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Synthesis of New Cationic Donor-Stabilized Phosphenium Adducts and Their Unexpected P-Substituent Exchange Reactions

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The reaction between two 1,3-dialkylimidazolium-2-carboxylates **1a** and **1b** and two different dichlorophosphines ($RPCl_2$, with R = Ph and NEt_2) led to new donor-stabilized phosphenium adducts. When the reaction was performed with the 1,3-dimethylimidazolium-2-carboxylate **1a** and $PhPCl_2$ in a 2:1 ratio, the phosphine **4a**, bearing two imidazolium moieties, was obtained and led to **5a**, after an anion exchange reaction with KPF_6, the latter being fully characterized by an X-ray structure analysis. In similar conditions, the bis-imidazolium phosphine or phosphene-di-ium, **4b**, which is analogous to **4a**, has been obtained by the addition of $PhPCl_2$ to the 1-dodecyl-3-methylimidazolium-2-carboxylate **1b**. However, by the use of dichloro(diethylamino)phosphine, $(Et_2N)PCl_2$, instead of $PhPCl_2$, the reaction with **1a** did not afford the biscationic phosphorus product **6a**, an analogue to **4a**, but, instead, the water-soluble mixed mono-imidazolium chlorophosphine **7a**. Subsequently, additional kinetic experiments have been investigated to rationalize the different reactivities observed with imidazolium-2-carboxylates and the phosphorus halide derivatives. We, thus, found that the bis-imidazolium phosphine **4b** was very rapidly formed in the above-mentioned reaction and was slowly converted, thereafter, back to the mixed mono-imidazolium chlorophosphine **8b** in the presence of the residual starting dichlorophosphine. Additionally, the addition of $PhPCl_2$ to the phosphene-di-ium **4b** represents, to our knowledge, the first example of a P-substituent exchange reaction involving a P−C bond formation in imidazolium phosphines. On the other hand, the air stability and the solubility of these new cationic functional phosphines in different media render such ligands very appealing in coordination chemistry for catalysis in mono- or biphasic media.

Introduction

In contrast to neutral phosphine ligands, imidazolium-functionalized phosphines represent an interesting opportunity to strongly decrease the metal leaching in homogeneous polyphasic catalysis, especially when using an ionic liquid phase.[1−4] Among these cationic ligands, the imidazolium-2-phosphines led to the very active rhodium catalysts in styrene hydroformylation[1] and palladium-catalyzed Heck reaction,[5] and they represent rare examples of base-donor/P-acceptor adducts involving an electron-rich P^{III} center as Lewis acceptor.[6] However, the access to a large library of imidazolium-2-phosphines is limited to a few examples because of their multistep preparation.[1,7−9] We have, thus, focused our investigations on such ligands and recently found a simple and straightforward synthesis of imidazolium-2-phosphines **2** and **3** by the addition of several monochlorophosphines to the 1,3-dimethylimidazolium-2-carboxylate **1a**[10] (see Scheme 1).

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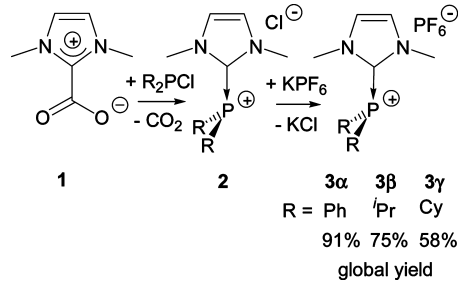
Scheme 1



Besides, the measurement of the A_1 symmetric stretching frequency of the related $Ni(CO)_3$(**3α**−***γ***) complexes has shown that ligands **2** and **3** behave as phosphite-like, strong π acceptors. This unexpected result seems to be the consequence of the C→P bond in imidazolium-2-phosphines that displaces the formal positive charge from the imidazolium ring to the phosphorus center. Since the combination of this electronic property with an ionic nature renders such ligands very promising in the development of new continuous-flow catalytic processes, we describe in this paper the reactivity of 1,3-dimethylimidazolium-2-carboxylate **1a** and 1-dodecyl-3-methylimidazolium-2-carboxylate **1b** toward other chlorophosphines to be able to the access new cationic donor-stabilized phosphenium adducts for coordination chemistry and catalysis.

Experimental Section

General Procedures. All reactions were performed in Schlenk-type flasks under an argon atmosphere. Solvents were purified and dried by conventional methods and distilled under argon. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded at 298 K on a Bruker Avance 300 MHz spectrometer for all compounds, with the exception of **4b**, for which NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer. All chemical shifts are relative to $SiMe_4$ (^{1}H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR) and are given in parts per million. Electrospray spectra were performed on a Bruker micrOTOF-Q instrument. The elemental analyses were performed on a Fisons EA 1108 apparatus. The chlorophosphines Ph_2PCl and $PhPCl_2$ were obtained from Aldrich and were used as received. The 1,3-dimethylimidazolium-2-carboxylate **1a** and 1-dodecyl-3-methylimidazolium-2-carboxylate **1b** were prepared according to the literature.[11,12] The dichloro(diethylamino)phosphine was prepared by the addition of diethylamine to phosphorus trichloride in diethylether solution, according to the procedure described in the literature.[13]

Syntheses of Cationic Imidazolium Phosphines. Ligand 4a. To a solution of 1,3-dimethylimidazolium-2-carboxylate (0.482 g, 3.439 mmol) in CH_2Cl_2 (5 mL) was rapidly added $PhPCl_2$ (0.307 g, 1.715 mmol). After 30 min of stirring, a white suspension appeared. The mixture was stirred for 18 h at room temperature. The precipitate was then filtrated, washed twice with 10 mL of CH_2Cl_2, and dried under vacuum; 0.571 g of **4a** was obtained, which was contaminated by 10% of the unreacted 1,3-dimethylimidazolium-2-carboxylate **1a**. ^{1}H NMR (D_2O): δ 7.72 (s, 4H, −CH=), 7.60−7.53 (m, 5H, aromatics), 3.61 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR (D_2O): δ 134.58 (d, $J_{P,C}$ = 24.2 Hz, 2C, NCN), 133.69−130.81 (m, 6C, aromatics), 128.37 (s, 4C, −CH=), 37.25 (d, $^3J_{P,C}$ = 7.5 Hz, 4C, NCH_3). ^{31}P{^{1}H} NMR (D_2O): δ −50.39 (s). ESI-MS (H_2O/MeOH) found for $C_{16}H_{21}N_4PCl_2$ (370.0881): m/z = 150.0826 [M − $2Cl^-]^{2+}$. Simulated: m/z = 150.0751. The compound was used without further purification.

Ligand 4b. To a solution of 1-dodecyl-3-methylimidazolium-2-carboxylate **1b** (0.074 g, 0.25 mmol) in CH_2Cl_2 (5 mL) was rapidly added $PhPCl_2$ (0.022 g, 0.123 mmol). The yellow solution was stirred for 10 min at room temperature. The solvent was removed under vacuum to afford 0.084 g of a yellow solid that was contaminated by a significant amount of compound related to the hydrolysis of **1b**. ^{1}H NMR ($CDCl_3$): δ 8.58 (s, 2H, CH^a=), 8.18 (s, 2H, CH^b=), 7.87−7.42 (m, 5H, aromatics), 4.22 (m, 4H, NCH_2), 3.75 (s, 6H, NCH_3), 1.59 (m, 4H, CH_2CH_2), 1.30−0.90 (br m, 36H, $(CH_2)_9$), 0.79 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.59 (d, $J_{P,C}$ = 41.4 Hz, 2C, NCN), 137.39−129.73 (m, 6C, aromatics), 126.28 (s, 2C, CH^a=), 124.72 (s, 2C, CH^b=), 50.90 (d, $^3J_{P,C}$ = 12.2 Hz, 2C, NCH_2), 38.15 (d, $^3J_{P,C}$ = 3.5 Hz, 2C, NCH_3), 31.81, 30.40, 29.50, 29.42, 29.39, 29.30, 29.24, 28.90, 26.28, 22.59 (s, 20C, CH_2), 14.02 (s, 2C, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −54.71 (s). The compound was used without further purification.

Ligand 5a. A mixture of bis-imidazolium-2-phosphine chloride **4a** (0.26 g, 0,63 mmol) and potassium hexafluorophosphate (0.296 g, 1.608 mmol) was introduced in 5 mL of absolute and degassed EtOH, and the resulting suspension was stirred for 24 h at room temperature. The solvent was then removed under vacuum to afford a white powder. The white solid was washed twice with 5 mL of degassed water. It was then dissolved in 10 mL of acetone, and the resulting solution was filtered over Celite. The solvent was removed under reduced pressure, leading to a white solid that was then dried under vacuum (0.30 g, 81%); mp 122 °C. Crystals suitable for X-ray structural analysis were obtained from an acetone/pentane mixture. ^{1}H NMR (acetone-d_6): δ 8.14 (s, 4H, −CH=), 7.78−7.70 (m, 5H, aromatics), 3.70 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR (acetone-d_6): δ 137.11 (d, $J_{P,C}$ = 39.2 Hz, 2C, NCN), 135.64−131.73 (m, 6C, aromatics), 129.76 (s, 4C, −CH=), 38.47 (d, $^3J_{P,C}$ = 8.3 Hz, 4C, NCH_3). ^{31}P{^{1}H} NMR (acetone-d_6): δ −50.85 (s), −144.40 (hept, $J_{P,F}$ = 712 Hz, PF_6^-). Anal. Calcd for $C_{16}H_{21}N_4P_3F_{12}$ (590.08): C, 32.53; H, 3.59; N, 9.49. Found: C, 31.99; H, 3.54; N, 9.37.

Ligand 7a. To a solution of 1,3-dimethylimidazolium-2-carboxylate **1a** (0.580 g, 4.14 mmol) in CH_2Cl_2 (5 mL) was rapidly added Et_2NPCl_2 (0.720 g, 4.14 mmol). After 15 min of stirring, a white precipitate appeared. The mixture was stirred for 18 h at room temperature. The precipitate was filtrated. The white solid was then washed twice with 10 mL of CH_2Cl_2 and dried under vacuum for 4 h (0.951 g, 85%); mp 192 °C. ^{1}H NMR (D_2O): δ 7.60 (s, 2H, −CH=), 3.66 (s, 6H, NCH_3), 3.17 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, NCH_2), 0.87 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CCH_3). ^{13}C{^{1}H} NMR (D_2O): δ 140.40 (d, $J_{P,C}$ = 50.6 Hz, 1C, NCN), 127.54 (s, 2C, CH=), 48.72 (d, $^2J_{P,C}$ = 17.4 Hz, 2C, NCH_2), 36.55 (d, $^3J_{P,C}$ = 8.3 Hz, 2C, NCH_3), 13.18 (d, $^3J_{P,C}$ = 5.3 Hz, 2C, $C\underline{C}H_3$). ^{31}P{^{1}H} NMR (D_2O): δ 9.71 (s). ESI-MS (H_2O/MeOH) found: m/z = 230.1561 [M − $2Cl^-$ + $CH_3O^-]^+$. Simulated: m/z = 230.1422. Anal. Calcd for $C_9H_{18}N_3PCl_2$ (269.06): C, 40.14; H, 6.74; N, 15.61. Found: C, 40.10; H, 6.69; N, 16.44.

Ligand 8a. To a solution of 1,3-dimethylimidazolium-2-carboxylate **1a** (0.180 g, 1.28 mmol) in CH_2Cl_2 (5 mL) was rapidly added $PhPCl_2$ (0.230 g, 1.28 mmol). After 30 min of stirring, a white suspension appeared. This suspension was stirred for 18 h at room temperature. After elimination of the precipitate through

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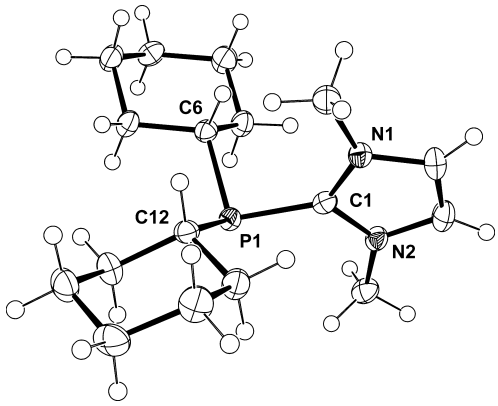

Figure 1. Molecular structure of **3γ** with thermal ellipsoids presented at a 50% probability level. Only one of both independent molecules is represented. The PF_6^- anions are omitted for clarity.

Table 1. Selected Bond Lengths [Å] and Bond Angles [°] for Compounds **3γ** and **5a**

bonds for **3γ**[a]		bonds for **5a**	
P(1)−C(1)	1.837(2), 1.838(2)	P(1)−C(1)	1.841(2)
P(1)−C(6)	1.860(2), 1.863(2)	P(1)−C(6)	1.828(2)
P(1)−C(12)	1.859(2), 1.861(2)	P(1)−C(11)	1.816(2)
C(1)−N(1)	1.353(2), 1.351(3)	C(1)−N(1)	1.343(3)
C(1)−N(2)	1.358(2), 1.358(3)	C(1)−N(2)	1.346(3)
		C(6)−N(3)	1.352(3)
		C(6)−N(4)	1.349(3)
angles for 3γ[a]		**angles for 5a**	
C(1)−P(1)−C(6)	99.05(9), 98.24(9)	C(1)−P(1)−C(6)	99.5(1)
C(1)−P(1)−C(12)	102.33(9), 103.87(9)	C(6)−P(1)−C(11)	101.5(1)
C(6)−P(1)−C(12)	107.54(9), 106.85(9)	C(11)−P(1)−C(1)	105.6 (1)

[a] Distances and angles for the two independent molecules. Labeling refers to the molecule represented in Figure 1.

filtration, the solvent was evaporated under vacuum to afford 0.206 g of a colorless, waxy oil contaminated by a byproduct that could not be identified. ^{1}H NMR ($CDCl_3$): δ 8.26 (s, 2H, −CH=), 7.70−7.40 (m, 5H, aromatics), 3.92 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.28 (d, $J_{P,C}$ = 47.55 Hz, 1C, NCN), 133.54−127.72 (m, 6C, aromatics), 127.53 (s, 2C, CH=), 37.78 (d, $^3J_{P,C}$ = 9.1 Hz, 2C, NCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.29 (s).

Ligand 8b. To a solution of 1-dodecyl-3-methylimidazolium-2-carboxylate **1b** (0.201 g, 0.68 mmol) in CH_2Cl_2 (5 mL) was rapidly added $PhPCl_2$ (0.120 g, 0.67 mmol). The mixture was stirred for 18 h at room temperature. The solvent was then evaporated to afford a colorless, waxy oil (0.23 g). The compound was contaminated by **4b**. ^{1}H NMR ($CDCl_3$): δ 8.72 (s, 1H, CH^a=), 8.42 (s, 1H, CH^b=), 7.63−7.30 (m, 5H, aromatics), 4.51 (t, $^3J_{H,H}$ = 7.1 Hz, 2H, NCH_2), 3.81 (s, 3H, NCH_3), 1.79 (m, 2H, NCH_2CH_2), 1.30−0.90 (br m, 18H, CH_2), 0.80 (t, $^3J_{H,H}$ = 6.8 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.94 (d, $J_{P,C}$ = 85.3 Hz, 1C, NCN), 134.19−125.26 (m, 6C, aromatics), 125.26 (s, 1C, CH^a=), 123.11 (s, 1C, CH^b=), 49.94 (d, $^3J_{P,C}$ = 12.8 Hz, 1C, NCH_2), 36.83 (d, $^3J_{P,C}$ = 5.3 Hz, 1C, NCH_3), 35.60, 30.87, 30.66, 29.47, 28.56, 28.45, 28.3, 27.97, 25.31, 21.66 (s, 10C, CH_2), 13.14 (s, 1C, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.81 (s). Satisfactory elemental analysis could not be obtained due to its high instability in the solid state.

Crystal Structure Determination for Compounds 3γ and 5a. Crystal data and refinement details are reported in Table 2. Data sets were collected on an Enraf-Nonius KappaCCD diffractometer at 115 K using Mo Kα radiation. The structures were solved by direct methods and refined with full-matrix least-squares methods[14] based on $|F^2|$, with the aid of the WINGX program.[15] For **3γ**, both PF_6^- anions are disordered over two positions (rotation about one F−P−F axis) and the occupation factors converged to 0.76/0.24 and 0.90/0.10. Except for the minor components of the disordered PF_6^- anions in **3γ**, which were isotropically refined, all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were either calculated or located on final Fourier difference maps and refined, after idealization, with a riding model. CCDC-702718 for **3γ** and CCDC-702719 for **5a** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk. Fax: +44−1223/336−033.

Table 2. Crystal Data and Structure Refinement Details

parameters	**3γ**	**5a**
chemical formula	$C_{17}H_{30}F_6N_2P_2$	$C_{16}H_{21}F_{12}N_4P_3$
M (g mol^{-1})	438.37	590.28
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	11.9511(2)	15.9951(4)
b (Å)	12.7627(2)	12.8993(3)
c (Å)	15.3238(3)	11.5831(3)
α (deg)	66.675(1)	90
β (deg)	81.664(1)	97.285(1)
γ (deg)	74.552(1)	90
V (Å^3)	2066.69(6)	2370.6(1)
Z	4	4
D_{calcd} (g/cm^3)	1.409	1.654
F(000)	920	1192
μ (mm^{-1})	0.268	0.358
reflections collected	18163	19278
independent reflections	9506	5448
observed reflections [$I > 2\sigma(I)$]	6538	3721
R(int)	0.038	0.066
R1, wR2 [$I > 2\sigma(I)$][a,b]	0.048, 0.104	0.044, 0.084
R1, wR2 (all data)[a,b]	0.082, 0.118	0.084, 0.096
goodness of fit	1.046	1.024
largest diff peak and hole e·Å^{-3}	0.56, −0.53	0.29, −0.38

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.76P]$ for **3γ** and $w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 1.92P]$ for **5a** and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Results and Discussion

In addition to our previous synthesis of heterocarbene donor-stabilized phosphenium adducts **2** and **3** and their characterization in $CDCl_3$ solution,[10] we report now the X-ray molecular structure for compound **3γ** obtained from a CH_2Cl_2/pentane mixture (Figure 1).

The ORTEP view shows one of the two identical, independent molecules found in the unit cell. Both adopt, however, exactly the same conformation with a root-mean-square error of 8.5 × 10^{-2} Å. The molecular structure arrangement is close to the one found for its analogue **3β** (see Table 1).[10] The imidazolium heterocycle is found in the bisector plane of the C(6)−P(1)−C(12) angle, due to the strong steric hindrance of the cyclohexyl groups. It is worth noting that both cyclohexyl groups adopt the more stable chair conformation, with the phosphenium fragment

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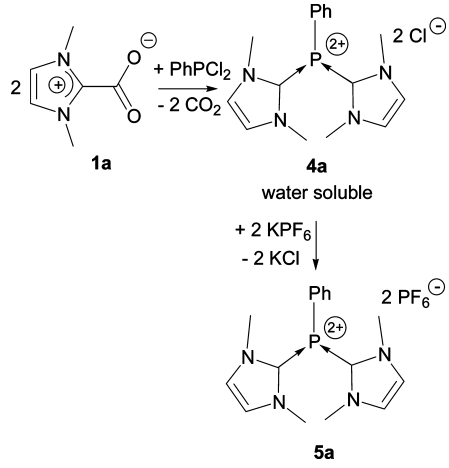
Scheme 2



linked to the cyclohexyl moiety in an equatorial position. Since the isopropyl and cyclohexyl substituents are very similar in terms of electronic and steric effects, no significant changes in P−C bonds and C−P−C angles are observed between the molecular structures of **3*β*** and **3*γ***. However, it is obvious that the latter structure gives an excellent view of the large volume that will be occupied by ligand **3*γ*** (versus **3*β***) in the metal coordination sphere.

We then extended our investigations on the reactivity of imidazolium-2-carboxylates from monochlorophenylphosphines to two different dichlorophosphines to evaluate the potential of such "masked heterocarbenes" in the preparation of new donor-stabilized phosphenium adducts, which would lead to a stronger π-acceptor character than for adducts **3α**,***γ***.[10]

A. Reactivity of Imidazolium-2-carboxylates toward $PhPCl_2$ and Et_2NPCl_2. We first explored the reactivity of imidazolium-2-carboxylate **1a** toward the very simple dichlorophenylphosphine $PhPCl_2$ (see Scheme 2) in CH_2Cl_2 solution. After half an hour, we observed the formation of large amounts of an insoluble product **4a** that was analyzed by NMR spectroscopy in deuterated water. The unique signal at −50.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum revealed a highly selective reaction and the formation of only one phosphorus compound. Although this ^{31}P chemical shift is very different from the ones reported for the bis-imidazolium-2-ethylphosphines,[16] the triphosphane-di-ium ions, [17] or the bis-*meta*-guanidinium-phenylphosphine bromides,[18] at − 30, −28, and −5 ppm, respectively, the presence of two imidazolium moieties linked to the P atom was unambiguously proven by an electrospray mass spectrometry analysis (see the Experimental Section for details and Scheme 2). The adduct **4a** is named phosphene-di-ium instead of phosphenium in order to precisely describe its dicationic structure by analogy with the comparable triphosphane-di-ium ligands $[RP(PR_3)_2]^{2+}$.[17] Moreover, no decomposition was

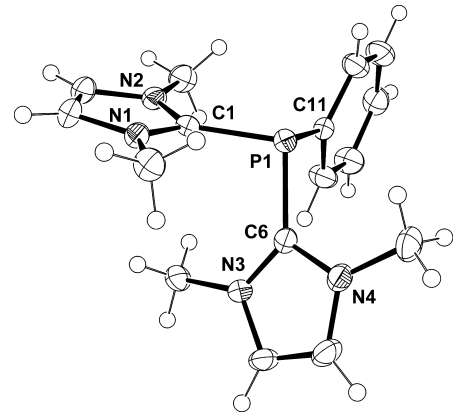


Figure 2. Molecular structure of **5a** with thermal ellipsoids presented at a 50% probability level. The PF_6^- anion is omitted for clarity.

observed with **4a** in water, which indicates its high stability in aqueous media.

We also observed in ^1H NMR the presence of about 10% of remaining **1a** and $PhPCl_2$, together with ligand **4a**, even after 18 h of reaction, which indicates an almost quantitative conversion of dichlorophenyl phosphine to **4a**. Since compounds **1a** and **4a** exhibit similar solubility properties, especially in aqueous media, we failed to find an efficient purification method to isolate the pure ligand **4a**. However, the carboxylate impurity was easily removed during the subsequent halide exchange reaction with KPF_6, described below.

It is interesting to note that the solubility of **4a** in water was also described in the literature for other dicationic phosphines like the bis-imidazolium-2-ethyl-[16] or the bis-*meta*-guanidinium-phenylphosphine bromides.[18] This peculiar physical property is likely due to the presence of the two cationic fragments linked to the same P atom and, consequently, to the two associated, strong hydrogen-bond acceptor halide counteranions. This assumption is supported by the following observations: First, the cationic phosphine **4a**, containing two halides as counteranions, is water soluble, whereas its monohalide analogues, **2α**−**2*γ***, are water insoluble. Second, when the nature of the counteranion is changed from the halide to the hexafluorophosphate anion, the resulting compound **5a** becomes totally insoluble in water, although well soluble in polar organic solvents like acetone or dimethylsulfoxide. This latter reaction, thus, allowed us to eliminate the unreacted imidazolium carboxylate **1a** from **5a** by simply washing the crude with water (see Scheme 2). Nevertheless, the nature of the P- and N-substituents also plays a major role in the control of the solubility properties of imidazolium ligands.

As mentioned above, among the few examples of biscationic phosphines reported in the literature, none contain a direct bond between the phosphorus atom and the N−C−N internal carbon atom. To get details on its molecular structure, suitable crystals for X-ray structure determination were obtained for **5a** from an acetone/pentane mixture (see Figure 2).

The P−C(imidazolium) bond distances of 1.828 and 1.842 Å in **5a** are comparable with the ones found in the monocationic imidazolium-2-diphenylphosphines **3*β*** (1.840

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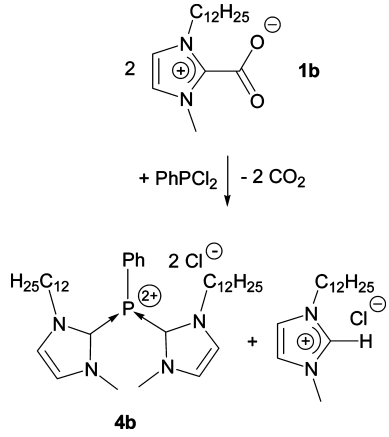
Scheme 3



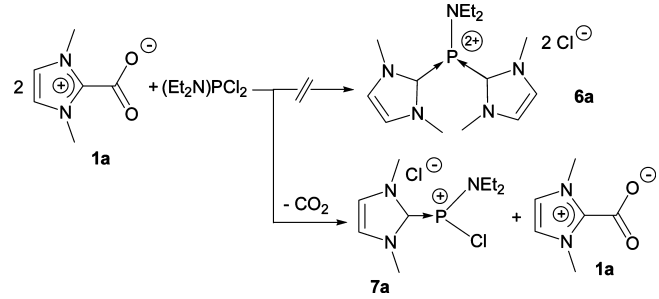
Å) and **3γ** (1.837 Å) (see Table 1). The pyramidal geometry of the P atom, together with the nonperpendicularity of the imidazolium rings with the P-doublet, clearly shows that this lone pair is selectively localized on the heteroatom, despite the presence of a second cationic fragment. A second interesting point to emphasize concerns the P−C(Ph) bond distance of 1.817 Å that is identical to those reported in the literature for the monocationic imidazolium-2-diphenylphosphine analogues of **3α** (ca. 1.810 Å).[9] The latter observation seems to indicate that the presence of a second cationic fragment does not affect the electronic density around the phosphorus atom center. However, this assumption will be confirmed by additional experiments based on the measurements of the ν_{CO} stretching frequencies of related metal−carbonyl complexes, which are currently in progress in our laboratory.

Since the coordination properties of donor ligands toward transition metals are generally examined in organic solvents rather than in water for solubility and/or stability reasons, we introduced a hydrophobic, long aliphatic chain on the carboxylate starting material. Subsequently, the reaction between $PhPCl_2$ and the 1-dodecyl-3-methylimidazolium-2-carboxylate **1b** was carried out in conditions analogous with those used for **1a** (see the Experimental Section and Scheme 3). After 10 min, the ^{31}P NMR spectrum of the related crude product showed a complete conversion and the presence of only one peak at −54.7 ppm. This signal was assigned to the new phosphene-di-ium **4b**, by analogy with the peak at −50.4 ppm found for **4a**.

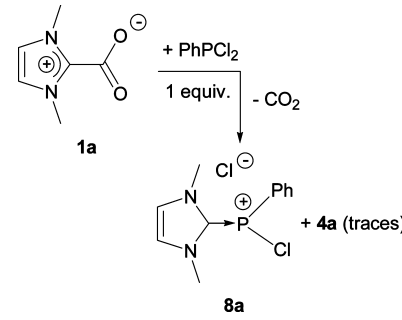
The proton NMR spectrum unfortunately revealed a significant amount (ca. 20%) of an inseparable byproduct resulting from the partial protonolysis of the acid-sensitive 1-dodecyl-3-methylimidazolium-2-carboxylate **1b**, which led to the corresponding ionic liquid.

To evaluate the potential of imidazolium-2-carboxylates in the synthesis of other donor-stabilized phosphenium ligands, we have investigated the reactivity of the above-mentioned starting material toward the dichloro(diethylamino)phosphine. We have, therefore, performed the reaction between Et_2NPCl_2 and the imidazolium-2-carboxylate **1a** in CH_2Cl_2 in the conditions described for **4a**. The reaction led, also in this case, to an insoluble product after 15 min. Surprisingly, the phosphorus NMR signal at 9.7 ppm

Scheme 4



Scheme 5



recorded in D_2O totally differed from the −50.4 ppm found for ligand **4a**. Furthermore, in its proton NMR spectrum, integration of the obtained signals showed an unexpected 1:1 ratio between the diethylamino and imidazolium fragments, thus, indicating the possible obtainment of the mono-imidazolium chlorophosphine intermediate **7a**, without any byproduct, instead of the double heterocarbene addition to the P atom center, leading to ligand **6a** (see Scheme 4). It should be pointed out that, to prevent any misinterpretation of the NMR spectra, the outstanding stability of the P−Cl bond toward water was confirmed by the similar chemical shifts obtained in the phosphorus and proton NMR spectra of **7a** in neat DMSO and in D_2O.

The nature of **7a** was confirmed by an electrospray measurement that showed the presence of a molecular peak corresponding to the monocationic phosphine (see the Experimental Section for details). A possible explanation for this selectivity in the formation of compound **7a** is its lower solubility in chlorinated solvents, which, upon precipitation, prevents any further reactivity with the remaining excess of imidazolium-2-carboxylate **1a**.

B. P-Substituent Exchange Reactions with Imidazolium Phosphines. Compound **7a** obtained above, however, demonstrated that mono-imidazolium chlorophosphines could be obtained using our synthetic pathway. We, thus, first explored the reactivity of the 1,3-dimethylimidazolium-2-carboxylate **1a** toward an equimolar amount of dichlorophenylphosphine. In contrast to the experiment performed with a double amount of **1a**, we observed, after 18 h, only traces of an insoluble product that was identified as ligand **4a** by phosphorus and proton NMR analysis in D_2O (see Scheme 5).

The removal of the traces of **4a** from the solution and subsequent evaporation of the solvent (see the Experimental Section) afforded a white residue that generated a new signal

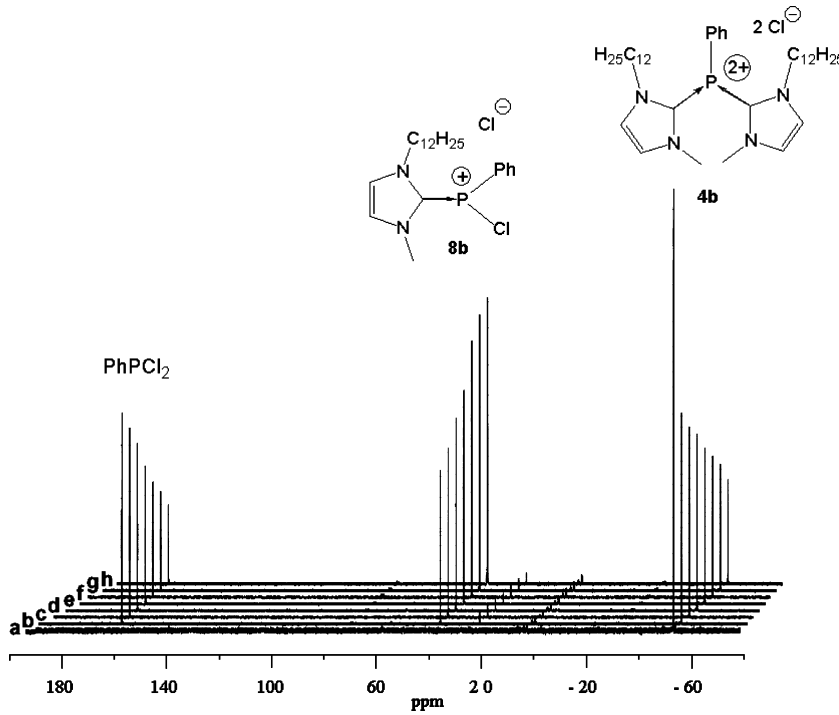


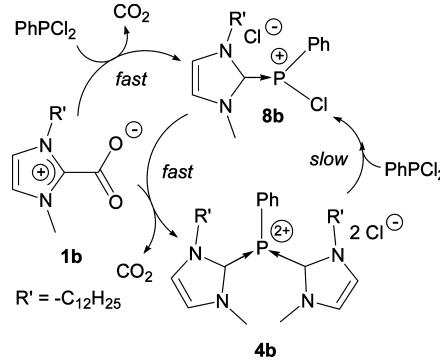
Figure 3. $^{31}P\{^{1}H\}$ NMR monitoring of the reaction between **4b** and $PhPCl_2$. Pure **4b** obtained by the reaction between **1b** and $PhPCl_2$, after a few minutes in a 2:1 ratio (a), followed by the addition of a second equivalent of $PhPCl_2$, after 8 min (b), after 22 min (c), after 56 min (d), after 101 min (e), after 239 min (f), after 274 min (g), and after 413 min (h).

at 37.7 ppm in the phosphorus NMR spectrum recorded in $CDCl_3$. In addition, a 1:1 ratio between the phenyl and imidazolium moieties was found by integration in the corresponding proton NMR spectrum. Both observations were, thus, consistent with the mono-imidazolium phenylphosphine **8a**. Unfortunately, compound **8a** could not be fully characterized due to its high thermal instability in the solid state, even at room temperature.

Nevertheless, according to these observations, one could propose that the mono-imidazolium chlorophosphines **8a** or **8b** can be selectively obtained, as we expected, in such stoichiometry. To confirm this assumption, we performed an additional study by phosphorus NMR monitoring of the dichlorophenylphosphine addition to the 1,3-dimethylimidazolium-2-carboxylate **1a**. However, solubility properties, which strongly differ between mono- and bis(cationic) ligands, prevented us from obtaining any accurate measurement. Subsequently, we overcame this problem by using the more hydrophobic and more soluble 1-dodecyl-3-methylimidazolium-2-carboxylate **1b**. Thus, a phosphorus NMR monitoring was performed with a mixture of **1b** and $PhPCl_2$ in a 2:1 ratio in $CDCl_3$. After less than 5 min, the spectrum indicated a complete conversion to the bis-imidazolium phosphine ligand **4b**, with the unique presence of its related phosphorus chemical shift at −54 ppm. Indeed, the signal at 37.7 ppm corresponding to the mono-imidazolium chlorophosphine intermediate **8b** could not be detected (see Figure 3, spectrum a).

This observation clearly indicates that compound **8b** is a very reactive intermediate in the formation of **4b** (see Scheme 6). An equimolar amount of $PhPCl_2$ was then added to ligand **4b** (prepared in situ) (see Figure 3, spectra b−h). After a

Scheme 6



few minutes, the peak at −54 ppm corresponding to **4b** had decreased, and a new signal appeared simultaneously at 38 ppm that was unambiguously assigned to the intermediate **8b**. A conversion of 94% was observed after 18 h, and the complete reaction was achieved after 8 days, leading to pure **8b**, as anticipated, with a 1:1 ratio between $PhPCl_2$ and **1b**. To the best of our knowledge, this reactivity of **4b** toward $PhPCl_2$ is the first example of P-substituent exchange involving a P−C bond cleavage in imidazolium phosphines.

It is also interesting to note the high reactivity of **8b** versus its stable analogue **7a**, which was obtained from **1a** and $(Et_2N)PCl_2$ (see Scheme 4). Indeed, the latter reaction should have led to **6a** in quantitative yield and not to **7a**. Subsequently, this confirms that the reaction stopped at **7a** because its lower solubility in the reaction medium prevented it from reacting with an additional imidazolium carboxylate **1a**.

The reactivity of phosphene-di-ium **4b** toward $PhPCl_2$ is comparable to other halogen and diethylamino- or ethoxy-group exchange reactions, previously reported with amino-

phosphines or phosphites in the presence of chlorophosphines. These reactions can lead to partial or complete internal phosphine reorganization, depending on the nature of the P-substituents. For example, the addition of CH_3PCl_2 to $CH_3P(NMe_2)_2$ in a 1:1 ratio led selectively to the pure $CH_3PCl(NMe_2)$,[19] similar to our reaction with **4b**, whereas an equilibrium mixture of $P(OPh)_3/PCl(OPh)_2/PCl_2(OPh)/PCl_3$ in a 1:7:7:1 ratio was obtained by the use of equal amounts of PCl_3 and $P(OPh)_3$.[20] These two observations could be explained by a higher reversibility of the P−O bond formation versus the P−N one, which renders the phosphites more unstable than the aminophosphines. Subsequently, we have performed an additional experiment to estimate the reversibility level of the P−C bond formation in ligands **4b** and **8b**. Thus, the mono-imidazolium chlorophosphine **8b**, obtained from **4b** and a slight excess of $PhPCl_2$, was washed three times with few milliliters of diethyl ether to eliminate the remaining $PhPCl_2$. A sample was then placed into an NMR tube and monitored using phosphorus NMR. However, no **4b** or $PhPCl_2$, which could be re-formed by the reverse reaction from **8b** to **4b**, was observed. This observation is, thus, consistent with the formation of a stable P−C bond in mono-imidazolium chlorophosphine **8b**.

In extension of this work, we have added phosphorus trichloride or triiodide to the imidazolium-2-carboxylate **1a** to get the related tris-imidazolium phosphine. Unfortunately, the phosphorus NMR spectra of the crude products showed a mixture of several compounds that have not yet been identified.

Conclusion

In this paper, we have reported that the reaction of 1,3-dimethylimidazolium-2-carboxylate with $PhPCl_2$ in a 2:1 ratio leads to the air-stable biscationic phosphine bearing two imidazolium moieties. These phosphorus compounds, together with the mixed mono-imidazolium chlorophosphines, represent a new type of water-soluble ligand. Moreover, their hydrophilicity can easily be tuned in favor of organic solvents by the introduction of a long alkyl chain onto the imidazolium-2-carboxylate starting material or simply by an anion exchange reaction. Nevertheless, a fine change in the nature of the P-substituent in dichlorophosphines allows one to change the selectivity of the reaction to the formation of a mixed mono-imidazolium chlorophosphine. The study of kinetic experiments has shown, first, that the bis-imidazolium phosphines are the kinetic products that are slowly converted, afterward, to the mixed mono-imidazolium chlorophosphines and, second, the first example of P−C cleavage in imidazolium phosphines by the addition of $PhPCl_2$ to the dicationic derivative. We have also described that the air stability and solubility of new ligands in different media strongly depend of the nature of the P- and N-substituents, which renders such phosphenium and phosphene-di-ium ligands very appealing for further applications in coordination chemistry and in catalysis in aqueous or in biphasic media.

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