doublet (J(CP) 8 Hz). In contrast, the resonance of the cyclopentadienyl carbon atoms bridged by the PhP group in I was observed at δ (C) 18.7 ppm (d, J(CP) 54 Hz). The corresponding carbon atom signal was found at δ (C) 18.3 ppm in the ^{13}C NMR spectrum of III. The 70 eV mass spectra of I, II and III showed the molecular ion as the most intense peak.

We have begun a study of the chemistry of I, II and III and report here some initial results. Reaction with elemental sulfur in benzene readily converted I and II to the corresponding moderately air-stable, red-brown, microcrystalline phos-

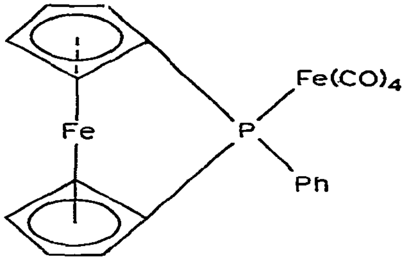


(V, R = Ph;
VI, R = CH_3)

phine sulfides, V and VI. The electronic spectrum of V (Et_2O) showed a band at 485 nm, which indicates that the [1]ferrocenophane system still is present. Metal carbonyl complexes of I and III also were prepared by reactions of both with THF· $W(CO)_5$ and of I with $Fe_2(CO)_9$ in THF. The [1]ferrocenophane structure also was retained in the air-stable, red, crystalline products, VII, VIII, and IX. Thus the electronic spectrum of VIII showed λ_{max} 492 nm (ϵ 33.0 m^2/mol).



(VII, M = P;
VIII, M = As)



(IX)

Of special interest are the reactions of I and III with organolithium reagents which proceeded via nucleophilic attack at the bridging atom with disruption of

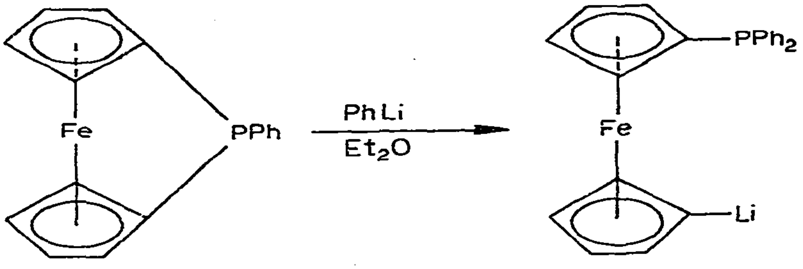
TABLE 1

SUBSTITUTED FERROCENES PREPARED BY REACTIONS OF THE LITHIUM REAGENTS DERIVED FROM (1,1′-FERROCENEDIYL)PHENYL-PHOSPHINE AND -ARSINE

RLi	Reactant	Product	M.p. (°C)	Yield (%)
A. Reagents derived from (1,1′-ferrocenediyl)phenylphosphine/RLi reactions				
PhLi	H_2O	$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4PPh_2)^a$	120—123	80
PhLi	Me_3SnCl	$(\eta^5\text{-}C_5H_4SnMe_3)Fe(\eta^5\text{-}C_5H_4PPh_2)$	oil	80
PhLi	Ph_2PCl	$Fe(\eta^5\text{-}C_5H_4PPh_2)_2{}^b$	184—185	79
PhLi	Me_3SiCl	$(\eta^5\text{-}Me_3SiC_5H_4)Fe(\eta^5\text{-}C_5H_4PPh_2)$	oil	98
MeLi	H_2O	$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4PMePh)$	69—71	29
B. Reagent derived from (1,1′-ferrocendiyl)phenylarsine/PhLi reaction				
PhLi	H_2O	$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4AsPh_2)$	129—130	73
PhLi	Ph_2PCl	$(\eta^5\text{-}C_5H_4AsPh_2)Fe(\eta^5\text{-}C_5H_4PPh_2)$	164—165.5	67

[a] Known compound; m.p. 120—122°C: ref. 4. [b] Known compound; m.p. 183—184°C; ref. 5.

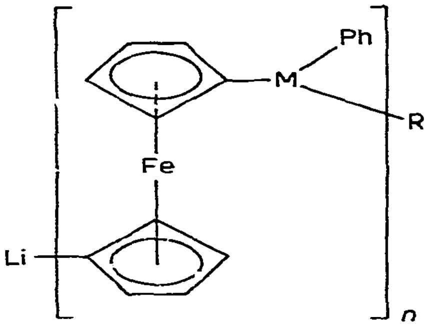
the [1]ferrocenophane systems as shown in eq. 1. The 1-lithio-1′-phosphino- (or -arsino)-ferrocenes thus produced were characterized by means of their reactions with various reagents as shown in Table 1. Product yields were uniformly high (65—95%). To obtain such high yields it is important to add I or III to an excess



(1)

(X)

of the organolithium reagent since the product of RLi attack on I or III is itself an organolithium reagent, and can compete effectively with RLi in attack at I or III. When a deficiency of RLi is added to I or III, novel phosphino- or arsinoferrocene polymers of type XI are obtained. These will be the subject of a later report.



(XI, M = P, As)

Such nucleophilic opening of [1]ferrocenophanes clearly is capable of wide extension. Coupled with the diversity of reactions which it is possible to effect with the reagents thus produced (e.g., X), this new functional ferrocene reaction provides access to a wide variety of new monosubstituted and 1,1′-disubstituted ferrocenes. Such reactions of I, II and III will be of interest since they can be used to prepare interesting and potentially useful new mono- and bi-dentate ligands, as, for instance, 1-diphenylarsino-1′-diphenylphosphinoferrocene (Table 1).

All new compounds were fully characterized by spectroscopy and analysis. Our efforts in this area are continuing. In conclusion, we note that the preparation and spectroscopy of I and III were reported independently by Osborne, Whiteley and Hollands at a poster session at the IXth International Conference on Organometallic Chemistry in Dijon in September 1979 [6].

Acknowledgment

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