

Efficient one-pot synthesis of diphenyl(pyrazin-2-yl)phosphine and its Ag^I, Au^I and Pt^{II} complexes

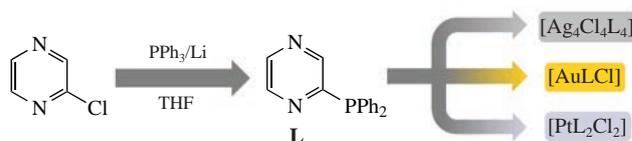
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A convenient one-pot synthesis of diphenyl(pyrazin-2-yl)phosphine has been developed based on reaction of Ph₃P with metallic lithium followed by treatment of the Ph₂PLi formed with 2-chloropyrazine. The Ag^I, Au^I and Pt^{II} chloride complexes derived from this phosphine have been synthesized and structurally characterized.



Keywords: diphenyl(pyrazin-2-yl)phosphine, lithiation, pyrazine, triphenylphosphine, silver(I) complexes, gold(I) complexes, platinum(II) complexes.

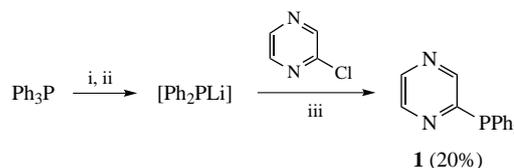
In the last two decades, pyridylphosphines have attracted interest as ligands for diverse molecular complexes and coordination polymers, which demonstrate excellent catalytic performance,^{1–8} luminescent properties,^{9–11} biological activity¹² and magnetic features.¹³ The specific disposition of the hard nitrogen and soft phosphorus atoms in pyridylphosphines provides an opportunity for design of poly- and heterometallic complexes including those with metallophilic interactions.^{14,15} Thus, about seven hundred mono- and polymetallic assemblies were prepared using commercially available diphenyl(pyridin-2-yl)phosphine.¹⁶ By contrast, the corresponding diazine analogues bearing pyrimidin-2-yl or pyrazin-2-yl substituents are much less investigated. As an example, diphenyl(pyrimidin-2-yl)phosphine was employed for the synthesis of Ag^I and Au^I complexes, Au^I–Ag^I clusters as well as several dinuclear clusters.^{17–20} For diphenyl(pyrazin-2-yl)phosphine, only few [Cu₂I₂] type complexes have been described.^{21,22} Concerning the synthesis of these phosphines, it was described for diphenyl(pyrimidin-2-yl)phosphine only,^{18,20,23,24} while the preparation procedure and spectral characteristics for diphenyl(pyrazin-2-yl)phosphine are still lacking. Among the close analogues of the latter, (3-methylpyrazin-2-yl)diphenylphosphine has been synthesized *via* metalation of diphenylphosphine with BuLi followed by reaction with 2-chloro-3-methylpyrazine.²⁵

Herein, we report one-pot organometallics-free synthesis of diphenyl(pyrazin-2-yl)phosphine **1** from air-stable and readily available precursors. As our experiments have revealed, this phosphine can readily be accessed *via* reaction of 2-chloropyrazine with lithium diphenylphosphide (Ph₂PLi) *in situ* generated by treatment of Ph₃P with metallic lithium in THF (room temperature, 5 h) followed by quenching of by-produced PhLi with Me₃SiCl (Scheme 1).[†] The non-optimized yield of **1**

obtained after recrystallization from MeOH/CH₂Cl₂ being 20%. The protocol elaborated has proved to be also relevant for the synthesis of diphenyl(pyrimidin-2-yl)phosphine **2** from 2-chloropyrimidine in 36% non-optimized yield.

Phosphine **1** was isolated as colorless powder which slowly oxidized in air to the corresponding phosphine oxide. Therefore, although this phosphine can be handled in air, it should be stored in inert atmosphere. The ¹H, ¹³C{¹H} and ³¹P{¹H} NMR as well as FT-IR spectra of compound **1** confirm its structure and demonstrate the expected signal patterns. The structure of phosphine **1** has also been established by X-ray diffraction technique^{26,27} featuring trigonal pyramidal geometry of phosphorus atom (Figure 1) with C–P–C angles ranging from 99.60(6) to 105.06(6)°.[‡]

Having in hands the title phosphine, we have surveyed its coordination ability toward Ag^I, Au^I and Pt^{II} centers aiming to



Scheme 1 Reagents and conditions: i, Li, THF, 25 °C, 5 h; ii, Me₃SiCl, 25 °C, 10 min; iii, 2-chloropyrazine, –20 to 25 °C, 3 h.

added on stirring, the resulting mixture was kept for 10 min and then cooled down to –20 °C. Suspension of 2-chloropyrazine (5.7 g, 0.05 mol) in THF (15 ml) was added dropwise, the resulting mixture was warmed to room temperature and stirred for 3 h. Water (50 ml) was added and the quenched mixture was extracted with CH₂Cl₂ (3 × 30 ml). The combined organic extract was washed with H₂O, dried with MgSO₄ and evaporated *in vacuo*. The crude residue was recrystallized from MeOH–CH₂Cl₂ (5:1, v/v) affording colorless crystals of product **1**. Yield: 3.0 g (20%).

[‡] Crystal data for **1**. C₁₆H₁₃N₂P, 0.50 × 0.20 × 0.10 mm, triclinic, space group P $\bar{1}$, *a* = 5.8848(3), *b* = 10.3298(5) and *c* = 11.9224(6) Å, α = 69.607(2)°, β = 87.818(2)° and γ = 83.598(2)°, *V* = 675.09(6) Å³,

[†] Synthesis of diphenyl(pyrazin-2-yl)phosphine **1**. To a solution of triphenylphosphine (13.0 g, 0.05 mol) in absolute THF (50 ml), pieces of lithium metal (1.2 g, 0.176 mol) were added, and the mixture was stirred at room temperature for 5 h. Hereupon, Me₃SiCl (5.4 g, 0.05 mol) was

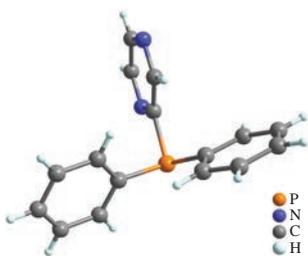


Figure 1 Molecular structure of diphenyl(pyrazin-2-yl)phosphine **1**.

design new potential pre-catalysts and luminescent materials.[§] The interaction of **1** with AgCl in a 1:1 molar ratio has been found to afford tetranuclear $[\text{Ag}_4\text{Cl}_4(\mathbf{1})_4]$ complex (54% yield), whose structure is represented by Ag_4Cl_4 cube supported by the ligands in P-monodentate manner (Figure 2).[‡] The closest Ag...Ag contacts of 3.607 Å rule out the appearance of argentophilic interactions within Ag_4Cl_4 module. Reaction of **1** with AuCl taken as Au(tht)Cl (tht = tetrahydrothiophene) results in linear $[\text{Au}(\mathbf{1})\text{Cl}]$ complex (81% yield)[§] with the pyrazine ring being non-coordinated (Figure 3).[‡] The packing of $[\text{Au}(\mathbf{1})\text{Cl}]$ features no intramolecular aurophilic contacts, typically found in crystals of such complexes. Again, the P-coordination of this phosphine has been observed in *cis*- $[\text{Pt}(\mathbf{1})_2\text{Cl}_2]$ complex (Figure 4),[‡] synthesized as CH_2Cl_2 solvate in 89% yield reacting with $\text{Pt}(\text{COD})_2\text{Cl}_2$ (COD = cycloocta-1,5-diene).[§] Considering the presence of one or several pyrazine rings in complexes

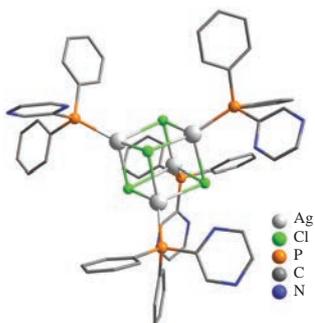


Figure 2 Molecular structure of complex $[\text{Ag}_4\text{Cl}_4(\mathbf{1})_4]$, H atoms are omitted for clarity.

$Z = 2$, $d_{\text{calc}} = 1.300 \text{ g cm}^{-3}$, $\mu = 0.19 \text{ mm}^{-1}$, data/restraints/parameters 3642/172/0, $S = 1.03$. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0431$, $wR_2 = 0.1002$. R indices (all data): $R_1 = 0.0554$, $wR_2 = 0.1087$.

Crystal data for $[\text{Ag}_4\text{Cl}_4(\mathbf{1})_4]$. $\text{C}_{64}\text{H}_{52}\text{Ag}_4\text{Cl}_4\text{N}_8\text{P}_4$, $0.20 \times 0.20 \times 0.10 \text{ mm}$, triclinic, space group $P\bar{1}$, $a = 11.5541(5)$, $b = 11.9705(5)$ and $c = 24.1849(9) \text{ \AA}$, $\alpha = 102.932(2)^\circ$, $\beta = 99.327(2)^\circ$ and $\gamma = 91.431(2)^\circ$, $V = 3210.5(2) \text{ \AA}^3$, $Z = 2$, $d_{\text{calc}} = 1.686 \text{ g cm}^{-3}$, $\mu = 1.52 \text{ mm}^{-1}$, data/restraints/parameters 14766/757/27, $S = 1.021$. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0444$, $wR_2 = 0.0984$. R indices (all data): $R_1 = 0.0838$, $wR_2 = 0.1141$.

Crystal data for $[\text{Au}(\mathbf{1})\text{Cl}]$. $\text{C}_{16}\text{H}_{13}\text{AuClN}_2\text{P}$, $0.40 \times 0.20 \times 0.20 \text{ mm}$, orthorhombic, space group $Pna2_1$, $a = 12.939(2)$, $b = 11.537(2)$ and $c = 10.849(2) \text{ \AA}$, $V = 1619.6(5) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 2.037 \text{ g cm}^{-3}$, $\mu = 9.34 \text{ mm}^{-1}$, data/restraints/parameters 2816/155/23, $S = 1.04$. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0475$, $wR_2 = 0.0985$. R indices (all data): $R_1 = 0.0782$, $wR_2 = 0.1121$.

Crystal data for *cis*- $[\text{Pt}(\mathbf{1})_2\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2$. $\text{C}_{33}\text{H}_{28}\text{Cl}_4\text{N}_4\text{P}_2\text{Pt}$, $0.50 \times 0.30 \times 0.10 \text{ mm}$, monoclinic, space group $P2_1/n$, $a = 10.6817(6)$, $b = 21.6533(11)$ and $c = 14.4428(7) \text{ \AA}$, $\beta = 91.266(2)^\circ$, $V = 3339.7(3) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.749 \text{ g cm}^{-3}$, $\mu = 4.65 \text{ mm}^{-1}$, data/restraints/parameters 9232/397/0, $S = 1.03$. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0413$, $wR_2 = 0.0829$. R indices (all data): $R_1 = 0.0787$, $wR_2 = 0.0961$.

CCDC 1966849–1966852 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

[§] See Online Supplementary Materials for details.

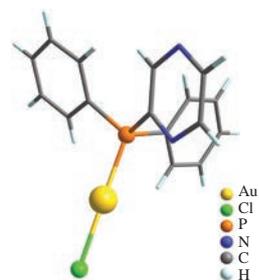


Figure 3 Molecular structure of complex $[\text{Au}(\mathbf{1})\text{Cl}]$.

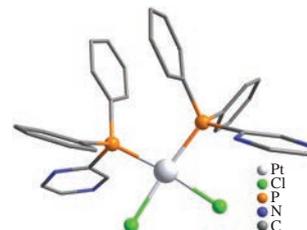


Figure 4 Molecular structure of complex *cis*- $[\text{Pt}(\mathbf{1})_2\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2$, H atoms and CH_2Cl_2 molecule are omitted for clarity.

presented, the latter seem to be promising metalloligands for coordination-driven assembly of diverse metal-organic polymers.

The phase purity of the above complexes has been verified by FT-IR, NMR and elemental analysis data.[§] The FT-IR spectra are in agreement with the X-ray results demonstrating vibrations of the coordinated phosphine **1** backbone. According to TGA and DTG analyses, the complexes have high thermal stability and start to decompose at least above 200 °C. Complex *cis*- $[\text{Pt}(\mathbf{1})_2\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2$ completely loses its solvate molecule at ~150 °C. Complexes $[\text{Au}(\mathbf{1})\text{Cl}]$ and *cis*- $[\text{Pt}(\mathbf{1})_2\text{Cl}_2]$ were soluble in organic solvents and thus were investigated by NMR spectroscopy, which confirmed a retention of their molecular structures upon dissolution. ¹H NMR resonances of the complexes are shifted downfield relative to those of free phosphine **1**. The ³¹P{¹H} NMR spectra of $[\text{Au}(\mathbf{1})\text{Cl}]$ and *cis*- $[\text{Pt}(\mathbf{1})_2\text{Cl}_2]$ contain sharp singlets at 26.97 and 6.79 ppm (*cf.* $\delta_{\text{P}} = -8.13 \text{ ppm}$ for phosphine **1**). The ³¹P{¹H} NMR peak of the Pt^{II} complex is flanked by a set of ¹⁹⁵Pt–³¹P satellites, with the specific ¹J_{Pt–P} coupling constant being 1835 Hz.

In summary, an efficient one-pot synthesis of diphenyl(pyrazin-2-yl)phosphine has been elaborated starting from available triphenylphosphine, 2-choropyrazine and lithium metal. The coordination behavior of this polydentate ligand has been examined in reactions with Ag^I, Au^I and Pt^{II} chlorides, revealing the P-monodentate ligation pattern in the complexes synthesized, namely $[\text{Ag}_4\text{Cl}_4(\mathbf{1})_4]$, $[\text{Au}(\mathbf{1})\text{Cl}]$ and *cis*- $[\text{Pt}(\mathbf{1})_2\text{Cl}_2]$. These findings contribute to the coordination chemistry of P,N-ligands and to the synthesis of organophosphorus compounds.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.014.

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