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Letter

1-Vinylimidazole – a versatile building block for the synthesis of cationic phosphines useful in ionic liquid biphasic catalysis

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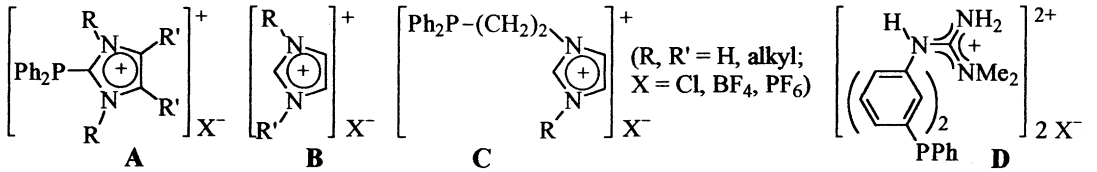
Abstract

Base catalyzed addition of 1-vinylimidazole to primary and secondary phosphines affords tertiary phosphines with terminal 1-imidazolyl substituents $C_3H_3N_2$ in high yields. The X-ray structure of the oxide $Ph_2P(O)$–$(CH_2)_2$–1-$C_3H_3N_2$ has been determined (space group $P\bar{1}$). By selective *N*-protonation and protected group *N*-quaternization novel cationic phosphines, e.g. **2a**, **2b**, **9** and **10**, with peripheral 1-imidazolium groups are obtained. These are interesting ligands for catalytic reactions in biphasic systems containing ionic liquids as polar phase and may be employed in hydroformylation of long-chain olefins like 1-octene.

Keywords: 1-vinylimidazole; 1-imidazolylphosphines; 1-imidazolium phosphines; Hydroformylation; Ionic liquids

1. Introduction

Phosphines bearing imidazolyl moieties have attracted substantial interest because of their potential to bind soft and hard transition metals via phosphorus [1] or nitrogen [2]. Due to the pronounced basicity of the heterocyclic group these ligands are, however, also capable to form cationic phosphine ligands by selective *N*-protonation or *N*-alkylation. The resulting imidazolium phosphines (**A**) contain structural elements of the ionic liquids (**B**, e.g. R = Me, R′ = *n*-Bu) which have very recently been employed as "designer solvents" in novel two-phase catalytical reactions [3–5]. While only very few 2-imidazolium phosphines (**A**) are known [6,7], phosphine ligands of type **C** bearing terminal *N*-imidazolium groups have, with one single exception [8], not been reported in the literature so far.



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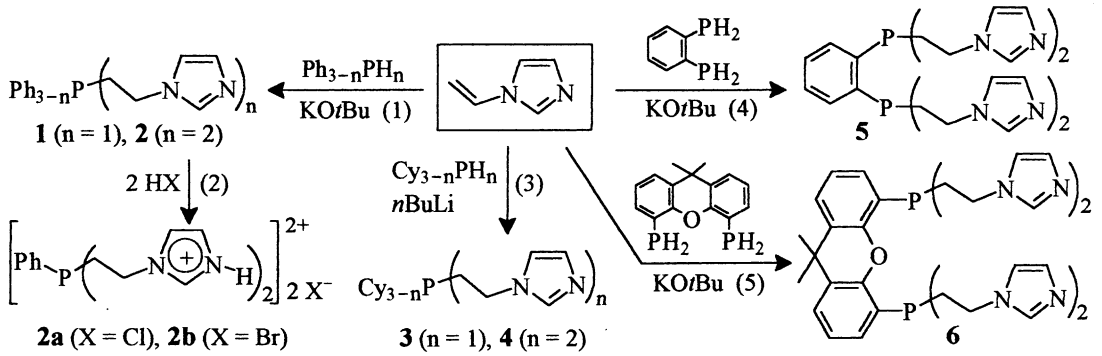
In context with of our ongoing research on catalyst ligands containing mesomeric cationic groups as in the guanidinium phosphines **D** [9] we report here on the synthesis and application of imidazolium phosphines of type **C**.

2. Results and discussion

2.1. Addition of 1-vinylimidazole to primary and secondary phosphines

In presence of catalytic amounts of strong bases PH functional phosphines are added to the exocyclic C=C double bond of *N*-vinylimidazole forming tertiary phosphine ligands **1–6** with 2-(1-imidazolyl)ethyl substituents in high yields. KO-*t*-Bu is preferably applied as the base if primary or secondary aromatic phosphines are used. In case of aliphatic phosphines, due to their lower PH acidity, stronger bases like *n*-BuLi have to be employed. This method has a broad applicability for the synthesis of all types of tertiary phosphines with terminal 1-imidazolyl groups (Eqs. (1), (3)–(5)) [10].

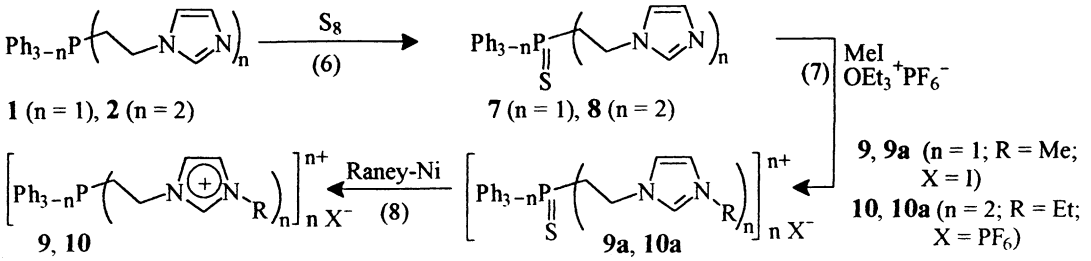


The anti-Markownikow addition of the P–H group to the exocyclic C=C double bond of *N*-vinylimidazole has been proved by the X-ray structure of **1a** (Fig. 1) [1], the oxide of **1**, and by analysis of the ^{1}H-NMR and $^{13}C\{^{1}H\}$-NMR spectra of **1–6** showing resonances for the N–CH_2–CH_2^{13}C–P unit (e.g. **1**: ^{1}H-NMR: 2.12 (2 H, m), 3.49 (2 H, m); $^{13}C\{^{1}H\}$-NMR: 30.5 (J(PC) = 16.3 Hz), 43.8 (J(PC) = 25.4 Hz)), no signals for N–CH(Me)–P bridges could be observed. In the $^{31}P\{^{1}H\}$-NMR spectra **1–6** show singlets in the range between $\delta P = -5$ and -43 typical for alkyl–aryl phosphines [11].

2.2. N-protonation and N-quaternization of the 1-imidazolylethylphosphines

In contrast to **2–6** which are formed as oily liquids, the *N*-protonated phosphines like **2a** and **2b** are obtained as solids (Eq. (2)). Selective *N*-quaternization of the neutral phosphines requires protection of the phosphorus atom against attack by the alkylating agent. This may be achieved by sulfurization (Eq. (6)) as shown for the synthesis of the imidazoliumphosphines **9** and **10**. The sulfides **7** and **8** have been *N*-quaternized with CH_3I or Et_3O^+ PF_6^- to yield **9a** or **10a**, respectively (Eq. (7)). Deprotection of **9a** or **10a** was achieved under mild conditions with Raney nickel, the imidazolium phosphines (**9**, **10**) being formed (Eq. (8)).

[1] X-ray analysis of **1a**: $C_{17}H_{17}N_2OP$, $M_w = 296.3$, Siemens P4 diffractometer, (MoKα radiation, $\lambda = 0.71073$ Å), triclinic, space group $P\bar{1}$, $Z = 2$, $a = 5.8272(12)$ Å, $b = 11.4309(23)$ Å, $c = 12.3024(25)$ Å, $\alpha = 84.56(3)°$, $\beta = 84.40(3)°$, $\gamma = 79.46(3)°$, $D_{calc} = 1.231$ g/cm^3. The structure was solved by direct methods using SHELX-86 and refined against F^2 using SHELXL-93 to $R_1 = 0.0457$ and $wR_2 = 0.1404$ for 2799 independent reflections. Additional crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155692. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK.



This method of desulfurization of phosphine sulfides was employed by Gilbertson et al. [13] in the synthesis of phosphino substituted polypeptides. The $^{31}P\{^1H\}$-NMR resonances of **9** ($\delta P = -20.4$) or **10** ($\delta P = -35.4$) are shifted ca. 60 to high field compared with **9a** ($\delta P = 39.7$) or **10a** ($\delta P = 30.9$), respectively. The *N*-quaternization of **1** and **2** is indicated by additional resonances in the ^{1}H-NMR (**9**: 3.87, **10**: 4.07, 1.40) and in the $^{13}C\{^1H\}$-NMR spectra (**9**: 36.6, **10**: 46.0, 15.3) which may be assigned to the N–Me or N–Et groups. *N*-quaternization of the neutral phosphine causes a significant high field shift of the resonance of the aza-nitrogen in the ^{15}N-NMR spectrum (**1**: $\delta N = -120.6, -210.6$; **9**: $-202.5, -214.2$). This was also observed for imidazole derivatives [12].

2.3. Hydroformylation of 1-octene in ionic liquids

The use of ionic liquids for the biphasic Rh-catalyzed hydroformylation of longer chain olefins has been suggested by Chauvin et al. [14]. Later it was clearly demonstrated that cationic ligands especially designed for being applied in ionic liquids show very promising results [15,16]. A first indication for the usefulness of the ligands of type **2a**, **2b**, **9** and **10** could be obtained by testing the easily accessible ligand **10** in the biphasic hydroformylation of 1-octene using 1-*n*-butyl-3-methylimidazolium hexafluorophosphate as the catalyst solvent. The active catalyst was prepared in-situ by mixing $Rh(CO)_2$acac with two equivalents of the ligand. The reaction was carried out at 100°C and 30 bar synthesis gas pressure ($CO/H_2 = 1/1$) for 1 h. The biphasic hydroformylation under these conditions showed a turnover frequency of 32 mol 1-octene per mol Rh and hour and a *n*:*i* ratio of 2.8. It should be noted that with ligand **10** no significant leaching (almost colourless organic layer) of the Rh-catalyst into the organic layer was observed.

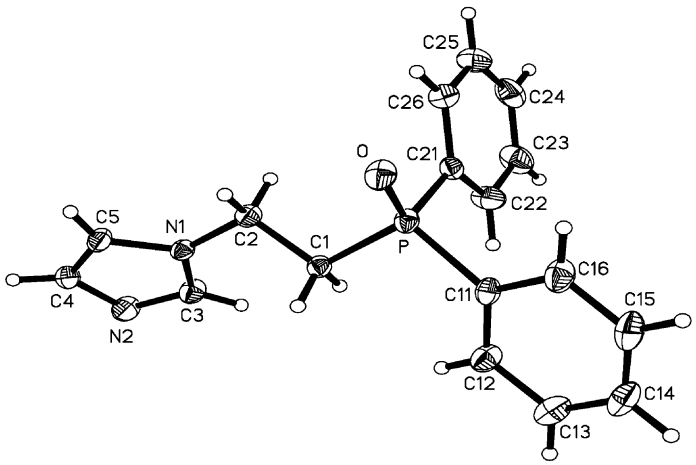


Fig. 1. X-ray structure of the oxide **1a**: P–C(1) 1.803(3); P–C(11) 1.807(3); P–C(21) 1.810(3); C(1)–P–C(11) 105.80(13); C(11)–P–C(21) 105.39(13); C(21)–P–C(1) 104.85(12).

3. Conclusion

Commercially available 1-vinylimidazole is a versatile starting material for the synthesis of tertiary phosphine ligands containing imidazolium moieties. These novel cationic phosphine ligands may be employed as catalyst components in biphasic ionic liquids systems.

Acknowledgements

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