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A Triazine-Phosphite Polymeric Ligand Bearing Cagelike P,N-Ligation Sites: As an Efficient ligand in Nickel-catalyzed Amination of Aryl Chlorides and Phenols

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Abstract

A novel P,N-ligand was introduced for efficient Ni-catalyzed amination of aryl chlorides. Reaction of cyanuric acid (1,3,5-triazine-2,4,6-triol) and trichlorophosphine (PCl₃) resulted in the production of a new porous material (TPPM) containing a triazine ring and phosphite moieties in sheet morphology. The cavities of prepared compound create appropriate sites on the surface of the material with ligation character to coordinate with metals for catalytic purposes. The nickel-catalyzed amination of aryl chlorides and also phenols as their 2,4,6-triaryloxy-1,3,5-triazines (TATs) protected form were efficiently accomplished in the presence of this easily prepared and reusable P,N-ligand under mild reaction conditions. More importantly, TPPM was reusable for 5 times in this protocol without significant decreasing in its activity.

Keywords: Polymeric Ligands, P,N-ligands, Nickel-catalyzed amination, Aryl chlorides, Phenols

Introduction

There is often an emphasis on the development of ligands that influence efficiency and selectivity in transition metal-catalysis (TMC).^[1] Heteroatomic bidentate ligands have received considerable attentions in the recent years due to their widespread applications in TMC.^[2] Phosphines are one of the most important class of ligands in this field, showing high efficiency and applicability.^[3] More importantly, the heteroatomic bidentate P,N-ligands revealed their superiority in activity and selectivity between other phosphorous containing ligands.^[4] The importance of P,N-ligands is resulted from this fact that, as soft/hard ligand able to coordinate reversibly to a metal center providing temporarily a vacant coordination site, a feature very desirable for catalysis.^[5] Therefore, the introduction of new, efficient, easily prepared and applicable P,N-ligands is of much current interest and is the subject of extensive research in this field.^[6] The ideal form is the synthesis of an active P,N-ligand with simple workup and purification process .

Supporting the ligands on a solid substrate is one of the subjects which allow the recycling of ligand and simplifying workup process.^[7] In this study we have focused on an easy approach, which relies on a polymeric structure containing P,N-ligation sites. Organic polymers that contain ligated metals for catalysis purposes, offer a variety of unique properties.^[8] The strong coordination of metals to these ligation centers resulted in the construction of catalytic positions for application in TMC.^[8c,d] On the other hand, the presence of catalytic sites on a flexible polymeric backbone can represent action of enzymes in natural systems which can increase the interactions between the catalyst and substrates by folding of main chains.^[9] Furthermore, these structures caused increase of the local concentration of both substrates and catalyst. Consequently, these functions not only lead to enhancements in reaction rates, but also provide an easy scaffold for recycling.^[10]

Herein, we disclosed the preparation of an easily prepared and reusable P,N-ligand from commercially available and cheap starting materials in a single step process. Reaction of PCl₃ with

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cyanuric acid produces an organic polymer (triazine-phosphite polymeric material, TPPM) which is introduced as a new P,N-ligand (Scheme 1).



Scheme 1. Synthesis of a triazine-phosphite polymeric material (TPPM) through the reaction of PCl_3 with cyanuric acid. Cyanuric acid as a white solid was reacted with PCl_3 (a clear liquid) and forms a yellow solid which is a triazine-phosphite compound. This material is unsolvable in solvents such as water, ethanol, ethyl acetate and *n*-hexane. The presence of P and N atoms in the structure of this material caused that it be usable as P,N-ligand in TMC organic transformations.

In this study, TPPM was employed as ligand in metal-catalyzed amination of aryl chlorides.^[11] The TMC amination of aryl halides is an important tool for the production of arylamines.^[12] The expansion of a simple metal catalyst system for the coupling of aryl electrophiles with NH₃ is an important challenge in the recent decade.^[13] Most of these catalyst systems have done coupling reactions of aryl chlorides with NH₃ in low yields, especially with unactivated substrates.^[14] The competition of solvent with NH₃ was observed in several cases and is a key limitation.^[15] In some of the used methodologies, the produced aniline product competes with ammonia in coupling reaction and the diaryl amine is the byproduct, resulting in the decreasing of the yield and complication of purification process.^[16] Furthermore, in most cases, harsh reaction conditions are needed and very expensive and complicated catalyst system or ligand was employed to accomplish this reaction.^[17] As a result, description of a simple and efficient catalyst system for the coupling of unactivated aryl chlorides with ammonia established the significance of our new P₃N-ligand to achieve high reactivity in TMC. Thus, the metal-catalyzed reaction between aryl

chlorides and NH₃ in the presence of this ligand was investigated. Furthermore, the amination of phenols as their 2,4,6-triaryloxy-1,3,5-triazines (TATs) protected form were evaluated in the presence of TPPM ligand.

Results and Discussion

Synthesis and Characterization of TPPM

The TPPM ligand was simply synthesized using the reaction of PCl₃ and cyanuric acid in the presence of (*n*-Pr)₃N. Cyanuric acid immediately reacts with PCl₃ and produces TPPM as a yellow solid (Scheme 1). The reaction proceeded rapidly and afforded almost quantitative product yield. This compound was characterized using ¹³CNMR, and FT-IR spectroscopies. There is one carbon atom at 149.8 ppm in ¹³CNMR spectrum of this compound which is attributed to the carbon of triazine ring (See supporting information). The FT-IR of TPPM shows the appearance of P-O bond peak at 851 cm⁻¹. Also, the peaks attributed to triazine ring with little shift appeared in the FT-IR spectrum (See supporting information).^[19]

The transmission electron microscopy (TEM) images of TPPM are shown in Figure 1. The TEM images show the both porous and sheet nature of the TPPM material. The sheets and the holes of TPPM are in the range of nanometers.



Figure 1. TEM images of TPPM from different positions and magnifications. The sheet morphology of the synthesized TPPM is shown in TEM images **a** and **b**. TEM image of TPPM with high magnification shows that the sheets are prose and cavities in the range of 10-40 nm are observable **c-f**. It seems that TPPM strings to forms skims in sheet morphology with cavities in the range of nanometers. This cavities are containing P,N-ligation sites which can be used as ligand in transition-metal catalysis.

The scanning electron microscopy (SEM) images of TPPM are shown in Figure 2. The SEM images also prove the porous structure of TPPM and show cavities in the range of nanometer scale (Fig 2).



Figure 2. The SEM images of TPPM. The SEM images of TPPM with different magnification are demonstrated the surface morphology of the material. The structure and surface of this material in terms of nanoscale is shown in these images. Pores in the range of nm are observable on the surface of TPPM.

High porosity surface can be observed in the SEM images of material for all magnifications. At higher magnification, the mesoporosity of material is becomes clear.

The sheet and porous structure of TPPM make it as a high surface area material which capable for catalytic and isolation purposes. The TPPM was also analyzed using nitrogen adsorption–desorption isotherms (Figure 3a). The adsorption isotherm is obtained by measuring the amount of nitrogen gas adsorbed across the relative pressures at a constant temperature of 77K and conversely desorption isotherms were achieved by measuring gas removed as pressure is reduced. The isotherm type is V according to the Brunauer defind.^[20] This type of isotherm shows small adsorbent-adsorbate interactions potentials which associated with pores in the range of 1.5-100 nm. According to the Brunauer–Emmett–Teller (BET) analysis, the specific surface area and pore volume of TPPM were calculated as 28.7 m².g⁻¹ and 0.16 cm³.g⁻¹, respectively (Figure 3a & b).^[21] The nano porous character of the TPPM was proved by the Barrett–Joyner–Halenda (BJH) method (Figure 3c).^[22] The BJH curve clearly displayed four peaks with the pore size centered at about 4.61, 6.0, 8.0 and 24.0 nm, for four types of pores. These different pores also confirm the nano-porous nature of TPPM. Thus, this porous material with nanometer range cavities and relatively good surface area is suitable for catalysis process.



Figure 3. The nitrogen adsorption-desorption isotherm of TPPM (3a). The type of isotherm shows small adsorbent-adsorbate interactions potentials which associated with pores in the range of 1.5-100 nm. The BET of TPPM (3b). The specific surface area and pore volume of TPPM were obtained using BET

analysis. The V_m, $a_{s,BET}$, C, total pore volume, and mean pore diameter for TPPM were 6.6 cm⁻³.g⁻¹, 28.7 m².g⁻¹, 24.9 nm, 0.16 cm³.g⁻¹, and 22.7 nm, respectively. The Barrett–Joyner–Halenda (BJH) analysis of TPPM (3c). According to the BJH-plot of TPPM the V_p, $r_{p,peak}$ and a_p were 0.17 cm³.g⁻¹, 4.61 nm, 40.7 m².g⁻¹, respectively. The BJH-plot also confirms the nano-porosity nature of TPPM.

The X-ray diffraction (XRD) pattern of TPPM material (Figure 4a) showed some strong peaks placed at 20 of 19.9, 22.6, 26.4, 29.9. These sharp peaks revealed highly crystalline nature of TPPM.^[23] The thermogravimetric analysis (TGA) of TPPM shows three main weight losses (Figure 4b). The first one is accounted for adsorbed water in the structure of the material (1.92%). The second one occurred at 180– 290 °C (5.34%). The main decreasing in the weight percentage of the material at 290-420 °C is related to decomposition of the compound structure. Thus, the TGA analysis indicates the high thermal stability of material. Deferential scanning calorimetry (DSC) is a technique used to investigate the response of polymers to heating. DSC can be used to study the melting of a crystalline polymer or the glass transition.^[24] The crystallization (T_c) and melting (T_m) peaks are only observed for polymers that can form crystals. The crystallization temperature (T_c) of TPPM is occurs at ~210 °C. The DSC of TPPM also shows an endothermic process which happens at ~390 °C. Purely amorphous polymers will only undergo a glass transition. For semi-crystalline polymers, the amorphous portion only undergoes the glass transition while the crystalline regions only undergo melting. According the DSC analysis, it seems that TPPM is a semi-crystalline polymeric material.

The energy-dispersive X-ray (EDX) spectra of the TPPM material (Fig. 4d) show the elements P, N, C and O with wt% of 14.62, 28.55, 24.61 and 30.93, respectively. Also the elemental analysis of the TPPM material demonstrates the presence of C and N atoms with wt% of 23.84% and 29.56%, respectively. Accordingly, it is possible to determine the experimental formula of this material approximately, which estimated to be $C_3N_3O_3P_{0.75}$.

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Figure 4. The XRD pattern of TPPM (a); the existence of sharp peaks shows the crystalline nature of this polymer. The TGA analysis of TPPM (b) shows three weights loses that the main loses (~76%) occur around 290-400 °C which is in parallel to a sharp peak in DTG curve (b, dash line) at 390 °C. The DSC curve of TPPM (c). The EDX analysis of TPPM (d) showed the elements of the compound including P, N, C, and O with the W percentages of 14.62, 28.55, 24.61 and 30.93, respectively.

The experimental formula is in good agreement with a subunit that shown in Figure 5a. The arrangements of triazine ring and phosphite groups generate chelation cavities which have role in the porosity of this material. An optimized structure of a part of TPPM is shown in Figure 5b. These nano-cavities with donor atoms of phosphorus and nitrogen can act as chelating ligand in the presence of a metal (Figure 5c). The coordination of TPPM and a metal form a heterogeneous polymeric material containing metal catalyst for application in organic transformations. The chemical structure of a Ni complex of TPPM is shown in Scheme 5d.



Figure 5. Subunit structure of TPPM (a); if we consider the complete reaction of cyanuric acid with trichlorophosphine it is possible to have subunits containing a phosphorous atom connected to three hydroxyl group of three triazine rings. The optimize structure of a part of TPPM using Austin Model 1 (AM1) and representation of PN chelation cavities (b, c). A schematic representation the available sites of TPPM for the chelation with metals such as Ni to generate heterogeneous catalyst systems for applications in organic transformations (d).

Nickel-catalyzed amination of aryl chlorides using TPPM ligand

In order to evaluate the applicability of TPPM as ligand in TMC it was employed in metal-catalyzed

amination of aryl chlorides. The metal-catalyzed reaction between chlorobenzene and NH₃ in the presence

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of this ligand was investigated to obtain excellent yield of aniline. Different metals including Cu, Pd and Ni (commonly used metal catalysts for this transformation) were used in order to determine which of them is more efficient for the conversion of chlorobenzene to aniline in the presence of TPPM ligand (Table 1).

Table 1. Optimization of metal in metal-catalyzed amination of aryl chloride in the presence of TPPM^a



Entry	Catalyst (mol%)	NH ₃	Yield 3a (%) ^b
1	CuI (10)	$(NH_4)_2SO_4$	75
2	$Cu(OAc)_2$ (10)	$(NH_4)_2SO_4$	70
3	$Pd(OAc)_2(2)$	$(NH_4)_2SO_4$	20
4	NiCl ₂ .5H ₂ O (10)	$(NH_4)_2SO_4$	none
5	Ni(PPh ₃) ₂ (CO) ₂ (10)	$(NH_4)_2SO_4$	90
6	Ni(COD) (10)	$(NH_4)_2SO_4$	92
7	Ni(PPh ₃) ₄ (10)	$(NH_4)_2SO_4$	75
8	Ni(PPh ₃) ₂ (CO) ₂ (10)	$(NH_4)_2SO_4$	35 ^c
9	Ni(PPh ₃) ₄ (10)	$(NH_4)_2SO_4$	22 ^c

^a Reaction conditions: chlorobenzene (1.0 mmol), ammonium source (3.0 mmol), NaOtBu (1.5 mmol), PEG-200 (2.0 mL). ^b Yields are isolated product. ^cNo TPPM was used.

First, CuI was used as catalyst and about 75% of product was obtained (Table 1, entry 1). Approximately same product was observed using Cu(OAc)₂ as catalyst (Table 1, entry 2). In the presence of Pd(OAc)₂ as catalyst the reaction yield was decreased significantly (Table 1, entry 3). Also, by the use of Ni(II) as catalyst no product was observed (Table 1, entry 4). However, maximum yield of product was obtained using Ni(0) catalysts (Table 1, entries 5-7). Among tested Ni(0) catalyst Ni(COD)₂ was the best one (Table 1, entry 6). In the absence TPPM ligand the reaction yield for Ni(PPh₃)₂(CO)₂ and Ni(PPh₃)₄ was significantly decreased, demonstrating the high efficiency of catalyst system for this transformation (Table 1, entries 8 & 9). All of the reactions were checked in the presence of 50 mg of ligand, (NH₄)₂SO₄

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as NH₃ source, NaO*t*Bu as base and PEG-200 as solvent. Then, amounts of Ni(0) and ligand was optimized (Figure 6a&b) and it was observed that about 50 mg of TPPM ligand and 10 mol% of Ni(COD)₂ are necessary to obtain high yield of aniline using coupling of NH₃ with chlorobenzene. In the absence of TPPM ligand, the reaction yield was decrease significantly (20%), demonstrating the important role of the ligand in this reaction. In the absence of metal catalyst no product was observed (Figure 6a &b).



Figure 6. Optimized amount of Ni(COD)₂ quantity (a). With increasing amount of Ni(0) from 3 mol% to 10 mol% the reaction yield was improved to 93% and after that no improvement was observed thus 10 mol% is the optimum amount of catalyst for this reaction. Optimization amount of TPPM ligand (b). In the absence of ligand about 18% of product was observed and with increasing amount of ligand the reaction yield was enhanced. About 50 mg of ligand is needed to obtain maximum yield of product.

Different ammonia source was used and $(NH_4)_2SO_4$ was the best one (c). The best solvent for this reaction was recognized PEG-200, among tested solvents (d). Some bases including NaOtBu, Cs₂CO₃, NaOH, K₂CO₃, and NaH was tested and maximum yield of product using NaOtBu was obtained (e). Amount of base was optimized and 1.5 mmol of base is enough for this reaction.

Among tested ammonia sources, $(NH_4)_2SO_4$ was recognized as the best one (Figure 6c). Other solvents were also checked and no superiority was observed (Figure 6d). Also, in order to prove the only solvent role of the PEG-200, ethylene glycol was used; however the reaction yield was decreased to 35%. This test clarify that the coordination capability of PEG-200 with metal is not the key factor on the superiority of this solvent related to other used. It should be mentioned that in ethanol and *tert*-butanol the reaction yields were 30 and 45%, respectively, confirming that alcoholic solvents are not suitable for this methodology. Since, the type of base is important for this transformation some bases were checked and best results were observed using NaOtBu (Figure 6e). Amount of base was optimized and 1.5 equivalent of base was selected as optimum (Figure 6f). The optimized conditions for conversion of aryl chlorides to anilines in the presence of TPPM ligand are shown in Scheme 2.

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CI + (NH₄)₂SO₄ <u>TPPM (50 mg)</u> NaO*t*Bu, PEG-200 100 °C, 12h

Scheme 2. Optimized conditions for amination of aryl chlorides using TPPM ligand. Reaction conditions: aryl chloride (1.0 mmol), (NH₄)₂SO₄ (2.0 mmol), NaO*t*Bu (1.5 mmol), PEG-200 (2.0 mL).

In another attempt the amination of phenols using their protected 2,4,6-triaryloxy-1,3,5-triazine $(TAT)^{17f,25}$ compounds as an aryl C-O electrophile was also examined in order to extend the applicability of the catalyst system in amination of phenolic-based compounds (Scheme 3).



2,4,6-tris(p-tolyloxy)-1,3,5-triazine

Scheme 3. Amination of 2,4,6-tris(*p*-tolyloxy)-1,3,5-triazine (TPTT) under optimized conditions. Reaction conditions: TPTT (0.35 mmol), (NH₄)₂SO₄ (2.0 mmol), NaO*t*Bu (1.5 mmol), PEG-200 (2.0 mL).

The Ni-catalyzed cross-coupling of NH₃ with a range of aryl chlorides and TAT derivatives were performed efficiently under our optimized conditions and the obtained results are shown in Scheme 4. As established in Scheme 4, the substrates bearing different functional groups were all efficiently coupled under these reaction conditions to provide the corresponding anilines in good to excellent isolated yields, representing this methodology is a general and practical for the synthesis of diverse anilines.

Aryl electrophiles with functional groups such as alkyl (**3b-d**), carbonyl (**3q**), methoxy (**3f-h**), nitro (**3i,j**), cyano (**3k**), acetyl (**3l**) and ether (**3o&3r**) reacted successfully. Some sterically hindered substrates (**3d&3f**) succeeded in producing aniline. Heteroaryl substrates (**3m&3n**) can also be employed to prepare their corresponding amine products. It should be mentioned that in all of the reaction the diaryl amine byproduct was not observed. It seems that, the isolated sites of TPPM resulting from the triazine ring and phosphite moiety can stabilize reactive intermediates on the surface toward the construction of product and thus decrease byproduct formation.

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Scheme 4. Products of Ni-catalyzed amination using TPPM as ligand. Reaction conditions: aryl chloride (1.0 mmol) or TAT (0.35 mmol), $(NH_4)_2SO_4$ (2.0 mmol), NaOtBu (1.5 mmol), PEG-200 (2.0 mL). Yields are isolated product. OTA= the leaving group of TAT.

We also employed the optimized conditions for the synthesis of various arylamines using other amine substrates which are depicted in Scheme 5.²⁶



Scheme 5. Products of Ni-catalyzed amination of different amines and aryl electrophiles using TPPM as ligand. Reaction conditions: aryl chloride (1.0 mmol) or TAT (0.35 mmol), amine (1.0 mmol), NaOtBu (1.5 mmol), PEG-200 (2.0 mL). Yields are isolated product. OTA= the leaving group of TAT.

As shown in Scheme 5, the reactions of different amines (indole, pyrrole, carbazole, imidazole, diphenylamine, and dodecyl amine) proceeded smoothly to furnish the corresponding arylamines with moderate to good yields.

In order to show the recyclability of this catalytic system, first, $Ni(COD)_2$ was complexed with TPPM in PEG-200 solvent at 100 °C and then applied in the coupling reaction between chlorobenzene and $(NH_4)_2SO_4$ and aniline was obtained in 90% isolated yield. The extracted catalyst from the reaction mixture (after filtration, washing and drying) was applied for the next run and 88% of the product was obtained. Overall, the catalyst system was reusable at least for 4 cycles (90, 88, 86, 84, 82%) with almost

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consistent efficiency, demonstrating that Ni/TPPM acts a heterogeneous catalyst system in amination of aryl chlorides. The ICP analysis from the catalyst after 4 cycle of reusability showed that less than 1 percent of Ni source was removed from the TPPM surface during the reaction progress. This result is in good agreement with the efficiency of catalyst after each recovery. The TEM image showed the porous network structure of the material after complexation no metal particle observed the image (Fig. 7a). The SEM of the Ni-TPPM complex shows that the morphology is not changed significantly during complexation process of Ni and TPPM (Fig. 7b). The EDX analysis shows the presence of Ni in the structure of Ni-TPPM complex (Fig. 7c).



Figure 7. A TEM image (a) and SEM image (b) of Ni-TPPM complex which show that the structure and morphology of TPPM ligand remained unchanged after complexation with Ni(COD)₂. The EDX analysis of the Ni-TPPM complex show the presence of Ni in the structure of the material.

This experiments and analysis revealed that the Ni moieties have good connection with ligation sites of TPPM.

Conclusions

In conclusion, we have introduced a new P,N-ligand which can be used as a reusable P,N-ligand in transition-metal catalyzed organic reactions. TPPM is a porous material in sheet morphology with cavities in the range of nanometer scale which can act as an efficient ligand in organic reactions. These nano-

cavities create appropriate sites on the surface of this material with ligation character to coordinate with metals for catalytic purposes. In this study, TPPM was used as ligand in metal-catalyzed amination of aryl chlorides and a combination of TPPM and Ni(COD)₂ was found as an efficient catalyst system for the conversion of aryl chlorides and protected phenols as their TAT substrates to anilines. Moreover, the TPPM ligand provides great promise towards further useful applications in other transition metal-catalyzed organic transformations in future.

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Graphical Abstracts:



A reusable polymeric material containing P,N-ligation sites was prepared by a facile one-step route for application in transition-metal catalysis as a reusable P,N-ligand. This material has cavities in the range of nanometer. It was used as ligand in amination of various aryl chlorides and phenols efficiently to synthesis corresponding aromatic amines in good to excellent yields.