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Sterically Encumbered Ligands in Coordination Chemistry

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Abstract : A bromo-functionalized 2,6-dimethylphenyl phosphate ligand (Dmpp-H_2) (3) was synthesized by using a simple methodology and further the Dmpp-H_2 was used in the synthesis of 4-bromo-2,6-dimethylphenoxy tert-butyl phosphonate ester (5) by reacting 3 with Tert-butyl phosphoryl chloride (1). The encumberedness of methyl and tert-butyl group provides solubility in the ligand systems. The all ligands were characterized analytical methods and further confirmed by spectroscopic methods.

Keywords: bromo-functionalized 2,6-dimethylphenyl phosphate ligand (Dmpp-H_2) (3) was synthesized by using a simple methodology and further the Dmpp-H_2 was used in the synthesis of 4-bromo-2,6-dimethylphenoxy tert-butyl phosphonate ester

Introduction

Sterically encumbered ligands are commonly explored to stabilize low coordinate metal centers. Steric bulk can support unusual coordination geometries in mononuclear complexes. The two-coordinate iron (II) thiolate complexes [Fe(SAr^{mes}){N ($SiMe_3$)$_2$}] and [Fe(SAr^{mes})$_2$] illustrate this application. Two mesityl groups flanking the metal binding sites apparently shield them against unwanted oligomerization reactions. Control over coordination number and geometry can thus be achieved by inter-ligand interactions in the second coordination sphere (figure 1.)[1]

Figure 1. [Fe (SAr^{mes})$_2$] Ligand[1]

In an extension of this approach we explored the chemistry of sterically more demanding monodentate and polydentate N-donor ligands. Our goal is to evaluate how variation in steric bulk and ligand donor strength would affect the nuclearity and coordination geometry of the resulting complexes.

Olefin polymerization by Ni(II) complexes; by using bulky substituents accessing high molecular weight polymer, because these bulky substituents are considered to retard chain transfer by blocking the axial positions on the metal center. By comparison to their Ni (II) counterparts, they are more tolerant towards polar reagents.[3]

Figure 2. Ni (II) catalyst with bulky ligand[3]

Because of the bulk of the ligands, their complexes are usually discrete and often monomeric. As such they are more reactive polymeric metal complexes; due to bulk of the complex exhibits high catatytic activity. For example the reaction of (η3-allyl) palladium complexes with nucleophiles to afford allylic alkylation products is of wide ranging synthetic utility. One of the most significant aspect of this chemistry is the prospect of controlling the chemo-, regio-, stereo-, and enantioselectivity of the nucleophilic attack on the allyl moiety through appropriate choice of the reaction conditions and the ancillary ligands attached to palladium. As a result, there is considerable current interest in investigating the electronic and steric interactions that govern the selectivity in catalytic transformations proceeding through (η^3-allyl) palladium intermediates.[2]

We are investigating the metal chemistry of PNP (Aminodiphosphine)[5-10] ligands, silanetrioles[17,19,20], synthesis of phosphate, phosphonate[21-22], and phosphinate ligands.

Recent literature survey reveals that alkyl phosphonate have rich and varied chemistry. A large part of this chemistry still remains to be explored with respect to chemical and structural properties. As the literature indicates that metal phosphonates can be used as potential zeolites and as material exhibiting good thermal properties, we plan to synthesize alkylphosphonates, and their metal complexes. The objective will be to form complexes with ligands which can undergo β-elimination and hence provide an opportunity to make layered one dimentional polymeric structures. Also the phosphonates which may not undergo β-elimination are to be studies as ligands stabilizing the unusual valency of actinides. This kind of coordination gives us the possibility of separating the actinides from other ions with similar charge to size ratio. Ligands specificity may even be controlled by alkyl substituents on the the ligand.

Results and Discussion

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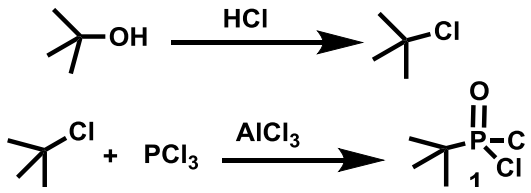
9,10 March 2018

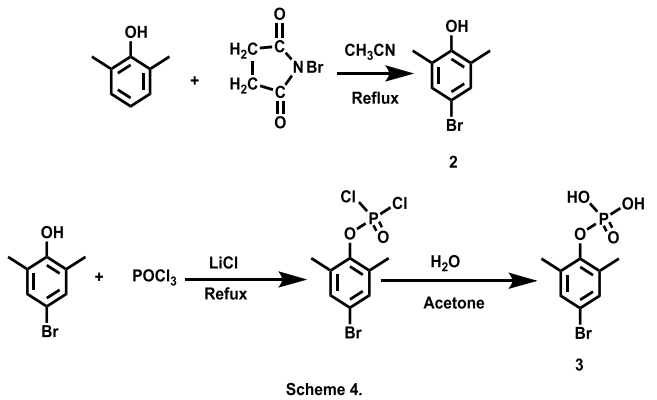
Synthesis and spectral studies of Tert-butyl phosphoryl chloride (1)*:* Tert-butyl-phosphorylchloride was prepared by the procedure given in literature[21-22]. First, we prepared tert-butyl chloride by SN^1 reaction of tert-butanol with HCl, to this added PCl_3 and anhydrous $AlCl_3$, as catalyst to obtain compound **1.**



Scheme 3.

This was characterized by ^1H & ^{31}P NMR, elemental analysis (Table 1), and mass spectrometry. In ^1H NMR there is a doublet at 1.45 ppm due to phosphorous and proton coupling, in ^{31}P NMR there is a single peak at 68.62 ppm, which shows the compound is formed. In mass spectrometry an M^+ at 175.0 (M.Wt. =174.99).

Synthesis and spectral studies of 4-bromo-2,6-dimethyl phosphate (**3**)*:* Chemistry of 2, 6-dimethyl phosphate has been explored to considerable extent by our group and is still expected to lead us to some novel aspects of its chemistry. We have tried to modified the basic constitution of 2, 6-dimethyl phosphate by brominating the starting material 2,6-dimethyl phenol (**2**) by refluxing with N-bromo-succinimide (NBS) in acetonitrile by proper work-up[16], which was characterized by ^1H NMR (Figure 3) ,elemental analysis (Table 1) and mass spectrometry. Presence of single peak in aromatic region at 7.09 ppm corresponding to aromatic H's and slight downfield replacement of singlet for methyl ($-CH_3$) support the fact that electronegative Br functionally is attached to ring at Para position. Compound **2** was converted to phosphate derivative compound **3**, by refluxing 2, 6-dimethyl phenol with $POCl_3$ in presence of catalytic amounts of LiCl and subsequent hydrolysis, compound **3** was obtained[13-14] and characterized by analytical and spectroscopic techniques. The single peak in ^{31}P spectroscopy -5.01 ppm (Figure 4.) is in agreement with the reported value for phosphorous in compound **3**, besides elemental analysis values are also in good agreement (Table 1) **.**In ^1H NMR spectrum shifting of aromatic singlet and methyl singlet, to downfield support that the compound is formed.



Scheme 4.

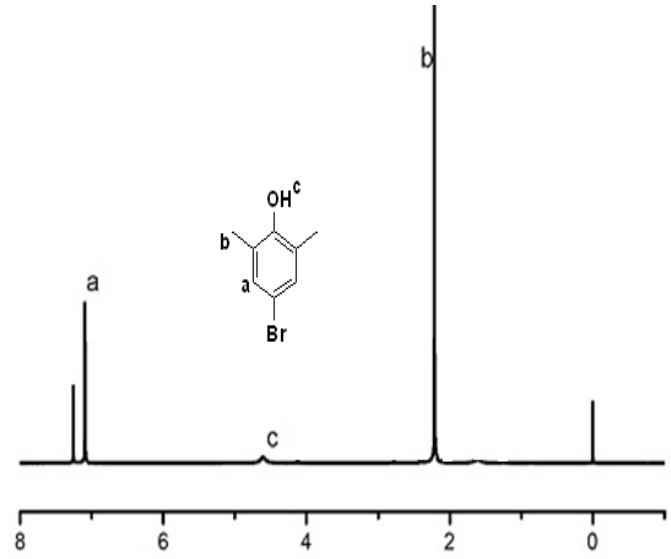


Figure 3. ^1H NMR of 4-bromo-2, 6-dimethylphenol **(2)** in $CDCl_3$

Table 1. Analytical data of compounds **1**, **2** and **3.**

Compounds	Elemental analysis found(Calculated)		M.P.	Yield (%)
	C	H		
1	22.08 (21.61)	3.81 (4.71)	109-110 ^oC	66
2	47.80 (47.79)	4.15 (4.51)	76-78 ^oC	91
3	33.05 (34.19)	2.96 (3.39)	188-190 ^oC	43

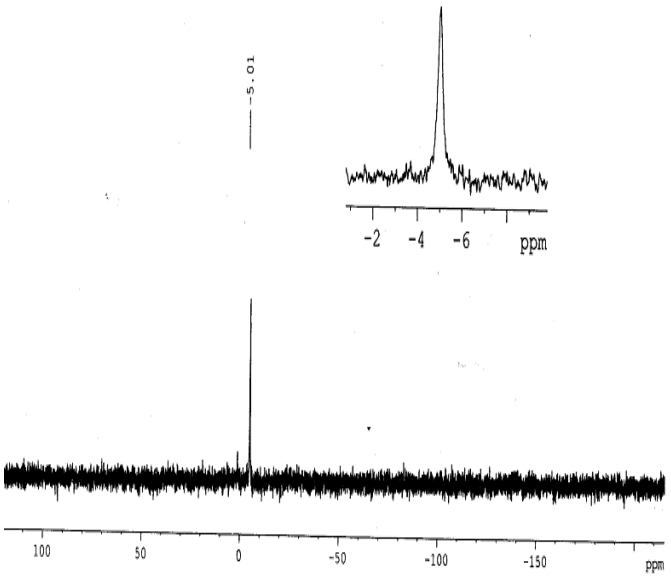


Figure 4. ^{31}P NMR spectrum of 4-bromo-2,6-dimethyl phosphate (**3**) in CD_3OD**.**

ISSN:2319-6890 (online),2347-5013(print)
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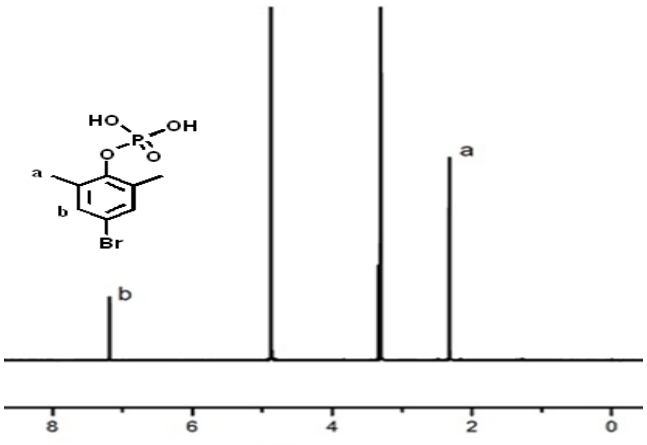


Figure 5. ^{1}H NMR spectrum of 4-bromo-2,6-dimethyl phosphate (**3**) in CD_3OD

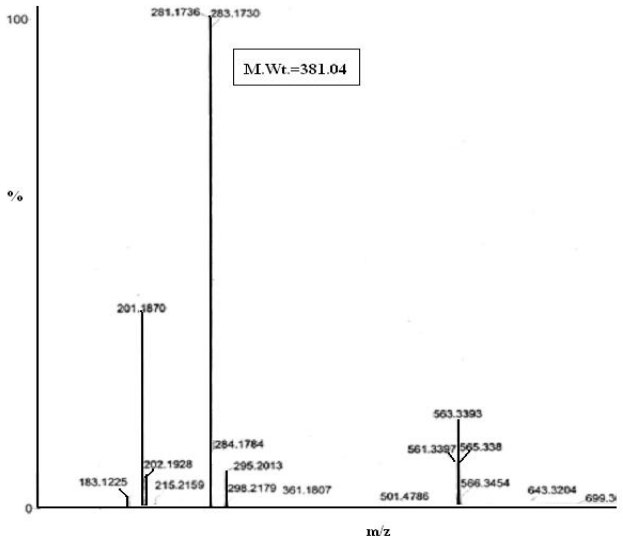
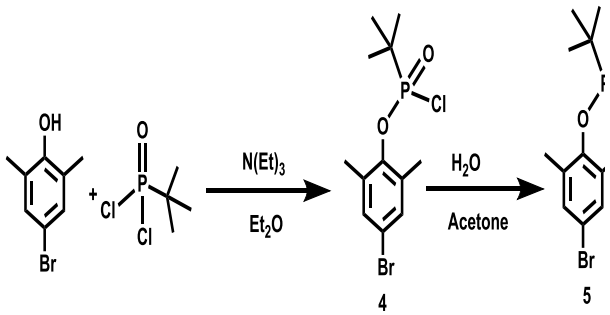


Figure 6. EI-MS spectrum of 4-bromo-2,6-dimethyl phosphate (**9**)

Synthesis of 4-bromo-2,6-dimethylphenoxy tert-butyl phosphonate ester:



Scheme 5.

To a dry ether solution of 4-bromo-2,6-dimethyl phenol, triethylamine was added and brought to temperature -78 ^{o}C. To this reaction mixture dry ether solution of tert-butyl-phosphoryl chloride was added drop wise for two hours at -78 ^{o}C. During the course of reaction $N(Et)_3$.HCl was appeared as white solid. The white precipitate was filtered off to get colorless clear solution. Solvent was removed under vacuum to get oily colorless compound as crude product. The oily material was washed several times with petroleum ether to obtain compound **4** in pure form, which was characterized by ^{1}H and ^{31}P NMR, mass spectrometry (M^+ peak at 339.08).

Compound **5** was obtained by hydrolysis of compound **4** with one equivalent of water to form 4-bromo-2,6-dimethylphenoxy tert-butyl phosphonate ester.

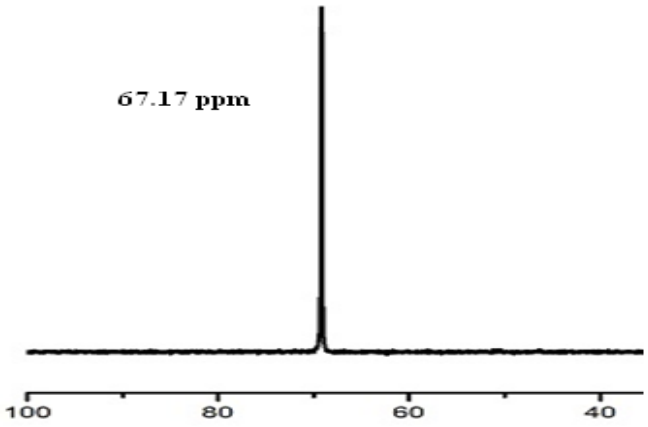


Figure 7.^{31}P NMR spectrum of 4-bromo-2,6-dimethylphenoxy tert-butylphosphorylchloride .

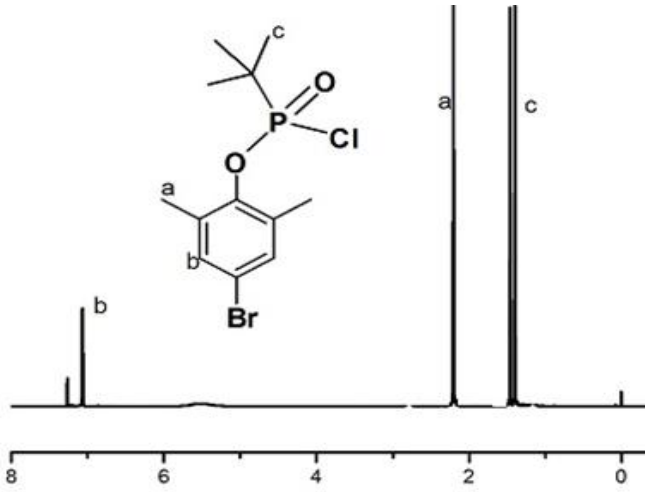


Figure 8. ^{1}H NMR of 4-bromo-2,6-dimethylphenoxy tert-butyl phosphorylchloride. (**4**)

Experimental Section

***Methods, Materials and Instruments*:**

All starting materials have been procured from commercial sources and used as received. Methods used for purification of solvents and starting materials are similar to those described in the literature. All the starting materials and the products were found to be stable towards moisture and air, and hence no specific precaution has been taken to rigorously exclude air. The melting points were measured in glass capillaries and reported uncorrected. Elemental analysis was performed on a Thermo Finnigan (FLASH EA 1112) micro analyzer. Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum One Infrared Spectroscopy as KBr diluted disks. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bucker 400 MHz instrument using Me_4Si as an internal reference for proton.

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The ESI mass spectra were recorded on Micro mass Q-Tof micro mass spectrometer.

Synthesis of tert-butyl chloride[21-22]**:** In a separating funnel 48.3 mL of tert-butyl alcohol with conc. HCl (127.5 mL) was added shacked time to time. During 20 min. 2 layers was separated, the lower layer discated, washed with 20 ml of 5% $NaHCO_3$, dried over $CaCl_2$, distilled to get ^tBuCl (Bp:50.4 ^oC/0.5 mmHg).

Synthesis of tert-butyl-phosphoryl chloride[21-22] **(1):** $AlCl_3$ was added to flax containing PCl_3 (23.89 g, 173.96 mmo) and ^tBuCl (16.8 g, 181.48 mmol), shacked for 1h. White powder was obtained, dissolved in 150 ml dichloromethane to give a clear solution. To this solution, 20 ml of water was added, $Al(OH)_2$ was precipitate out, which was filtered and the solvent was removed to give white crystalline solid. Yield: 20 g (66%).Mp.109-110 ^oC. Anal.Calc. for ($C_4H_9Cl_2OP$), Found (calc.): C, 21.61(22.08); H, 4.71(3.81). ^1H NMR ($CDCl_3$, 400MHz), δ 1.45 (d, 9H, ^tBu-H). ^{31}P NMR ($CDCl_3$, 161 MHz) 68.62 ppm. EI-MS *m*/*z* 174.1(M^+).

Synthesis of 4-bromo-2,6-dimethylphenol[16] **(2):** To the solution of 2,6-dimethylphenol (16.37 mmol, 2.00 g) in acetonitrile (20 mL) was added NBS (17.189 mmol, 3.06 g), and it was refluxed overnight. After the completion of reaction as indicated by TLC, the reaction mixture was concentrated under reduced pressure and residue reconstituted in ethyl acetate. The organic solution was washed with water and brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude residue was subjected to column chromatography (eluent: ethyl acetate/hexanes) to yield 91%. M.P. 76-78^o C^1H NMR (400 MHz, $CDCl_3$): *δ* 7.09 (s, 2H), 4.60 (s, 1H), 2.21 (s, 6H) ppm. EI-MS *m*/*z* 201.3(M^+). Anal. Calc. for (C_8H_9BrO), Found (calc.) C, 47.80(47.79); H, 4.15 (4.51).

Synthesis of 4-bromo-2,6-dimethylphosphate (Dmpp-H_2)[13-14] **(3):** To the 3.29 g, 16.40 mmol of 4-bromo-2,6-dimethylphenol was added catalytic amount (50 mg) of LiCl (anhydrous) and 10.0 ml of $POCl_3$ and the reaction mixture was refluxed for 72 h at 130 ^oC. The reaction was cooled to room temperature under N_2 atmosphere, and the contents were filtered to remove LiCl, Concentrated under vacuum to remove excess of $POCl_3$, distilled to give 3.14 mmol of dichloro derivative, which then hydrolysed with 2 equivalent of water in 50 ml of acetone ,stirred for 36h. M.P. 188-190 ^oC Yield: (2.0) 43%.Anal. Calc.for ($C_8H_{10}BrO_4P$) Found (Calc.): C, 33.05 (34.19); H, 2.96 (3.39). ^{31}P NMR (CD_3OD, 161 MHz) δ -5.08 ppm. ^1H NMR (CD_3OD, 400 MHz) δ 7.18(s, 2H, Ar-H), 2.32 (s, 6H, CH_3-H).

Synthesis of 2,6-dimethylphenoxy-tert-butyl phosphorylchloride **(4):** To a dry ether solution of 2.0 g (9.950 mmol) 4-bromo-2,6-dimethyl phenol, 1.0g (9.950 mmol) triethylamine was added and brought to temparature -78 ^oC. To this reaction mixture dry ether solution of 1.58 g (9.950 mmol) tert-butyl-phosphoryl chloride was added dropwise for two hours at -78 ^oC. During the course of reaction N $(Et)_3$.HCl was appeared as white solid. The white precipitate was filtered off to get colorless clear solution. Solvent was removed under vacuum to get oily colorless compound as crude product. Yield 3.0 g (93%) ^{31}P NMR ($CDCl_3$, 161 MHz) δ 67.17 ppm. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.07 (s, 2H, Ar-H), 2.20(s, 6H, CH_3-H), 1.41 (s, 9H, ^tBu-H). EI-MS *m*/*z* 339.08 (M^+). The oily material was washed several times with petroleum ether to obtain compound **5** in pure form.

Conclusions

The bromo-functionalized phosphate ligand **3** was synthesized and characterized with various analytical and spectroscopic methods. *Dmpp-H_2* was used in the synthesis of *4-bromo-2,6-dimethylphenoxy tert-butyl phosphonate ester* (**5**) by reacting **3** with Tert-butyl phosphoryl chloride (**1**). The utilization of these phosphate and phosphonate ligands to make functional D4R-Zn-Cubanes, with the aid of metal acetate and ancillary ligands, is being going on in our laboratory. The idea behind using bromo functionality on the system, the halogen substituents on ligands can be exploited by Suzuki coupling for further functionalization of these systems. These systems with high encumberedness can lead to formation of highly soluble covalently linked 3-dimensional assemblies of D4R-Zn-cubanes.

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