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# A 4,5-Diphosphino-Substituted Imidazolium Salt: A Building Block for the Modular Synthesis of Mixed Diphosphine–NHC Heterometallic Complexes

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Phosphine ligands functionalized with imidazolium salts have recently received a widespread interest owing to the multiple applications that the corresponding transition-metal complexes have found in organometallic chemistry and catalysis. Most known examples contain the phosphino substituent linked to the nitrogen atoms of the imidazolium cycle through a carbon spacer (Figure 1, **I**), and these imidazolium salts have been widely used in the synthesis of complexes with chelating or pincer N-heterocyclic carbene (NHC)–phosphine ligands,[1] and as ionophilic phosphines for ionic-liquid, biphasic catalysis.[2] A few examples of imidazolium salts substituted at the 2-position with a phosphinomethyl group have also been prepared (**II**) and used in the design of valuable recyclable catalysts.[3] Imidazolium salts containing a phosphino group directly bonded to a nitrogen atom (**III**)[4] or to the C2 atom (**IV**)[5] are also known, the latter is a good example of a strong π-acceptor phosphorus ligand[6] and hence better considered as an NHC–phosphenium adduct.[6b,c]

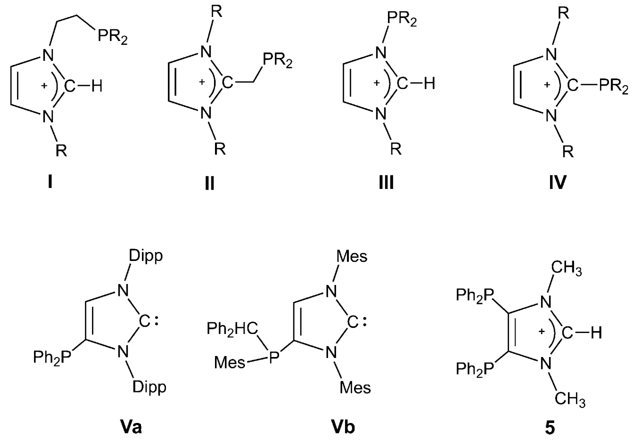

Figure 1. Examples of phosphino-functionalized imidazolium cations (**I**–**IV**), 4-phosphino-substituted NHCs (**Va**, **Vb**), and the 4,5-diphosphino-substituted imidazolium cation **5**.

To the best of our knowledge, imidazolium-4-phosphines that are unsubstituted at the 2-position are unknown. A recent breakthrough in this chemistry has been the synthesis of the corresponding deprotonated derivatives, 4-phosphino-substituted *N*,*N′*-diaryl-imidazol-2-ylidenes, from 4,5-unsubstituted NHCs by the groups of Bertrand (**Va**)[7] and Gates (**Vb**).[8] These new molecules behave as bifunctional ligands that allow the synthesis of a variety of dimetallic complexes.[8,9] Another remarkable example of NHC functionalized at the backbone, containing an imidato functionality, has recently been described by César and Lavigne and used as a ditopic ligand in the preparation of polymetallic derivatives.[10]

Considering the ubiquity of diphosphine and NHC ligands in organometallic chemistry and catalysis,[11] we aimed to prepare diphosphino-functionalized imidazole-2-ylidenes, or the corresponding imidazolium cations, to achieve the first molecule with both functionalities.[12] We have successfully found a straightforward approach for the synthesis of the 4,5-bis(diphenylphosphino)-1,3-dimethyl-imidazolium salt ([**5**]($CF_3SO_3$); Figure 1) and proved its suitability for easy modular formation of mixed diphosphine–NHC heterometallic complexes.

For the preparation of [**5**]($CF_3SO_3$) we have followed a one-pot, multi-step, experimental procedure that starts from 1-methylimidazole (**1**). As summarized in Scheme 1, imidazole **1** was reacted with *n*BuLi at −78 °C in THF and then treated with $ClPPh_2$ to form 2-diphenylphosphino-1-methylimidazole **2**.[13] This was reacted with an equivalent amount of methyl triflate, allowing for the selective methylation of the N3 atom of the imidazole ring, leaving the phosphino substituent unreacted, to give the 2-imidazolium phosphine **3**. Subsequent addition of $LiN(SiMe_3)_2$ (2 equiv) and $ClPPh_2$ (1 equiv) and quenching with water afforded the diphosphinoimidazole salt [**5**]($CF_3SO_3$), which was isolated as colorless crystals in high yield (85 %). Based on the pioneering work of Bertrand on mesoionic carbenes[14] and double functionalization of NHCs at the carbon–carbon double bond,[7] we propose that the reaction is very likely to proceed through the formation of mesoionic carbenes **A** and **D** (Scheme 1), which spontaneously evolve to the normal NHC isomers **B** and **4**, before protonation.

Very interestingly, Arduengo has described a double-chlorination reaction at the carbon backbone of the imida-

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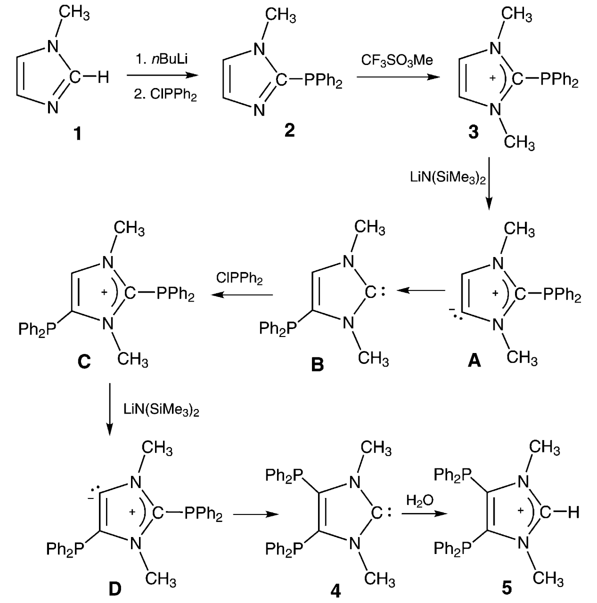


Scheme 1. Proposed mechanism for the formation of imidazolium cation **5**, starting from 1-methylimidazole.

zole ring by treatment of 1,3-dimesitylimidazol-2-ylidene with two equivalents of $CCl_4$,[15] suggesting that the reaction proceeds through mesoionic intermediates similar to **A** and **D**.

Compound [**5**]($CF_3SO_3$) was fully characterized by spectroscopic methods (see the Experimental Section; note the presence of a singlet signal at −30.4 ppm for the two equivalent phosphino groups in the $^{31}P\{^1H\}$ NMR spectrum). The crystal structure of [**5**]($CF_3SO_3$) has been determined by an X-ray diffraction study (Figure 2).[16] The endocyclic bond lengths, ranging from 1.322(3) to 1.396(3) Å, reflect the expected electronic delocalization within the heterocycle. The C2−N bond lengths (1.324(3) Å on average) and the N1-C2-N3 bond angle (109.5(2)°) are typical of imidazolium salts.

The imidazolium cation **5** can be deprotonated by treatment with $LiN(SiMe_3)_2$ (Scheme 2) to afford the new diphosphino-functionalized NHC **4** (assumed as an intermediate in Scheme 1), which was fully spectroscopically characterized. The signal of the phosphino groups in the $^{31}P\{^1H\}$ NMR spectrum of **4** is only slightly shifted high-field (3 ppm) with respect to the imidazolium precursor **5**. In the $^{13}C\{^1H\}$ NMR spectrum the resonance of the carbene carbon appears at 208.4 ppm,[17] that is 6 ppm lower in frequency than the unsubstituted 1,3-dimethyl-imidazol-2-ylidene (214.4 ppm).[18]

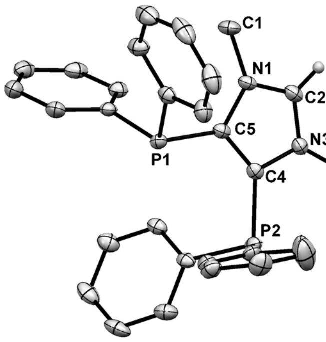
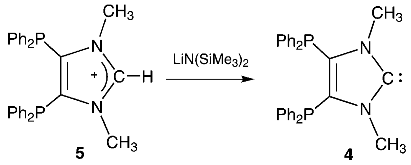


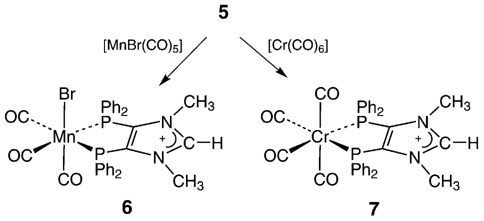
Figure 2. Molecular structure of imidazolium cation **5** shown with 50 % thermal ellipsoids. Hydrogen atoms (except C2−H) are omitted for clarity. Selected interatomic distances (Å) and angles (°): C2−N1 1.322(3), C2−N3 1.325(3), N1−C5 1.396(2), N3−C4 1.392(2), C4−C5 1.373(3), C5−P1 1.823(2), C4−P2 1.827(3); N1-C2-N3 109.5(2).



Scheme 2. Deprotonation of **5** to afford diphosphino-functionalized NHC **4**.

Note that this experimental approach, for the functionalization of the imidazole ring with phosphino groups at positions 4 and 5, involves air- and moisture-stable imidazoles and imidazolium salts to avoid the use of free carbenes as starting material. 1,3-Dialkyl-substituted NHCs, such as 1,3-dimetyl-imidazol-2-ylidene, are usually liquid at room temperature, very moisture sensitive, thermally labile, and decompose after a few days in room temperature.[18] In addition, the preparation of these carbenes involves the use of corrosive and toxic ammonia as solvent.

The potential coordination capability of the imidazolium salt [**5**]($CF_3SO_3$) combined with the stability and easy handling, prompted us to study their behavior as ligand in transition-metal complexes. We first checked the reaction with prototypic carbonyl complexes, such as $[MnBr(CO)_5]$ and $[Cr(CO)_6]$. The treatment of these species with an equivalent amount of **5** in refluxing toluene afforded the cationic complexes **6** and **7**, respectively, which contain the new imidazolium–diphosphine as a chelating ligand (Scheme 3).



Scheme 3. Coordination of **5** to $Mn^I$ (**6**) and $Cr^0$ (**7**) carbonyl complexes.

The cationic nature of **5** makes this ligand a poorer electron-donor than classical, neutral, diphosphine ligands, such as 1,2-bis(diphenylphosphino)ethane (dppe); this is reflected in the IR spectra of **6** and **7** (see the Experimental Section) that show $\tilde{\nu}$(CO) bands at higher frequencies (14 $cm^{-1}$ on average) than the neutral counterparts $[MnBr(CO)_3(dppe)]$[19] and $[Cr(CO)_4(dppe)]$.[20] The structure of **6** was confirmed by an X-ray diffraction study (Figure 3),[16] show-

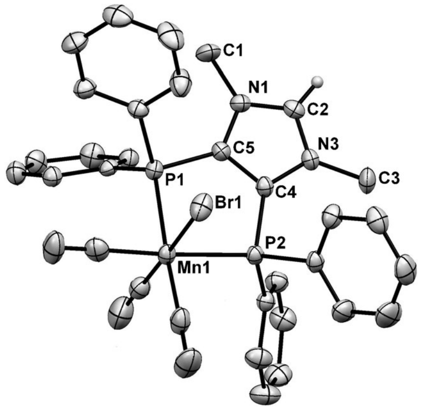
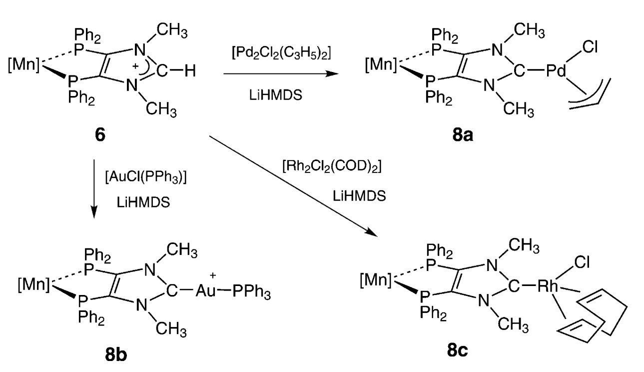


Figure 3. Molecular structure of complex **6** shown with 50 % thermal ellipsoids. Hydrogen atoms (except C2−H) are omitted for clarity. Selected interatomic distances (Å) and angles (°): C2−N1 1.335(4), C2−N3 1.327(4), N1−C5 1.388(4), N3−C4 1.380(4), C4−C5 1.363(4), C5−P1 1.808(3), C4−P2 1.800(3); N1-C2-N3 109.3(3).

ing that the structural parameters of the ligand remain essentially constant upon coordination.

The metal-containing imidazolium salts [**6**](CF$_3$SO$_3$) and [**7**](CF$_3$SO$_3$) readily react with a variety of metal complexes, in the presence of a deprotonating agents, such as LiN(SiMe$_3$)$_2$ (LiHMDS), to yield mixed, diphosphine–NHC, heterometallic derivatives. Selected examples are shown in Scheme 4 and involve coordination of the in situ generated carbene to [PdCl($\eta^3$-C$_3$H$_5$)], [AuPPh$_3$]$^+$, and [RhCl(COD)] fragments to give complexes **8a**, **8b** and **8c**, respectively. The most significant spectroscopic features of the new compounds are the disappearance of the C2−H resonances in the $^1$H NMR spectra and the presence of the low-field carbene-carbon resonances around 200 ppm in the $^{13}$C{$^1$H} NMR spectra (for full spectroscopic data see the Experimental Section and the Supporting Information).[17] Additionally, the crystal structure of **8a**, as a representative example, has been determined (Figure 4).[16]



Scheme 4. Formation of heterodimetallic complexes **8a–c** with diphosphino-functionalized NHC **4** ([Mn] = [MnBr(CO)$_3$]).

Considering the extraordinary coordination capability of diphosphines and NHCs, we envisage that a plethora of predesigned heterodimetallic complexes could be prepared by using the methodology above. We also anticipate that the use of other imidazoles and chlorophosphines as starting materials can further expand the synthetic utility of the present experimental approach.

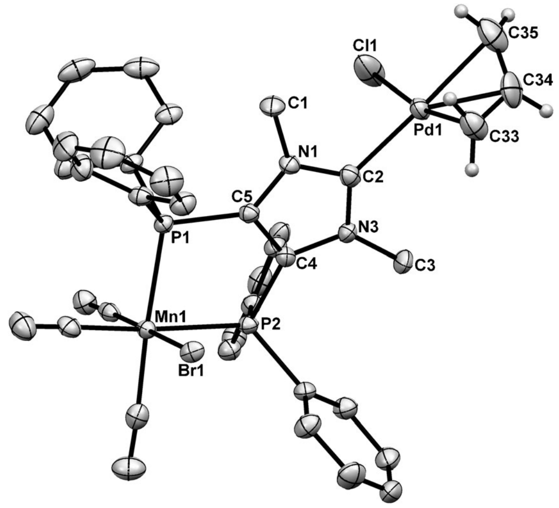


Figure 4. Molecular structure of the heterometallic complex **8a** shown with 50 % thermal ellipsoids. Hydrogen atoms (except those of the allyl group) are omitted for clarity. Selected interatomic distances (Å) and angles (°): C2−N1 1.352(4), C2−N3 1.358(4), N1−C5 1.388(4), N3−C4 1.386(4), C4−C5 1.360(4), C5−P1 1.804(3), C4−P2 1.803(3), Pd1−C2 2.035(3); N1-C2-N3 105.5(3).

In summary, we have described herein the synthesis of the unique 4,5-diphosphino-1,3-dimethyl-imidazolium salt [**5**](CF$_3$SO$_3$), which generates, in a modular manner, different heterometallic complexes with the mixed diphosphine–NHC ligand **4**. For future applications in organometallic synthesis and dual catalysis, these results could be extended to the preparation of a great variety of target heterometallic complexes containing carbene **4**. The new imidazolium–diphosphine ligand **5** is also promising as an ionophilic diphosphine for ionic-liquid, biphasic catalysis.

## Experimental Section

Selected spectroscopic data for the new compounds:

**Ligand [5](CF$_3$SO$_3$)**: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 9.50$ (s, 1 H, N$_2$CH), 3.47 ppm (s, 6 H, Me); $^{13}$C{$^1$H} NMR (100.61 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 144.8$ (s, C2), 139.9 (m, C4 and C5), 36.6 ppm (s, Me); $^{31}$P{$^1$H} NMR (162.14 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = -30.4$ ppm (s, PPh$_2$).

**Ligand 4**: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 3.48$ ppm (s, 6 H, Me); $^{13}$C{$^1$H} NMR (100.61 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 208.4$ (s, C2), 136.7 (br, C4 and C5), 37.6 ppm (s, Me); $^{31}$P{$^1$H} NMR (162.14 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = -33.3$ ppm (s, PPh$_2$).

**Complex [6](CF$_3$SO$_3$)**: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 9.41$ (s, 1 H, N$_2$CH), 3.48 ppm (s, 6 H, Me); $^{13}$C{$^1$H} NMR (75.5 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 218.5$ (s, CO), 217.2 (s, CO), 144.9 (s, C2), 134.7 (br, C4 and C5), 43.0 ppm (s, Me); $^{31}$P{$^1$H} NMR (121.4 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 47.3$ ppm (s, PPh$_2$); IR (CH$_2$Cl$_2$): $\tilde{\nu}$(CO) = 2036 (vs), 1975 (s), 1936 cm$^{-1}$ (s).

**Complex [7](CF$_3$SO$_3$)**: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 9.64$ (s, 1 H, N$_2$CH), 3.37 ppm (s, 6 H, Me); $^{13}$C{$^1$H} NMR (100.61 MHz, CD$_2$Cl$_2$,

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25 °C): $\delta = 225.7$ (s, CO), 218.1 (s, CO), 150.9 (s, C2), 147.2 (br, C4 and C5), 36.5 ppm (s, Me); $^{31}P\{^1H\}$ NMR (162.14 MHz, $CD_2Cl_2$, 25 °C): $\delta = 56.2$ ppm (s, $PPh_2$); IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 2022$ (s), 1936 (s), 1913 $cm^{-1}$ (vs).

**Complex 8a**: $^1H$ NMR (300 MHz, $CD_2Cl_2$, 25 °C): $\delta = 3.47$ ppm (s, 6H, Me); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CD_2Cl_2$, 25 °C): $\delta = 217.9$ (br, CO), 203.0 (s, C2), 143.5 (m, C4 and C5), 38.7 ppm (s, Me); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CD_2Cl_2$, 25 °C): $\delta = 38.1$ ppm (s, $PPh_2$); IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 2031$ (vs), 1968 (s), 1929 $cm^{-1}$ (s).

**Complex [8b](CF₃SO₃)**: $^1H$ NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta = 3.39$ ppm (br, 6H, Me); $^{13}C\{^1H\}$ NMR (100.61 MHz, $CD_2Cl_2$, 25 °C): $\delta = 219.5$ (s, CO), 217.5 (s, CO), 201.5 (s, C2), 144.1 (br, C4 and C5), 39.1 ppm (s, Me); $^{31}P\{^1H\}$ NMR (162.1 MHz, $CD_2Cl_2$, 25 °C): $\delta = 41.9$ (s, $PPh_3$), 39.7 ppm (s, $PPh_2$); IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 2028$ (vs), 1963 (s), 1932 $cm^{-1}$ (s).

**Complex 8c**: $^1H$ NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta = 3.69$ ppm (s, 6H, Me); $^{13}C\{^1H\}$ NMR (100.61 MHz, $CD_2Cl_2$, 25 °C): $\delta = 219.2$ (s, CO), 217.6 (s, CO), 205.4 (br, C2), 143.5 (br, C4 and C5), 38.3 ppm (s, Me); $^{31}P\{^1H\}$ NMR (162.1 MHz, $CD_2Cl_2$, 25 °C): $\delta = 37.3$ ppm (s, $PPh_2$); IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 2029$ (vs), 1967 (s), 1929 $cm^{-1}$ (s).

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**Keywords:** diphosphines · imidazolium · phosphines · N-heterocyclic carbenes · phosphanes

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