Inorganica Chimica Acta 402 (2013) 116–122

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

The preparation of electrophilic and electroneutral phosphane ligands and their substitution chemistry with $Mo(CO)_6$

Natalia G. Petrochko, Jaimee M. Ash, Michelle M. Choate, Justin Spott, R. Peters *

Department of Chemistry, Wilkes University, 84 W. South St., Wilkes-Barre, PA 18766, USA

ARTICLE INFO

Article history:
Received 1 August 2012
Received in revised form 13 March 2013
Accepted 15 March 2013
Available online 29 March 2013

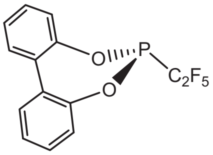
Keywords:
Phosphane
Fluoroalkylphosphane
Coordination complex
Molybdenum carbonyl complexes
Second order fluorine NMR
Amino phosphanes

ABSTRACT

The synthesis, characterization and coordination chemistry of electroneutral and electron-poor phosphane ligands is reported. The addition of diaminochlorophosphanes [compounds of the type $(R_2N)_2PCl$] to ether solutions of C_2F_5Li produced the corresponding diaminopentafluoroethylphosphane compounds $(R_2N)_2PC_2F_5$ ($R_2N = C_4H_8ON$, **1**; $C_5H_{10}N$, **2**; and C_8H_8N, **3**). Similar treatment of aminodichlorophosphanes with two equivalents of C_2F_5Li produced compounds of the type $(R_2N)P(C_2F_5)_2$ ($R = C_4H_8ON$, **4**; $C_5H_{10}N$, **5**; C_4H_8N, **6**; and C_8H_8N, **7**). These phosphanes were isolated as high boiling liquids (1, 2, 4–7) or as a solid (**3**) in moderate yields (44–71%). Substitution reactions of one equivalent of **1**–**6** with $Mo(CO)_6$ yielded the corresponding pentacarbonyl complexes $(L)Mo(CO)_5$ (**1a**–**6a**). Thermolysis of **7** with $Mo(CO)_6$ did not yield the expected pentacarbonyl complex. The phosphane compounds **1**–**7** and their molybdenum derivatives **1a**–**6a** were characterized by multinuclear NMR; the CF_2 region in the ^{19}F NMR for compounds **4**–**7** and complexes **4a**–**6a** displayed second-order character which complicated their interpretation. Compounds **1a**–**6a** were also characterized by IR spectroscopy; the IR stretching frequencies for these complexes suggest that ligands **1**–**3** are electroneutral (and approximate the electronic influence of phosphites) while similar stretching frequencies for **4a**–**6a** clearly establish these ligands as electrophilic.

1. Introduction

The systematic manipulation of metal center properties via alteration of their ancillary ligands continues to attract attention in the field of inorganic chemistry. Phosphane ligands (compounds of the type PR_3) have been used extensively for this purpose due to the wide variety of available substituents which bind to the phosphorus atom. The steric and electronic properties of phosphane ligands are readily controlled by the careful selection of the appropriate R group(s). Despite this variety of substituents, an a priori study of the stereoelectronic profile (a plot of sterics versus electronics character) of known phosphane ligands showed two large voids: sterically demanding, electronically neutral phosphanes as well as large, electron-poor phosphanes [1]. One rationale for this void postulated that the lack of commercial reagents to introduce electron-poor substituents stunted its development. However, techniques which introduce electron-poor substituents such as fluorocarbons have come from our lab [2–4], and others [5–18]; this suggests that the lack of synthetic methodologies no longer impedes the development of this field. Indeed, the subject of fluoroalkyl phosphines was the subject of a very recent review [19]



Previous work from our lab involved the synthesis, characterization and coordination chemistry of electroneutral phosphane ligands. We recently reported the synthesis of a versatile starting material to produce electroneutral phosphane ligands containing an electron-poor C_2F_5 group (seen at right) [4]. Cleavage of the two P–O bonds occurs using any commercially available Grignard or alkyllithium reagent and produced a variety of R_fPR_2 and $(R_f)_2PR$ phosphane ligands (R = Me, Et, iPr). We developed this starting material because of the difficulty in preparing R_2PCl and $RPCl_2$ starting materials incorporating typical hydrocarbon substituents; stepwise introduction of sterically undemanding hydrocarbon R groups to PCl_3 results in a mixture of products ($R_{3-x}PCl_x$). More recently, we reported the synthesis and coordination chemistry of a group of phosphane ligands containing secondary amido substituents. In that study, we examined the subtle fine-tuning of the electronics of a phosphane ligand without significantly altering the steric demands.

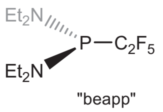
---

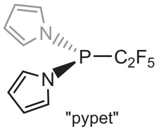
* Corresponding author. Permanent Address: Department of Chemistry, The University of Findlay, 1000 North Main Street, Findlay, OH 45840, USA. Tel.: +1 419 422 5754; fax: +1 419 434 4822.

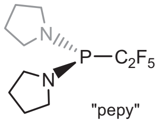
E-mail address: gpeters@findlay.edu (R. Peters).

0020-1693/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2013.03.035

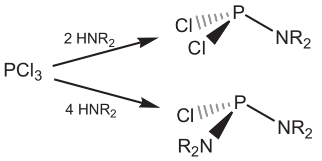
Ligands incorporating diethylamino (beapp), pyrrole (pypet) and pyrrolidino (pepy) substituents were prepared; IR data from the $Mo(CO)_5(L)$ derivatives we prepared clearly indicated the impact that subtle manipulation of ancillary phosphane substituents has on the electronics of the metal center itself. The lone pair electrons of the pyrrole substituents on the pypet ligand form part of an aromatic system; this reduced availability results in a more electron-poor phosphorus ligand (relative to both beapp and pepy) and a higher $A_1^{(2)}$ IR stretching frequency in the corresponding $Mo(CO)_5(L)$ derivative (2081 cm^{-1} for pypet; 2077 and 2080 for pepy and beapp, respectively).


"beapp"


"pypet"


"pepy"

The present work continues our investigation into the synthesis, characterization and coordination chemistry of phosphane ligands incorporating secondary amine substituents and pentafluoroethyl group(s). We selected these groups for two reasons; the steric variety of secondary amines is quite large and preparing $(R_2N)PCl_2$ and $(R_2N)_2PCl$ starting materials from PCl_3 occurs in a straightforward and stepwise manner. Treatment of PCl_3 with either two or four equivalents of a secondary amine produces precursor compounds of the type $(R_2N)PCl_2$ or $(R_2N)_2PCl$ along with the ammonium salts Eq. (1). This stepwise substitution of an amido group for a chloro group on PCl_3 stands in contrast to traditional hydrocarbon substituents; these tend to form product mixtures unless the substituent is sterically demanding. Herein, we report the synthesis and characterization of several new electroneutral phosphane ligands of the type $(R_2N)_2PR_f$ ($R_f = C_2F_5$) and electron poor phosphane ligands of the type $(R_2N)P(R_f)_2$. The steric demand of each ligand type was modified by altering the size of the secondary amine—from the relatively undemanding pyrrolidine substituent to a much larger indoline substituent. The substitution chemistry of these ligands with $Mo(CO)_6$ was also examined in an effort to establish the steric and electronic influence of these ligands.

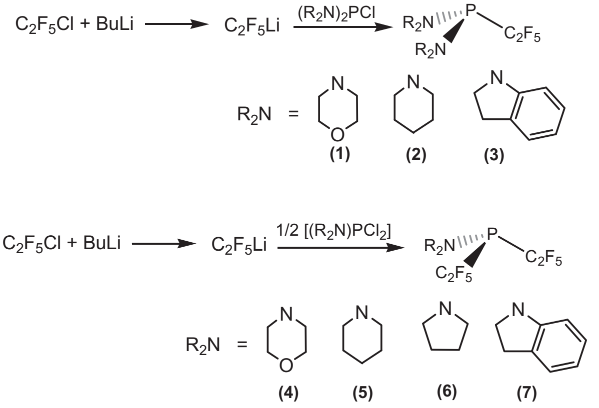


(1)

2. Results and discussion

2.1. Syntheses of phosphanes **1**–**7**

Treatment of P–Cl bonds with C_2F_5Li leads to the formation of P–C_2F_5 bonds and LiCl without cleaving any existing P–N bonds. Accordingly, compounds **1**–**3** were prepared by the reaction of C_2F_5Li with one equivalent of the appropriate diaminochlorophosphane starting material while ligands **4**–**7** were prepared from the reaction of C_2F_5Li with half an equivalent of the aminodichlorophosphane starting material. The chlorophosphane precursors are prepared from the reaction of PCl_3 with either four equivalents (for precursors to compounds **1**–**3**) or two equivalents (for precursors to **4**–**7**) of a secondary amine in CH_2Cl_2. Filtration of the ammonium salts followed by solvent removal under vacuum yielded the chlorophosphane precursors as high-boiling liquids or oily solids which were used without further purification Eq. (1).



(2)

Pentafluoroethyl lithium, C_2F_5Li, is generated in an ethereal solution at −78 °C from the reaction of BuLi with chloropentafluoroethane and is best kept at temperatures below −70 °C to avoid elimination of LiF. Treatment of an ether solution of C_2F_5Li with $(C_4H_8ON)_2PCl$ yielded $(C_4H_8ON)_2PC_2F_5$ (**1**, pentafluoroethyldimorpholinophosphane, or “mopey”). Similar reactions with $(C_5H_{10}N)_2PCl$ and $(C_8H_8N)_2PCl$ yielded **2** and **3** respectively (**2**, pentafluoroethyldipiperidinophosphane or “pippy”; **3**, pentafluoroethylbisindolinophosphane or “bipp”). Separate additions of $(C_4H_8ON)_2PCl_2$, $(C_5H_{10}N)PCl_2$, $(C_4H_8N)PCl_2$ and $(C_8H_8N)PCl_2$ to two equivalents of C_2F_5Li produced ligands **4**–**7** respectively (**4**, bispentafluoroethylmorpholinophosphane, or “2-mopey”; **5**, bispentafluoroethylpiperidinophosphane, or “2-pippy”; **6**, bispentafluoroethylpyrrolidinophosphane, or “2-pepy”;[2] **7**, bispentafluoroethylindolinophosphane, or “2-bipp”). The syntheses of compounds **1**–**7** are shown in Eq. (2). All compounds were isolated as high-boiling liquids (**1**, **2**, **4**–**7**) or as a solid (**3**) in moderate to good yields (44–71%).

2.2. NMR characterization of compounds **1**–**7**

2.2.1. Characterization of compounds **1**–**3**

Multiple spin-active nuclei allowed these ligands to be well characterized by NMR. The ^1H NMR data of ligands **1**–**7** is relatively insensitive to the incorporation of a pentafluoroethyl group onto the phosphorus atom, and look similar to the ^1H NMR spectra of the chlorophosphane starting materials; we have noted this previously with amidophosphane systems [2]. Ligands **1**–**3** all posses two resonances in the ^{19}F NMR spectrum due to the CF_2 (~ -110 ppm) and CF_3 (~ -80 ppm) groups; both of which couple to the phosphorus atom ($^2J_{PF}$ values are consistently ~70 Hz; $^3J_{PF}$ values range from 17–21 Hz). $^3J_{FF}$ is only observed for **1** (2.3 Hz). As expected based on the fluorine data, the ^{31}P NMR spectra for phosphanes **1**–**3** all showed a simple triplet of quartets with chemical shifts between 40–75 ppm.

2.2.2. Characterization of compounds **4**–**7**, second order ^{19}F NMR data

In contrast to the relatively straightforward interpretation of compounds **1**–**3**, the interpretation of NMR data for **4**–**7** was more complicated. The spin system for ligands **4**–**7** is described by an ABM_3X pattern, with $^3J_{FF} \sim 0$ Hz between the two diastereotopic fluorines of the CF_2 groups and the CF_3 groups. Like compounds **1**–**3**, the CF_3 groups for 4–7 also consistently appear as simple doublets around −80 ppm with $^3J_{PF} \sim 17$ Hz. However, second order effects impact the CF_2 region of these compounds (ratios of $\Delta\delta/J$ were between **1** and **2** for all four phosphanes). Fig. 1 shows an expanded view of the CF_2 region of **6**, which appears as a deceptively simple doublet of quartets around −110 ppm. This pattern is seen for compounds **4**, **6** and **7**. Fig. 2 shows the same expanded region for **5**, which looks like