Synthesis of phenylamino bis(dichlorophosphine oxide) and its complexes with group 12 metals

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The high yield one pot synthesis of bis(dichlorophosphinoyl)aniline, PhN[P(O)Cl]₂ and its complexes with group 12 metals is described.

The coordination chemistry of bis (phosphino)amines is extensively studied⁴, whereas that of the corresponding bis(dichlorophosphino) amines and their dichalcogen derivatives is sparse. This may be due to the sensitivity of phosphorus-chloride bonds towards acid or base catalysed hydrolysis. The coordination chemistry of bis (dichlorophosphino) amines and their chalcogen derivatives would be interesting because the nucleophilic substitution reactions can be carried out conveniently even after the coordination of either P(III) or chalcogens to the metal centers. Further, bis(dichlorophosphino)amines can behave as strong π-acids, whereas their chalcogen derivatives can readily stabilize organometallic derivatives of hard transition metals and also lanthanides and actinides⁵.

As a part of our interest on aminophosphines,³ herein we report the modified and simple one pot synthesis of bis(dichlorophosphinoyl)aniline and its group 12 metal derivatives.

Experimental

All manipulations were performed under anaerobic conditions using standard Schlenk techniques. All solvents were dried and distilled under argon. Commercial reagents were used without further purification except for aniline. The ¹H and ³¹P NMR spectra were recorded using Varian VXR 300 and Bruker AMX 400 spectrometers operating at the appropriate frequencies using tetramethysilane and 85% H₃PO₄ as internal and external references respectively. Positive shifts lie downfield in all cases. IR spectra were recorded on a Nicolet Impact 400 FT IR instrument in KBr matrix. Microanalyses were performed on a Carlo Erba model 1112 elemental analyser. Melting points were determined in capillary tubes and are uncorrected.

PhN[P(O)Cl]₂ (1)
Aniline (15.0 g, 0.161 mol) was added dropwise to a round-bottomed flask containing POCI₃ (98.7 g, 0.644 mol) at 0°C. The white suspension was warmed to room temperature then heated (95-100°C) till the clear solution was obtained (~2 days). Then the solution was filtered through glass wool and concentrated to half the volume and cooled to 0°C to get white crystalline solid. The solid was recrystallized from diethyl ether at 0°C. Yield: 76% (40.0 g, 0.122 mol). Mp: 82-84°C. Anal. Calcd for C₆H₅NO₂P₂Cl₂: C 22.05; H 1.54; N 4.29%. Found: C 22.30; H 1.94; N 4.32%. FTIR (KBr disk) cm⁻¹: νₚ0 1102 s. ³¹P [¹H] NMR (CDCl₃): δ 7.3 (s).

Preparation of zinc, cadmium and mercury complexes, PhN[P(O)Cl]₂ (M = Zn, X = Cl and M = Cd, Hg; X = CH₂COO)
To a solution of an appropriate metal precursor (0.10 g) in methanol (10 mL), stoichiometric amount of PhN[P(O)Cl]₂ also in ethanol (5 mL) was added and the solution was stirred for 6 h at room temperature. The solvent was removed under reduced pressure and the residue obtained was washed with n-hexane and recrystallized from EtOH—n-hexane to give the products.

PhN[P(O)Cl]₂[ZnCl₂] (2)
Yield: 91% (0.650 g, 1.400 mmol). Mp: 66-70°C. Anal. Calcd for C₆H₅NCI₂O₂P₂Zn: C 15.56; H 1.08; N 3.02%. Found: C 15.34; H 1.28; N 2.69%. FTIR (KBr disk) cm⁻¹: νₚ0 1086 s. ³¹P [¹H] NMR (CDCl₃): δ 8.3 (s).

PhN[P(O)Cl]₂[Cd(CH₂COO)₂] (3)
Yield: 67% (0.150 g, 0.253 mmol). Mp: 202-205°C. Anal. Calcd for C₆H₅NO₂P₂Cl₂Cd.2H₂O: C 20.24;
H 2.55; N 2.36%. Found: C 20.49; H 2.76; N 2.31%. 

FTIR (KBr disk) cm⁻¹: v(CH₃): 3323 br s; v(CO): 1607 s; v(PO): 1042 s. ¹H NMR (DMSO-d₆): δ 1.21 (s, CH₃, 6H), 7.01-7.56 (m, phenyl, 5H). ³¹P{¹H} NMR (DMSO-d₆): δ -0.3 (s).

[PhN[P(O)Cl₂]₂Hg(CI₂COO)](4)

Yield: 70% (0.141 g, 0.218 mmol). Mp: 148-152 °C. Anal. Calc'd for C₁₈H₁₁N₀₆P₂Cl₄Hg: C 18.61; H 1.72; N 2.16%. Found: C 17.25; H 2.16; N 2.31%. 

Results and discussion

The bis (dihalophosphino) amines and their chalcogen derivatives of the type, X₂P(E)(N)(R)P(E')X₂, (E = E' = O, S, Se; E = O, E' = S, Se etc.; R = Me, Et, Ph; X = Cl or F) are known for several decades. Several synthetic methods are available for the preparation of these bis(dichlorophosphinoyl) compounds and their sulfide and selenide analogues, which involve multistep reactions:

a) By the condensation of amines X₂P(O)NHR (X = Cl, F) with phosphoryl chloride in the presence of tertiary amines as shown in Eq.1.

b) Oxidation of P(III) derivatives with KMnO₄, H₂O₂, TMNO or 'BuOOH, elemental sulphur in the presence of AlCl₃ as given in Eq.2.

Inspite of the involvement of multistep, method (a) is suitable for making unsymmetrical dichloro/difluoro phosphinoyl derivatives.

The reaction of aniline with excess of POCl₃ at 95-100 °C afforded the phospine oxide, PhN[P(O)Cl₂] (1) in good yield. The ³¹P NMR spectrum of 1 exhibits a single resonance at 7.3 ppm (lit. 7.4 ppm).

The compound 1 with two oxygen donors can bind readily to the oxophilic metal centers. Changing the substituents by nucleophilic substitution on phosphorus can alter the ligating behaviour of the ligand 1. Nucleophilic substitutions can also be performed at phosphorus centers even after their coordination to the metal centers. The reaction of phosphate 1 with ZnCl₂ results in the formation of a tetrahedral six-membered metalacycle. [ZnCl₂{PhN(P(O)Cl₂-kO,kO)}] (2) in 70% yield. The ³¹P NMR spectrum of the complex 2 shows a single resonance at 8.3 ppm and the lowering of ν(PO) frequency by 15 cm⁻¹ shows the interaction of P=O with the metal center.

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\text{PhNH}_2 + \text{POCl}_3 \xrightarrow{95-100^\circ \text{C}} \quad 1
\]

The reaction of 1 with metal acetates, M(OAc)₂ (M = Cd and Hg) affords the chelate complexes [M(OAc)₂(PhN[P(O)Cl₂-kO,kO])] (M = Cd, 3; Hg, 4). The lowering of ν(PO) frequency in the complexes compared to the free ligand indicates the interaction of P=O with metal center. The ³¹P NMR spectra of the complexes 3 and 4 show single resonances at -0.3 and 0.9 ppm respectively indicating equivalent nature of phosphorus centers. Further support for the formation of complexes comes from the micro analytical data. Further utilization of this class of compounds as anchoring ligands in organolanthanide chemistry is in progress in our laboratory.

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\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{M} & \quad \text{X} \quad \text{X} \\
\text{M} & \quad \text{Zn, X = Cl} \\
M & \quad \text{Cd, X = OAc} \\
M & \quad \text{Hg, X = OAc}
\end{align*}
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References


