

3, 5-Di-substitued Cyano-Scorpionate Ligand

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Abstract

Polypyrazolylborates are popular ligands in inorganic chemistry, largely due to the relative ease with which one can synthesize the ligands with a variety of different substituents, giving rise to ligands with desired steric and electronic properties. Reported here are the improved syntheses of 4-cyano-3,5-bisphenyl pyrazole and the corresponding ligand potassium bis(4-cyano-3,5-diphenylpyrazolyl)borate, which will expand the potential of the scorpionate ligand chemistry.

Keywords: Ligand, Polypyrazolylborates, Cyano-Scorpionate

1. Introduction

Polypyrazolylborates are popular ligands due to the relative ease with which one can synthesize the pyrazole rings with different substituents. Usually the ligands consist of a tetra-substituted boron atom attached to two or more pyrazoles through one N atom of the ring (Figure 1). The other N atoms of the pyrazole rings become the donor atoms of the ligand. Because they always adopt a multi-dentate mode, polypyrazolylborates are also known as “scorpionate” ligands.

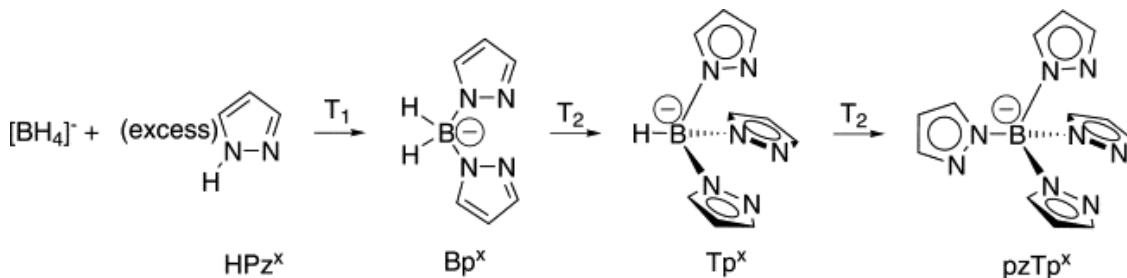


Figure 1: Naming conventions for degree of pyrazole substitution on boron atom. HPz^X indicates a pyrazolyl group where X represents an unspecified substituent. Bp^X , Tp^X , and $pzTp^X$ indicate that the boron has been substituted with two, three, and four pyrazolyl groups, respectively.¹

We have reported to NCUR the syntheses of 4-cyano-3,5-bisphenyl pyrazole and 4-cyano-3,5-bis(tert-butyl) pyrazole, in order to study the steric and electronic properties of the substituents in coordination chemistry². In addition, the coordinating capability of cyano group allows the construction of coordination polymers through a fully conjugated

pathway connecting the pyrazole- and cyano coordinated metals.^{3,4} Reported here are the improved synthesis of 4-cyano-3,5-bisphenyl pyrazole with better yield, and the potassium bis(4-cyano-3,5-diphenylpyrazolyl)borate ligand.

2. Experimental

Unless otherwise stated, all solvents and reagents were used as received from Alfa Aesar and Fisher Scientific without further purification. Toluene was dried over sodium/benzophenone. A BUCHI SWITZERLAND Rotavapor RII was used to remove solvents from solutions under reduced pressure. Glassware were soaked in a KOH/isopropanol/water bath, rinsed with de-ionized water, and dried over night at 80°C. FT-IR spectra were recorded on a PerkinElmer Spectrum100 FTIR spectrometer. ¹H NMR spectra were measured on a Eft-90 NMR spectrometer from Anasazi Instrument in CDCl₃ solution with TMS as internal standard.

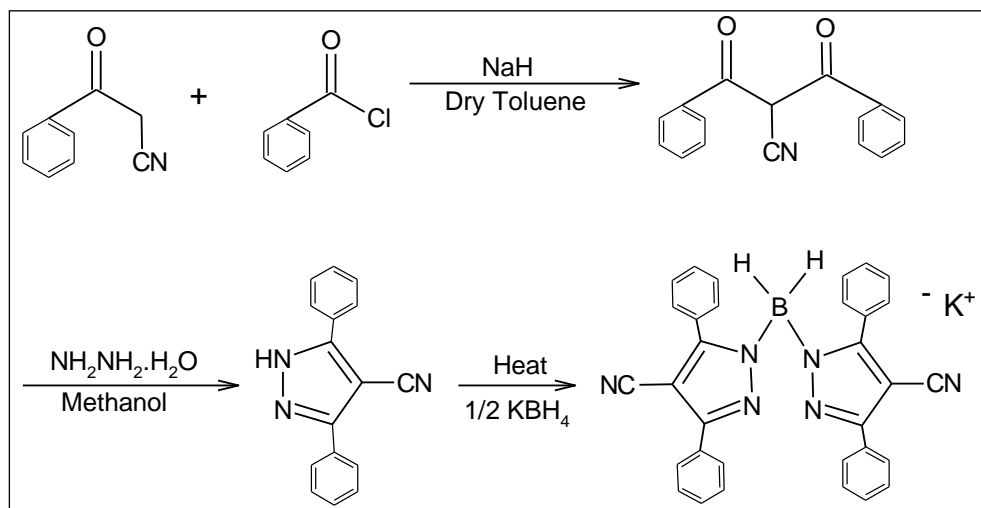


Figure 2. Synthesis scheme of the scorpionate ligand.

Figure 2 above shows the overall synthesis route of the scorpionate ligands. To synthesize of 4-cyano-3,5-bisphenyl pyrazole, 0.97 g (24.25 mmol, 60% dispersion in mineral oil) of sodium hydride was added to 100 mL dry toluene. To this solution was added 2.50 g of benzoylacetone nitrile (17.24 mmol), resulting in the immediate appearance of bubbles. The mixture was stirred for 18 hours before benzoyl chloride (2.43 g, 17.24 mmol) was added. The reaction mixture was stirred overnight followed by three extractions using 100 mL of 0.2 M NaOH solution each time. The aqueous layers were combined and acidified with HCl/H₂O (50/50) solution to pH~1. A white precipitate appeared immediately and was extracted with three portions of 100 mL of ethyl acetate and dried over anhydrous MgSO₄. Removal of the solvent under reduced pressure yielded 3.38 g (13.57 mmol, yield 78.72%) of crude product, which was chromatographed using a silica gel column (100-200 mesh) with 80/20 ethyl acetate/hexane as the mobile phase. The desired product had a very low retention time, and almost all other products adsorbed onto the silica very strongly. Eluent from the column was evaporated under reduced pressure, yielding 2-cyano-1,3-diphenyl-1,3-propanedione as a yellow solid (2.79 g, 11.21 mmol, 64.99%). Infrared spectroscopy showed a signal at 2216 cm⁻¹ for the C≡N stretch. The ¹H NMR (chloroform-d) showed chemical shifts at 7.59 ppm (m, 6H) and 8.12 ppm (m, 4H). This diketone compound (2.79 g, 11.21 mmol) was then reacted with hydrazine monohydrate (0.58 g, 11.60 mmol) in 100 mL of methanol and stirred overnight. The solvent was removed under reduced pressure to yield ~10 mL solution of the crude product, which was chromatographed using a silica gel column (100-200 mesh) with 70/30 ethyl acetate/hexane as the mobile phase. 10 mL eluent was collected each fraction, and the fraction number 7 to 13 were combined to yield the pure product. The solvent was evaporated under reduced pressure, yielding 4-cyano-3,5-bisphenyl pyrazole as a yellow solid (1.06 g, 4.33 mmol, 25.10%). Infrared spectroscopy showed characteristic peaks at 3177 cm⁻¹ and 2227 cm⁻¹ for N-H and C≡N stretches respectively. The ¹H NMR (chloroform-d) showed chemical shifts at 8.06 ppm (d, 4H), 7.64 ppm (t, 4H), and 7.54 ppm (t, 2H).

To synthesize potassium bis(4-cyano-3,5-diphenylpyrazolyl)borate, 0.789 g (3.22 mmol) of 4-cyano-3,5-bisphenyl pyrazole and 0.087 g of potassium borohydride (1.61 mmol) (2:1 ratio) were combined in a 100 mL round bottom flask

fitted with a reflux condenser. The mixture was then heated in an oil bath at $\sim 140\text{ }^{\circ}\text{C}$ whilst stirring for an hour. The pyrazole began to melt at about $110\text{ }^{\circ}\text{C}$ and reacted with KBH_4 producing hydrogen bubbles. The mixture solidified after 45 minutes and the resulting solid was then dissolved in 15 mL acetonitrile and filtered to remove any unreacted KBH_4 . The solvent was then removed under reduced pressure and the residue was boiled in toluene to further remove any unreacted pyrazole. Upon filtration and drying, a fine yellow powder of potassium bis(4-cyano-3,5-diphenylpyrazolyl)borate ($\text{KBp}^{\text{Ph}_2.4\text{CN}}$) (0.15 g, 0.28 mmol, 8.69%) was obtained. FT-IR showed the B-H and $\text{C}\equiv\text{N}$ stretches at 2349 cm^{-1} and 2228 cm^{-1} respectively. ^1H NMR (chloroform-d): 7.89 ppm (d, 8H), and 7.50 ppm (t, 12H).

3. Results And Discussion

The yield of 4-cyano-3,5-bisphenyl pyrazole was improved from 17.01% to 25.10% through chromatographs, which was applied in the attempt of synthesizing $\text{KBp}^{\text{Ph}_2.4\text{CN}}$. The FT-IR and NMR spectra showed promising results for the final product although X-ray quality crystals haven't been obtained yet. The low yield of the $\text{KBp}^{\text{Ph}_2.4\text{CN}}$ ligand might suggest the different solubility from its precursor compounds such as $\text{KBp}^{\text{Ph}.4\text{CN}}$ and $\text{KTp}^{\text{Ph}.4\text{CN}}$,^{3,4} indicating the effects of two symmetrical phenyl substituents, which will be the future direction of research.

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5. References

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