



Synthesis and structure of ferrocenylmethylphosphines, their borane adducts, and some related derivatives

Mitchell A. Pet^a, Matthew F. Cain^a, Russell P. Hughes^a, David S. Glueck^{a,*}, James A. Golen^b, Arnold L. Rheingold^b

^a 6128 Burke Laboratory, Department of Chemistry, Dartmouth College, Hanover, NH 03755, United States

^b Department of Chemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, United States

ARTICLE INFO

Article history:

Received 10 December 2008

Received in revised form 9 February 2009

Accepted 10 March 2009

Available online 18 March 2009

Keywords:

Phosphine

Ferrocenyl

ABSTRACT

Syntheses of the known ferrocenylmethylphosphines FcCH_2PH_2 (**2**, $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$), $(\text{FcCH}_2)_2\text{PH}$ (**3**), and $(\text{FcCH}_2)_3\text{P}$ (**4**) have been reinvestigated. The reaction of $[\text{FcCH}_2\text{NMe}_3][\text{I}]$ with $\text{P}(\text{CH}_2\text{OH})_3$, generated from $[\text{P}(\text{CH}_2\text{OH})_4][\text{Cl}]$ and KOH , gave a mixture of the major product $(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OH})$ (**1**) and over-alkylated $(\text{FcCH}_2)_3\text{P}(\text{CH}_2\text{OH})$ (**9**). Treatment of pure **9** with $\text{Na}_2\text{S}_2\text{O}_5$ gave the secondary phosphine **3**; slow addition of $\text{Na}_2\text{S}_2\text{O}_5$ to **1** gave **2** in improved yield. Reaction of **1** with $[\text{FcCH}_2\text{NMe}_3][\text{I}]$, followed by treatment with NEt_3 , gave the tertiary phosphine $(\text{FcCH}_2)_3\text{P}$ (**4**), along with the known phosphonium salt $[(\text{FcCH}_2)_4\text{P}][\text{I}]$ (**5**), which could be prepared in higher yield by adjusting the stoichiometry. Phosphine **4** oxidized slowly in air to yield $(\text{FcCH}_2)_3\text{P}(\text{O})$ (**12**), was protonated by $\text{HBF}_4(\text{OMe}_2)$ to give $[(\text{FcCH}_2)_3\text{PH}][\text{BF}_4]$ (**13**), and reacted with $\text{Pt}(\text{COD})\text{Cl}_2$ or PtCl_2 to yield a mixture of *cis*- and *trans*- $\text{Pt}(\text{P}(\text{CH}_2\text{Fc})_3)_2\text{Cl}_2$ (**14**). Silylation of **2** with *n*-BuLi/ Me_3SiCl gave $\text{FcCH}_2\text{P}(\text{SiMe}_3)_2$ (**10**); treatment of **1** with $\text{Me}_3\text{SiCl}/\text{Et}_3\text{N}$ gave $\text{FcCH}_2\text{P}(\text{CH}_2\text{OSiMe}_3)_2$ (**11**). The phosphine-borane adducts $\text{FcCH}_2\text{PH}_2(\text{BH}_3)$ (**6**), $(\text{FcCH}_2)_2\text{PH}(\text{BH}_3)$ (**7**), $(\text{FcCH}_2)_3\text{P}(\text{BH}_3)$ (**8**) and $(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OSiMe}_3)_2(\text{BH}_3)$ (**15**) were prepared from the corresponding phosphines and $\text{BH}_3(\text{SMe}_2)$. The phosphines **2**, **3**, and **4**, phosphonium salts **5** and **13**, phosphine oxide **12**, Pt complex *trans*-**14**, and phosphine-boranes **6**, **7** and **8** were structurally characterized by X-ray crystallography. The solid cone angle of $(\text{FcCH}_2)_3\text{P}$, 139° , in Pt complex **14** showed that **4** was bulkier than PPh_3 , but less sterically demanding than $\text{P}(t\text{-Bu})_3$. The structural changes observed on quaternization of P (shorter P–C bonds and larger angles at P), along with results from NMR and IR spectroscopy and DFT calculations, were consistent with the expected rehybridization at phosphorus. Related observations for analogous methylphosphines suggest that methyl and ferrocenylmethyl phosphorus substituents have similar properties.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Alkylphosphines are useful ligands for transition metals in coordination and organometallic chemistry and catalysis, but their air-sensitivity and unpleasant smell have discouraged their routine use [1]. For this reason, the recent syntheses of the air-stable ferrocenylmethylphosphine derivatives $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$ (**1**, $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$) [2] and, more strikingly, the primary and secondary phosphines FcCH_2PH_2 (**2**) [3] and $(\text{FcCH}_2)_2\text{PH}$ (**3**) [4] were significant advances in preparing “user-friendly” ligands for various applications [5]. Although these phosphines can be prepared readily from inexpensive, commercially available $[\text{P}(\text{CH}_2\text{OH})_4][\text{Cl}]$, their potential as ligands and as building blocks in phosphine synthesis

remains little explored [6]. More recently, the analogous tertiary phosphine $(\text{FcCH}_2)_3\text{P}$ (**4**) was prepared in a mixture and isolated in 1.5% yield after separation from **2** and **3**; no metal complexes of this potentially useful ligand have yet been reported [4d]. In order to explore structure-property relationships as a basis for further applications of the FcCH_2 group in phosphine chemistry, we report here synthetic and structural studies of ferrocenylmethylphosphines, their borane adducts, and related derivatives.

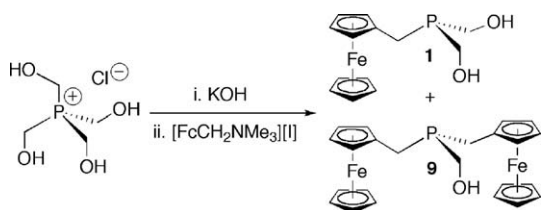
2. Results and discussion

2.1. Synthesis of ferrocenylmethylphosphines and some derivatives

As reported previously, treatment of $[\text{P}(\text{CH}_2\text{OH})_4][\text{Cl}]$ with KOH , followed by reaction with $[\text{FcCH}_2\text{NMe}_3][\text{I}]$ and workup with NEt_3 , yielded not only $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$ (**1**), as originally described [2], but also the over-alkylation byproduct, $(\text{FcCH}_2)_2\text{P}(\text{CH}_2\text{OH})$ (**9**, Scheme 1) [7]. Earlier, phosphine **9** was characterized only by

* Corresponding author.

E-mail addresses: Glueck@Dartmouth.Edu, David.Glueck@dartmouth.edu (D.S. Glueck).



Scheme 1. Synthesis of ferrocenylmethyl(hydroxymethyl)phosphines [2,7].

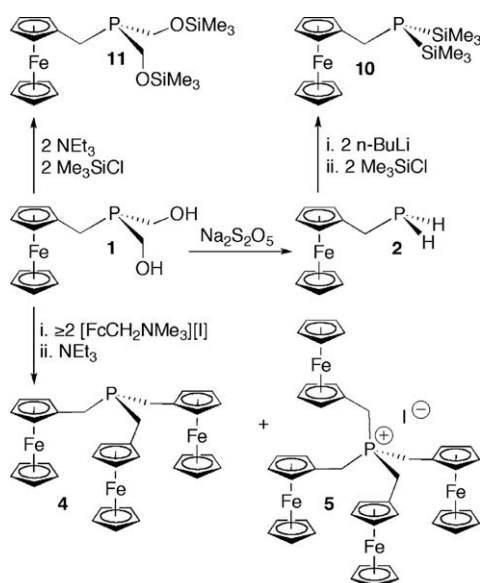
elemental analyses and mass spectroscopy; additional NMR data is given in Section 4.

The original synthesis [3] of **2** was improved by slow addition of $\text{Na}_2\text{S}_2\text{O}_5$ to **1** (Scheme 2) [8]; the workup could also be performed more conveniently by recrystallization instead of sublimation. These changes enabled synthesis of **2** on a 2-g scale in 79% yield.

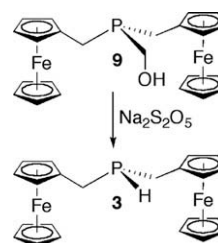
The secondary phosphine **3** was prepared earlier by deformylation of a mixture of hydroxymethylphosphines formed in the reaction of $[\text{P}(\text{CH}_2\text{OH})_4][\text{Cl}]$ with KOH and $[\text{FcCH}_2\text{NMe}_3][\text{I}]$, yielding a separable mixture of **2**, **3** and the tertiary phosphine $(\text{FcCH}_2)_3\text{P}$ (**4**, see below) [4d,8]. Phosphine **3** was more conveniently synthesized by treatment of isolated **9** with $\text{Na}_2\text{S}_2\text{O}_5$ (Scheme 3). However, because **9** was obtained in only 8.5% yield, an efficient synthesis of **3** is not yet available (the previously reported separation gave it in 21% yield) [4d].

The original synthesis of **4** required multiple recrystallizations before the tertiary phosphine was isolated in low yield from a mixture of the other ferrocenylmethylphosphines [4d]. Instead, heating **1** with 2 equiv. of $[\text{FcCH}_2\text{NMe}_3][\text{I}]$ in toluene/1-butanol gave a mixture of phosphonium salts. Subsequent treatment with NEt_3 gave a mixture of **4** and salt **5**, whose low solubility facilitated its separation (Scheme 2). Phosphonium salt **5** could be prepared deliberately in higher yield by adjusting the stoichiometry of this reaction. Previously, **5** was synthesized from $[\text{FcCH}_2\text{NMe}_3][\text{I}]$ and primary phosphine **2** [4d].

Two other tertiary ferrocenylmethylphosphines were prepared for comparison to **4**. Double deprotonation/silylation of **2** gave the bis(silyl)phosphine $\text{FcCH}_2\text{P}(\text{SiMe}_3)_2$ (**10**), which underwent hydrolysis rapidly on exposure to traces of water, while a similar sequence with **1** yielded air-stable $\text{FcCH}_2\text{P}(\text{CH}_2\text{OSiMe}_3)_2$ (**11**, Scheme 2) [9].



Scheme 2. Synthesis of ferrocenylmethylphosphines [3,4d,8].



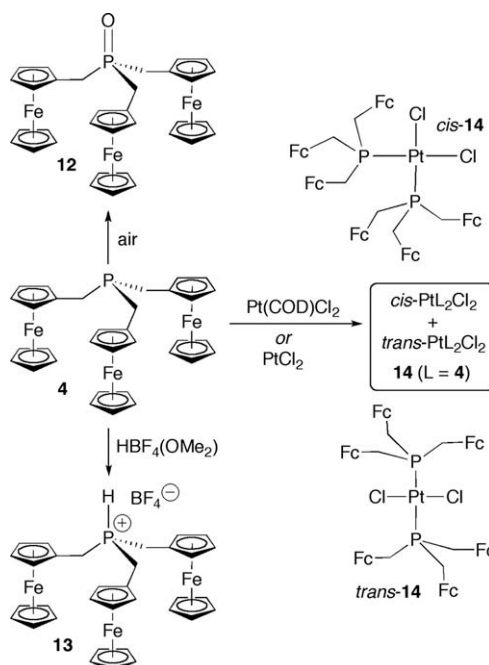
Scheme 3. Synthesis of bis(ferrocenylmethyl)phosphine [3,4d,8].

The reactivity of tertiary phosphine **4** was briefly surveyed (Scheme 4). In contrast to air-stable primary and secondary phosphines **2** and **3**, it slowly oxidized in air to yield phosphine oxide **12**. Protonation of **4** with $\text{HBF}_4(\text{OMe}_2)$ gave the air-stable phosphonium salt **13**. Although it was reported that **4** did not react with some Ta, Mo, and W complexes [4d], treatment of $\text{Pt}(\text{COD})\text{Cl}_2$ or PtCl_2 with two equiv of **4** yielded the complex $\text{Pt}(\text{P}(\text{CH}_2\text{Fc})_3)_2\text{Cl}_2$ (**14**) as a mixture of *cis* and *trans* isomers. Although we have not investigated in detail the dependence of product ratio on starting material, or the possibility of *cis*–*trans* isomerization, using PtCl_2 resulted in enrichment of the *trans* isomer, which was isolated by recrystallization.

Treatment of phosphines **2**, **3**, **4**, and **11** with $\text{BH}_3(\text{SMe}_2)$ gave the phosphine–borane adducts **6**, **7**, **8** and **15** (Scheme 5). Although the secondary and tertiary phosphine derivatives **7** and **8** were robust and could be purified by chromatography on silica gel, treatment of $\text{FcCH}_2\text{PH}_2(\text{BH}_3)$ (**6**) with water or attempted chromatography removed the borane to regenerate **2**.

2.2. X-ray crystallographic and computational studies of ferrocenylmethylphosphines and their derivatives

The crystal structures of phosphines **2** and **4**, phosphine–boranes **6**, **7**, and **8**, phosphine oxide **12**, and Pt complex **14** are shown in Figs. 1–7. We also determined the structures of secondary phosphine **3** and of salt **5**. While this work was in progress, the struc-



Scheme 4. Reactions of tertiary phosphine **4**.

Download English Version:

<https://daneshyari.com/en/article/1326482>

Download Persian Version:

<https://daneshyari.com/article/1326482>

[Daneshyari.com](https://daneshyari.com)