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Improved synthesis of a trisphosphine ligand and crystallographic characterization of the ligand and nickel thiocyanate complex

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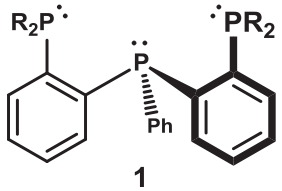
ABSTRACT

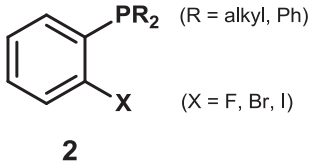
Improved syntheses of *o*-$C_6H_4(PEt_2)(X)$ (X = F, Br, I) and the trisphosphine $PhP[o\text{-}C_6H_4(PEt_2)]_2$ have been developed and are applicable to a wide variety of phosphine substituents. The trisphosphine, $PhP(o\text{-}Ph\text{–}PEt_2)_2$, has been fully characterized spectroscopically and, for the first time, crystallographically. Reaction of the P3 ligand with one equivalent of $NiCl_2$ or $Ni(BF_4)_2$ followed by 2.5 equivalents of KNCS produces the monometallic complexes $Ni(X)_2[\kappa^3\text{-}PhP(o\text{-}Ph\text{–}PEt_2)_2]$, (X = Cl or NCS). The nickel thiocyanate complex has been characterized via a crystal structure. The nickel center has a square pyramidal structure with one of the NCS ligands occupying the apical coordination site. The Ni complex crystallizes in the $P\bar{1}$ space group with an unusual six molecules in the asymmetric unit ($Z' = 6$), and twelve in the unit cell.

1. Introduction

The strongly chelating trisphosphine, $PhP(o\text{-}C_6H_4\text{–}PR_2)_2$, **1** (R = Et), was first prepared by Hart in 1960 [1]. Hartley, Venanzi and coworkers reported the synthesis of the more commonly used phenyl-substituted $PhP(o\text{-}C_6H_4\text{–}PPh_2)_2$, ligand in 1963 [2]. Since then this P3 ligand, mainly in the form of the R = Ph, or sometimes Me substituted versions, has been used to prepare a variety of monometallic transition metal complexes and occasionally multimetallic systems [3–6]. The difficulty and low yields in synthesizing this ligand, especially the alkyl-substituted versions, has limited its use in transition metal coordination chemistry.



1



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The key to the synthesis of **1** is to improve the yield of the commonly used precursor **2**. Early preparations **2** have reported yields of: 21% (R = Cl, X = Br), 36% (R = Ph, X = Br) [2], 26% (R = Et, X = Br), and 50% (R = Et, X = Cl) [1]. More recently, higher yields have been obtained using Pd-catalyzed coupling route (R = Ph, X = Br) [7] and better solvents when using lithium reagents (R = Me, X = F) [8]. The yields on preparing the trisphosphine ligand **1** from the appropriate precursor **2** have also been quite low with yields of 16% (R = Et) [1] and 35% (R = Ph) [2].

We report here improved and straightforward syntheses for **1** (R = Et) and especially **2** (R = Et, X = F, Br, I) along with the crystallographic characterization of **1** and the nickel complex formed from the reaction of $Ni(NCS)_2$ and **1**. This was part of our efforts to synthesize a new, far more strongly chelating and bridging tetraphosphine ligand for catalytic studies, which will be reported elsewhere.

2. Experimental

All manipulations were carried out under an inert atmosphere of nitrogen and in oven-dried glassware using a Vacuum Atmospheres Company glovebox or by using standard Schlenk techniques unless noted otherwise. Tetrahydrofuran (THF), diethyl ether, CH_2Cl_2, hexane, and *N*,*N*-dimethylformamide (DMF) were obtained dry from Aldrich and processed through a Innovative Technology Inc. PURESOLV™ solvent purification system under inert atmosphere (N_2). All other solvents were obtained anhydrous from Aldrich and were used as received. Deionized water was degassed by purging with nitrogen gas for 30 min prior to use.

Reagents and starting materials were obtained from commercial suppliers and used as received, except for phenylphosphine [9], which was prepared according to literature methods. Isopropylmagnesium bromide was produced from magnesium turnings

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and isopropyl bromide in THF. Other organolithium and Grignard reagents were obtained as commercial solutions from Aldrich and were titrated over salicylaldehyde phenylhydrazone [10] immediately preceding their use. $Ni(BF_4)_2{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$ were obtained from Strem Chemicals and used as received.

^1H NMR spectra were recorded on a Bruker DPX-250, an ARX-300, or a DPX-400 spectrometer with chloroform (7.26 ppm), benzene (7.15 ppm) or dichloromethane (5.32 ppm) as the internal standard. The ^{13}C NMR spectra were recorded on the same instruments with chloroform (77.0 ppm), or benzene (128.02 ppm) as the internal standard. The ^{31}P NMR spectra were recorded on the same instruments with 85% phosphoric acid (0.0 ppm) as the external reference. Multiplicity is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, om = overlapping multiplets, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets, and br = broad. The multiplicity reported in the $^{13}C\{^1H\}$ spectra refers to the ^{31}P–^{13}C coupling.

Mass spectral analyses were conducted at the LSU Mass Spectrometry Facility. ESI-MS was performed by an Agilent 6210 Electrospray Time-of-Flight Mass Spectrometer. Samples of **3** and **4** were dissolved in DCM and analyzed in both positive and negative-ion mode.

2.1. Preparation of 1-(diethylphosphino)-2-iodobenzene, **2i**

The following procedure was performed in a Schlenk flask covered with aluminum foil in order to exclude light. The iodo-products are light sensitive so it is important to protect them from even fluorescent lab lights. A solution of 1,2-diiodobenzene (25.0 g, 75.77 mmol) in THF (80 mL) was treated at 0 °C with a 0.44 M THF solution of *i*-PrMgBr (171.0 mL, 75.77 mmol). The resulting solution was stirred at 0 °C for 6 h. It was subsequently cooled to −25 °C, and slowly treated with a solution of Et_2PCl (9.72 g, 78.0 mmol) in THF (90 mL). The yellow solution was allowed to warm to room temperature and stirred overnight. Water (80 mL) was added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 50 mL), the organic extracts were combined and dried over Na_2SO_4, and the solvents were removed *in vacuo* to yield a slightly yellow liquid. The product was distilled *via* short-path distillation *in vacuo* to yield 16.0 g (72%) of an air- and light-sensitive colorless liquid: bp = 116–122 °C (0.6 Torr). Typical isolated yields are 70–75%, and the purity of the product is typically greater than 99% based on NMR.

$^{31}P\{^1H\}$ NMR (101.2 MHz, δ ppm, C_6D_6): 0.3 (s). ^1H NMR (250 MHz, δ ppm, C_6D_6): 7.7 (br m, 1H), 7.2 (sharp m, J = 7.3 Hz, 2H), 6.8 (sharp m, J = 7.3 Hz, 1H), 1.5 (m, 4H), and 0.9 (m, J = 7.3 Hz, $J_{P,H}$ = 7.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (62.8 MHz, δ ppm, C_6D_6): 142.3 (d, J = 15.3 Hz), 139.5 (s), 139.4 (d, J = 15.3 Hz), 108.5 (d, J = 40.3 Hz), 77.4 (d, J = 30.7 Hz), 76.6 (s), 19.3 (s), and 9.5 (d, J = 13.4 Hz).

2.2. Preparation of 1-(diethylphosphino)-2-bromobenzene, **2b**

The procedure described above was repeated on a 0.148 mol scale using 1,2-dibromobenzene. The bromo products are not light sensitive. The reaction afforded the product in 75–80% isolated yield (28.3 g): bp = 83 °C (0.4 Torr, lit. bp = 111–112 °C/0.8 Torr [1]).

$^{31}P\{^1H\}$ NMR (101.2 MHz, δ ppm, C_6D_6): −13.6 (s). ^1H NMR (250 MHz, δ ppm, C_6D_6): 7.4 (br m, 1H), 7.1 (d, J = 4.5 Hz, 2H), 7.0 (m, 1H), 1.6 (m, J = 7.3 Hz, 4H), and 0.9 (m, J = 7.3 Hz, $J_{P,H}$ = 7.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (62.8 MHz, δ ppm, C_6D_6): 139.8 (d, J = 17.2 Hz), 134.5 (s), 131.4 (d, J = 28.8 Hz), 129.3 (s), 78.1 (d, J = 32.6 Hz), 77.4 (s), 19.1 (s), and 10.3 (d, J = 13.4 Hz).

2.3. Preparation of 1-(diethylphosphino)-2-fluorobenzene, **2f**

Compound **2f** was prepared by using the procedure described for **2i**. The fluoro product is not light sensitive. The reaction was performed on a 0.171 mol scale using 1-bromo-2-fluorobenzene, and afforded the production of **2f** in 70–75% isolated yield (23.0 g): bp = 77–80 °C (0.3 Torr).

$^{31}P\{^1H\}$ NMR (101.2 MHz, δ ppm, C_6D_6): −21.6 (d, $J_{P,F}$ = 29.8 Hz). ^1H NMR (250 MHz, δ ppm, C_6D_6): 7.2 (br m, 1H), 6.8 (m, 3H), 1.6 (m, 4H), 0.9 (m, J = 7.3 Hz, $J_{P,H}$ = 7.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (62.8 MHz, δ ppm, C_6D_6): 133.8 (dd, J = 5.7 Hz, J = 13.4 Hz), 130.6 (d, J = 7.7 Hz), 124.2 (t, J = 3.8 Hz), 115.4 (d, J = 24.9 Hz), 18.8 (d, J = 3.8 Hz), 18.5 (s), 10.0 (d, J = 13.4 Hz).

2.4. Preparation of $PhP(o\text{-}C_6H_4\text{–}PEt_2)_2$, **1**

A 1.0 M THF solution of $o\text{-}C_6H_4(PEt_2)(I)$, **2i**, (10.0 g, 34.25 mmol) was cooled in an ice bath and slowly treated with 2.9 M *i*-PrMgBr (11.81 mL, 34.25 mmol) in THF, then allowed to stir at 0 °C for 8 h. This solution was then cooled to −25 °C by an acetone/dry ice bath and slowly treated with a 1.0 M THF solution of $PhPCl_2$ (3.064 g, 17.124 mmol), then allowed to warm to room temperature and stirred for an additional 8 h. The solution was warmed to 70 °C for 4 h and then allowed to cool to room temp. This solution was quenched with 100 mL of an aqueous NH_4Cl solution. The organic layer was extracted and any remaining organic product was extracted from the aqueous layer with three 20 mL portions of ether. The combined organic fractions were dried over Na_2SO_4 and a gravity filtration through celite was performed. The solvent was removed by vacuum evaporation and short path vacuum distillation was used to remove any unreacted $o\text{-}C_6H_4(PEt_2)(I)$, **2i** (0.5 torr, oil bath of 155 °C). The remaining product can be recrystallized from methanol or DMF. Typical isolated yields were 38–42%, although ^{31}P NMR of the crude reaction mixture showed a yield of 70+%.

$^{31}P\{^1H\}$ NMR (101.2 MHz, δ ppm, C_6D_6): forms an AB_2 second order pattern that was simulated to give the two external phosphorus atoms at −26.2 ppm and the internal phosphorus at −17.0 ppm with a calculated J_{P-P} = 152.7 Hz (see Fig. 1). ^1H NMR (250 MHz, δ ppm, C_6D_6): 7.5 (m, 2H), 7.4 (m, 2H), 7.2 (dd, J = 14.1 Hz, J = 6.8 Hz, 7H), 7.0 (t, J = 7.3 Hz, 2H), 1.7 (dq, $J_{H,H}$ = 7.7 - Hz, $J_{H,P}$ = 20.1 Hz, 8H), 1.02 (td, $J_{H,P}$ = 7.3 Hz, $J_{H,H}$ = 13.7 Hz, 12H. $^{13}C\{^1H\}$ NMR (62.8 MHz, δ ppm, C_6D_6): 135.2 (d, J = 19.2 Hz), 134.7 (m), 130.5 (d, J = 7.7 Hz), 129.0 (d, J = 15.3 Hz), 20.6 (m), 10.4 (t, J = 7.6 Hz).

2.5. Preparation of $Ni(NCS)_2[\kappa^3\text{-}PhP(o\text{-}C_6H_4\text{–}PEt_2)_2]$, **3**

In a Schlenk flask 0.879 g (2.00 mmol) of ligand **1** were dissolved in 70 mL of ethanol. Another Schlenk flask was charged with 0.682 g (2.00 mmol) $Ni(BF_4)_2{\cdot}6H_2O$ and dissolved in 15 mL of ethanol. The ligand solution was added dropwise via cannula to the $Ni(BF_4)_2$ solution. As the addition proceeded the solution became very dark red in color. After the addition, a solution of 0.487 g (5.00 mmol 2.5 equivalents) KSCN dissolved in 15 mL of ethanol was added to the dark red solution. This solution was allowed to stir overnight during which a red solid precipitated out of solution. The next day the solid was collected via filtration and washed with ethanol and diethyl ether and dried under vacuum. NMR analysis revealed it to be the desired complex with a 65% isolated yield. Dark red needle crystals for the X-ray analysis were grown by slow evaporation of a THF solution.

$^{31}P\{^1H\}$ NMR (101.2 MHz, δ ppm, CD_2Cl_2): 59.2 (P_{ext}, d, J_{P-P} = 56 Hz), 89.6 (P_{int}, t, J_{P-P} = 56 Hz). ^1H NMR (CD_2Cl_2): 0.95–1.04 (m, 6H), 1.27–1.36 (m, 6H), 2.08–2.28 (om, 6H), 2.45–2.55 (m, 2H), 6.67–6.72 (m, 2H), 7.32–7.36 (m, 2H), 7.44–7.49 (m, 1H), 7.73–7.87 (om, 8H).