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Manganese-Mediated Synthesis of NHC-Phosphine Ligand Precursors

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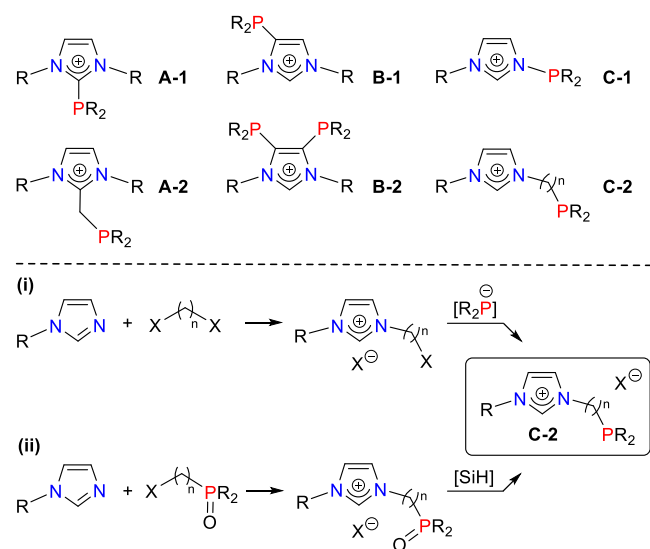
Dedicated to Professor Andrea Vasella on the occasion of his 80th birthday

Alkylation of *N*-substituted imidazoles ImR' (R' = 2,4,6-trimethylphenyl, 2,6-diisopropylphenyl, 1-adamantyl) with Mn(I) methylenephosphonium complexes [Cp(CO)₂Mn(η²-P,C-R₂P=C(H)Ph)](BF₄) (PR₂ = PPh₂, PCy₂, *trans*-PC(H)PhCH₂CH₂C(H)Ph) followed by photochemical demetallation afforded a series of bidentate NHC-phosphine ligand precursors [R₂PC(H)PhImR'](BF₄) in moderate to good yield. The same strategy was successfully applied to *N*-functionalized imidazoles ImL (L = 2-pyridyl, CH₂SMe, CH₂ImMe) to afford selectively NHC core pincer pre-ligands featuring phosphine/thioether, phosphine/NHC and phosphine/pyridine side arms. For PCy₂ derivatives, free NHCs in both bidentate and pincer series generated by deprotonation of the corresponding cationic precursors were shown to be persistent at room temperature.

Keywords: Bidentate ligands, manganese, *N*-heterocyclic carbenes, phosphines, pincer ligands.

Introduction

Phosphines are cornerstone ligands in organometallic chemistry and catalysis. Over the last three decades *N*-heterocyclic carbenes (NHCs) progressively gained a privileged position as L-type^[1] ligands resulting in widespread applications in coordination chemistry,^[2–5] homogeneous catalysis,^[6–9] functional materials^[10–13] or metallopharmaceuticals.^[14,15] The intrinsic properties of these two scaffolds motivated the research community to explore the tight association between phosphines and the most common imidazole-based NHC derivatives leading to the development of a large variety of *C,P*-ligands, in which the phosphorus group can be formally connected to any atoms of the heterocycle (Scheme 1).^[16] Indeed, the PR₂ fragment can be attached to the carbenic C2-center (A-1,^[17] A-2^[18]), or to the so-called abnormal carbenic C4/C5 positions (B-1,^[19] B-2^[20]), or to the adjacent N-atoms (C-1,^[21] C-2^[22–24]) (Scheme 1, *up*).



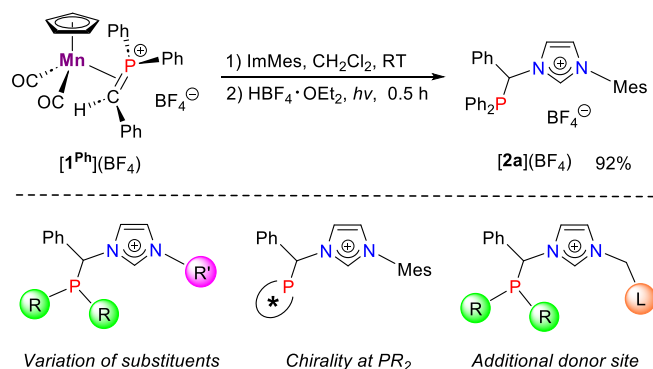
Scheme 1. Representation of known classes of phosphino-imidazolium salts A-C (*up*), and two main strategies described for the preparation of *N*-tethered phosphino-imidazolium salts C-2 (*down*).

In compounds A-B, the positioning of the PR₂ fragment excludes the *C,P*-chelating coordination mode but gives access to cationic phosphine ligands where the close proximity of the positive charge has an impact on the electronic properties^[25–27] and can favor catalytic processes requiring electron-poor metal complexes.^[28–30] For systems C-1, different coordination modes have been evidenced, namely the monodentate coordination of the NHC,^[31–33] the chelating coordination of NHC and phosphine donors,^[34,35] and the bridging coordination mode where the two L-type donors can be linked to different metal centers.^[31,36,37] However, given the limited number of *N*-phosphorylated imidazolium salts C-1 due in part to the lability of N–P bond, and more generally among all the possible NHC/phosphine combinations A-C, the *N*-tethered phosphino-imidazolium salts C-2 with different bridges between two donor moieties are by far the most common model.

To access species C-2 featuring different alkyl spacers, two main general approaches have been devised (Scheme 1, *down*): (i) the quaternization of a *N*-substituted imidazole with a dihalogenated derivative followed by a phosphination step using metal phosphide,^[38,39] (ii) the reaction of a *N*-substituted imidazole with a phosphorylalkyl halide followed by the reduction of the phosphine oxide extremity with silane.^[22–24] These two synthetic methods were also extended to the preparation of different NHC core pincer ligands featuring two pending phosphine arms.^[40–43]

Owing to the predominant role of NHC-phosphine ligands in different applications, the development of other synthetic methods is essential in order to provide a larger structural diversity to adjust the properties of the resulting metal complexes. With this objective in mind, we have developed an alternative metal-mediated strategy towards such pre-ligands bearing a C(H)Ph bridge exploiting the specific reactivity of methylenephosphonium ions in the coordination sphere of manganese.^[44] Indeed, the alkylation of *N*-mesitylimidazole (ImMes) with highly electrophilic Mn(I) methylenephosphonium complex [1^{Ph}](BF₄) followed by demetallation of the resulting phosphine intermediate [Cp(CO)₂Mn(κ²-P-

Ph₂PC(H)PhImMes]](BF₄) under visible light irradiation in the presence of HBF₄·OEt₂ provided the corresponding *N*-phosphinoimidazolium salt [2a](BF₄) in high yield under mild conditions (Scheme 2, up). This methodology was then applied to the preparation of NHC core pincer ligands featuring phosphine/phosphine,^[44] phosphine/pyridine^[45] and phosphine/phosphonium arms.^[46] Later, it was shown that beyond the creation of chirality element^[44] the presence of phenyl substituent on the NHC-phosphine ligand bridge can facilitate its deprotonation in transition metal complexes, which can stabilize unconventional P-ylide species,^[46] support the chemical non-innocence of this ligand scaffold,^[47,48] and even improve catalytic activity.^[48]

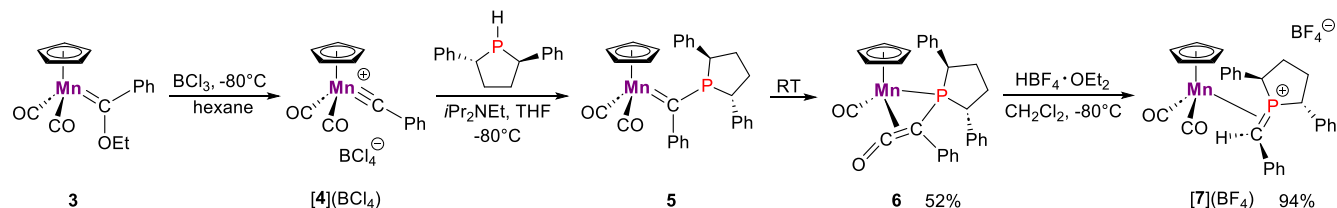


Scheme 2. Metal-mediated synthesis of the NHC-phosphine pre-ligand [2a](BF₄) (up), and generalization of this methodology to access C,P-chelating NHC-phosphine ligand precursors by varying the substituents at the *N*- and *P*-atoms (down).

In this context, we report herein the generalization of this methodology by extending the substitution pattern at the phosphorus atom of Mn(I) methylenephosphonium complex and/or at the *N*-substituted imidazole providing a library of new bidentate and pincer-type NHC-phosphine ligand precursors that could be further implemented in organometallic chemistry and homogeneous catalysis (Scheme 2, down).

Results and Discussion

The synthetic strategy initially developed for [1^{Ph}](BF₄) and ImMes was first extended to other *N*-substituted imidazoles. Thus, addition of sterically hindered *N*-2,6-diisopropylphenyl- (Dipp) and *N*-1-adamantylimidazoles to [1^{Ph}](BF₄) in CH₂Cl₂ at RT followed by demetallation afforded after purification by column chromatography on silica under nitrogen atmosphere the corresponding *N*-phosphinoimidazolium salts [2b-c](BF₄) in 67 and 64% yield, respectively (Scheme 3). The ³¹P NMR spectra of cations [2b](BF₄) and [2c](BF₄) displayed resonances at δ_P -5.8 and -6.1 ppm, respectively, being in the typical range for diarylalkylphosphine derivatives.



In the ¹H NMR spectra, the N₂CH imidazolium protons were evidenced by characteristic deshielded singlets at δ_H 9.12 and 8.65 ppm. The benzylic protons in [2c](BF₄) appeared as a doublet with small coupling with the phosphorus nuclei (δ_H 6.76 ppm, ²J(P,H) = 2.9 Hz). Next, we considered the modification of the phosphine moiety. For this purpose the Mn(I) complex [1^{Cy}](BF₄)^[44] bearing P-cyclohexyl substituents was reacted with ImMes under the same experimental conditions to give the NHC-phosphine pre-ligand [2d](BF₄) in 50% yield (Scheme 3). The lower yield of this product compared to [2a-c](BF₄) may be caused by an easier oxidation of trialkylphosphine derivatives. The identity of [2d](BF₄) was first established by ¹H and ³¹P NMR spectroscopy, which showed the presence of singlets at δ_H 9.33 ppm and δ_P 13.8 ppm, attributed to the N₂CH imidazolium proton and trialkylphosphine moiety, respectively. The benzylic proton was observed at δ_H 6.47 ppm (d, ²J(P,H) = 3.1 Hz) being slightly shielded compared to that of PPh₂ derivatives.

Scheme 3. Synthesis of phosphine-imidazolium salts [2b-d](BF₄) from Mn(I) η²-methylene phosphonium complexes [1^R](BF₄).

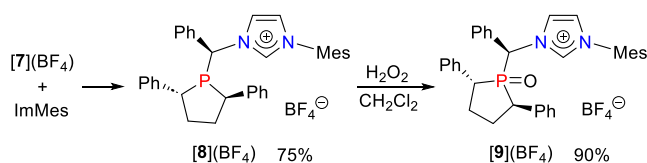
We next considered the possible incorporation of a chirality element at the phosphorus fragment in NHC-phosphine pre-ligands and concentrated our efforts on the Mn(I) methylenephosphonium complex [7](BF₄) based on the *trans*-2,5-diphenylphospholane fragment being one of the privileged motifs in enantioselective catalysis.^[49] The latter was synthesized following a two-step protocol previously developed for [1^{Cy}](BF₄) (Scheme 4).^[44] The Mn(I) η³-phosphinoketene complex **6** was first prepared in a 52% overall yield from the readily available Fischer-type alkoxy carbene **3**^[50] by an ethoxide group abstraction with BCl₃ to form the electrophilic carbyne complex [4](BCl₄), followed by its reaction at low temperature with racemic *trans*-2,5-diphenylphospholane^[51,52] in the presence of base. The resulting phosphinocarbene intermediate **5** finally rearranges into the ketene **6** upon intramolecular CO insertion (Scheme 4). In a last step, the protonation of **6** with HBF₄·OEt₂ in CH₂Cl₂ at -80°C led to the desired Mn(I) methylenephosphonium complex [7](BF₄) in 94% yield.

The chemical identity of complexes **6** and [7](BF₄) was confirmed by spectroscopic methods. The IR spectrum of **6** in CH₂Cl₂ shows an intense ν_{CO} band at 1925 cm⁻¹ for the metal-coordinated CO ligand and several broad

Scheme 4. Synthesis of Mn(I) methylenephosphonium complex [7](BF₄) based on the *trans*-2,5-diphenylphospholane fragment.

$\nu_{\text{C}=\text{O}}$ bands in the 1740-1655 cm^{-1} region attributed to the ketene moiety, similarly as it was observed for related Mn(I) complexes.^[53] The ^{31}P and ^{13}C NMR spectra of **6** exhibit a signal for the coordinated phosphine moiety at δ_{P} 68.7 ppm, and two doublet resonances for the $\text{R}_2\text{P}(\text{Ph})\text{C}=\text{O}$ fragment, one appearing at very low field (δ_{C} 240.2 ppm, $^2J(\text{P},\text{C}) = 23.6$ Hz, $\text{C}=\text{C}=\text{O}$) and a second one being strongly shielded (δ_{C} -30.7 ppm, $^3J(\text{P},\text{C}) = 15.4$ Hz, $\text{C}=\text{C}=\text{O}$).^[53] The IR spectrum of $[\mathbf{7}](\text{BF}_4)$ shows two strong ν_{CO} bands at 2032 and 1988 cm^{-1} being slightly higher in frequencies than those of dialkyl-substituted methylenephosphonium complex $[\mathbf{1}^{\text{Cy}}](\text{BF}_4)$ (ν_{CO} 2021 and 1970 cm^{-1}).^[44] The NMR spectra of $[\mathbf{7}](\text{BF}_4)$ in CD_2Cl_2 at room temperature showed very broad signals belonging to a mixture of two species in ca. 1:1.1 ratio according to the ^{31}P data (δ_{P} 66.7 and 45.5 ppm). Cooling to -40°C allowed to freeze this dynamic process tentatively attributed to the rotation of the η^2 -methylenephosphonium ligand around the metal atom/centroid of the $\text{P}=\text{C}$ bond axis.^[44] The isomers of $[\mathbf{7}](\text{BF}_4)$ likely differing by the orientation of the ligand related to $[\text{Cp}(\text{CO})_2\text{Mn}]$ moiety were fully characterized at -40°C revealing in particular two sets of characteristic NMR signals for the $\text{C}(\text{H})\text{Ph}$ moiety for major (δ_{H} 3.32 ppm (s), δ_{C} 21.7 ppm (br. s) and minor (δ_{H} 2.72 ppm; δ_{C} 20.4 ppm (d, $^3J(\text{P},\text{C}) = 9.3$ Hz)) species.

The application of previously optimized protocol to a combination of $[\mathbf{7}](\text{BF}_4)$ and ImMes allowed to isolate the targeted NHC-phosphine pre-ligand $[\mathbf{8}](\text{BF}_4)$ exhibiting the *trans*-2,5-diphenylphospholane in 75% yield (Scheme 5). To our delight, the ^{31}P NMR spectrum evidenced a unique resonance at δ_{P} 16.7 ppm speaking for the complete diastereoselectivity of the nucleophilic addition of imidazole on the η^2 -methylenephosphonium ligand in $[\mathbf{7}](\text{BF}_4)$. ^1H NMR data further confirm this conclusion with the presence of single set of signals for the N_2CH imidazolium (δ_{H} 9.14 ppm, s) and benzylic proton of the ligand bridge (δ_{H} 6.20 ppm, d, $^2J(\text{P},\text{H}) = 3.2$ Hz). Taking into account the fluxional behavior of complex $[\mathbf{7}](\text{BF}_4)$ at room temperature, we assume that this remarkable diastereoselectivity was caused by the higher reactivity of one of the rotamers with an incoming nucleophile. Since only few examples of optically active NHC-phosphine ligands featuring five-membered chelating cycle are known in literature,^[53] this result may open a new avenue for their efficient synthesis starting from optically active Mn(I) methylenephosphonium complexes. Facing difficulties to grow single crystals of $[\mathbf{8}](\text{BF}_4)$ eventually allowing to determine its absolute configuration, we decided to prepare the *P*-oxidized form $[\mathbf{9}](\text{BF}_4)$, which was isolated in 90% yield upon treatment with H_2O_2 in CH_2Cl_2 at RT (Scheme 5). As expected, the ^{31}P NMR resonance of the cationic phosphine oxide $[\mathbf{9}](\text{BF}_4)$ (δ_{P} 58.5 ppm) shifted downfield compared to the parent phosphine $[\mathbf{8}](\text{BF}_4)$ (δ_{P} 16.7 ppm).



Scheme 5. Synthesis of phosphine-imidazolium salt **8**(BF₄) from Mn(I) methylenephosphonium complex **7**(BF₄) using a standard protocol depicted in Scheme 4 and its oxidation to **9**(BF₄).

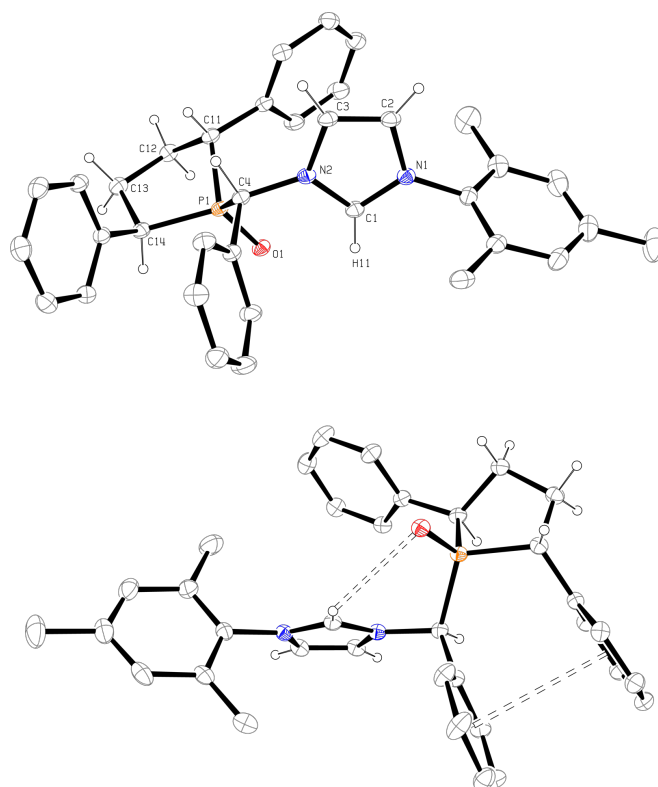
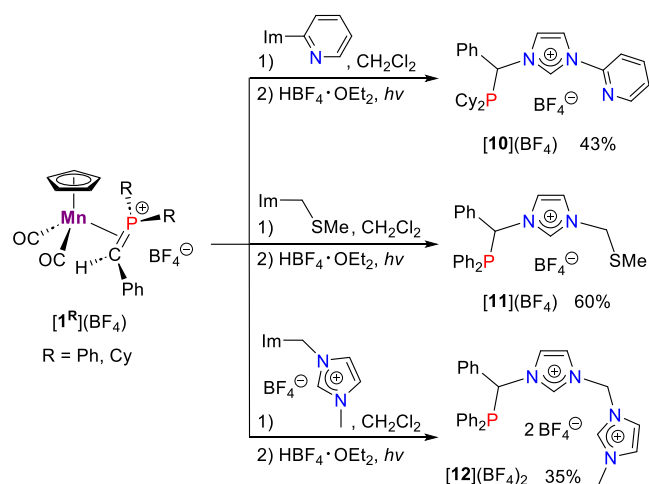


Figure 1. Perspective view of the cationic part of phosphine-oxide imidazolium salt **9**(BF₄) with thermal ellipsoids drawn at the 25% probability level (top, $S_{\text{C}44}, R_{\text{C}33}, R_{\text{C}14}$ isomer, hydrogen atoms of the aryl groups and BF₄⁻ anion are omitted for clarity) and non-covalent interactions identified for this compound in the solid state (bottom). Selected bond lengths [Å] and angles [°]: C1-N1 1.3366(18), C1-N2 1.3402(18), C2-C3 1.345(2), P1-O1 1.4877(10), N1-C1-N2 107.57(12), N2-C4-P1 107.77(9), C4-P1-O1 112.40(6), C11-P1-C14 95.56(7). CCDC Deposition number 2324142.

To our delight, the crystallization of **9**(BF₄) from a CH_2Cl_2 /hexane mixture at RT afforded single crystals suitable for X-ray diffraction analysis (Figure 1). The arrangement of *N*-tethered 2,5-diphenylphospholane oxide and imidazolium moieties is stabilized in the solid state by two types of non-covalent interactions, namely weak hydrogen bonding between the polarized $\text{P}=\text{O}$ bond and imidazolium proton ($\text{O1}\cdots\text{H11}$ 2.69 Å, $\text{O1}\cdots\text{H11}-\text{C1}$ 104.88°), and π - π stacking between the phenyl rings located at the bridge position and phospholane fragment ($\text{C}\cdots\text{C} \approx 3.26$ Å) (Figure 1, bottom). Finally, the configuration of the newly created stereogenic center in the ligand bridge was determined to be the opposite relative to the *trans*-2,5-diphenyl-phospholane scaffold ($S_{\text{C}44}, R_{\text{C}33}, R_{\text{C}14} / R_{\text{C}44}, S_{\text{C}33}, S_{\text{C}14}$).

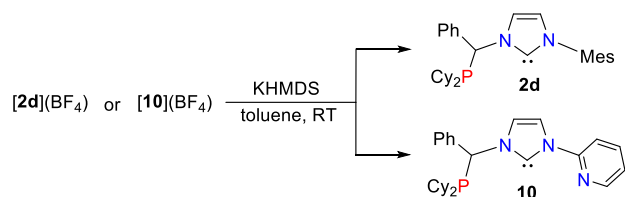
We then applied the same methodology to different functionalized imidazoles in order to increase the structural diversity of pincer ligand precursors incorporating the $\text{R}_2\text{P}-\text{C}(\text{H})\text{Ph}-\text{NHC}$ motif.^[44-46] First, we have expanded the access to phosphine-NHC-pyridine pincer ligands previously known in the Ph_2P versions^[43,45] to the aliphatic phosphine derivative (Scheme 6). The treatment of $[\mathbf{1}^{\text{Cy}}](\text{BF}_4)$ with 2-pyridylimidazole using the same protocol afforded the compound **10**(BF₄) in 43% yield. Then, the variation of the third sidearm was attempted by the reactions of $[\mathbf{1}^{\text{Ph}}](\text{BF}_4)$ with imidazole derivatives bearing thiomethyl- and imidazolium substituents to give the corresponding products **11**(BF₄), and **12**(BF₄)₂ in 60, and 35%



Scheme 6. Synthesis of pincer-type pre-ligands $[10](BF_4)$, $[11](BF_4)$ and $[12](BF_4)_2$ from Mn(I) methylenephosphonium complexes $[1^R](BF_4)$.

yield, respectively (Scheme 6). The identity of these compounds was established by multinuclear NMR and HRMS. In the ^{31}P NMR spectra, characteristic singlets at δ_P 12.2, -6.9, and -5.6 ppm for $[10](BF_4)$, $[11](BF_4)$ and $[12](BF_4)_2$, respectively, were observed in agreement with the alkyl or aryl nature of P-substituents. The signals of imidazolium (δ_H 10.10 ppm) and benzylic (δ_H 6.37 ppm, d, $^2J(P,H) = 2.8$ Hz) protons in $[10](BF_4)$ were significantly shifted compared to those of its Ph_2P analogue (δ_H 9.40 (s, N_2CH), 6.85 (d, $^2J(P,H) = 3.0$ Hz, $CHPh$).^[45] The most pertinent 1H NMR data for the pre-ligands $[11](BF_4)$ and $[12](BF_4)_2$ rest in the characteristic imidazolium resonances observed in the 8.93–9.00 ppm range and in the AB spin systems centered at δ_H 4.94 ($^2J(H,H) = 12.0$ Hz) and 6.25 ($^2J(H,H) = 16.0$ Hz) ppm, respectively for the two diastereotopic methylene bridge protons. To the best of our knowledge, $[11](BF_4)$ represents the first example of NHC core pincer pre-ligand exhibiting phosphine and thioether arms as only symmetric analogues with two neutral S-donor extremities have been previously reported.^[54–56] While some tridentate phosphine-core bis(NHC) pincers are known,^[57–60] the phosphine-NHC-NHC ligand topology in $[12](BF_4)_2$ is also unprecedented.

Considering that free bi- and tridentate NHCs bearing Ph_2PCHPh wingtip have been already shown to be sufficiently stable for successful coordination to transition metals,^[45,48,61] we decided to check whether the newly prepared derivatives based on aliphatic phosphines could have the same behavior. The NHC-phosphine ligands **2a** and **10** were thus quantitatively generated upon deprotonation of corresponding cationic precursors $[2d](BF_4)$ and $[10](BF_4)$ with KHMDS in toluene at RT and fully characterized by NMR spectroscopy (Scheme 7).



Scheme 7. Generation of free bidentate and tridentate NHC ligands **2d** and **10** from the corresponding imidazolium salts.

The formation of free NHCs was first assigned by the disappearance of the C–H imidazolium protons in the 1H NMR spectra and the occurrence of highly deshielded ^{13}C NMR doublet resonances attributed to the carbenic carbon atoms (**2d**: δ_C 216.2 ppm, br. s; **10**: δ_C 216.0 ppm, s; $^3J(P,C) = 7.0$ Hz). The ^{31}P NMR signals were observed (**2d**: δ_P 8.5 ppm, s; **10**: δ_P 7.8 ppm) in the same region as that of their precursors. Both free carbenes were persistent in C_6D_6 solution under an inert atmosphere at RT for several hours being largely sufficient for their future implementation in coordination chemistry.

Conclusions

We have demonstrated that a metal-mediated strategy for the synthesis of phosphine-imidazolium salts allows to modulate easily the nature of the substituents at both phosphine and imidazolium moieties to provide a straightforward access to a family of original bi- and tridentate NHC pre-ligands. Remarkable level of stereocontrol observed in the reaction of the Mn(I) methylenephosphonium complex incorporating the chiral *trans*-2,5-diphenylphospholane moiety with *N*-mesitylimidazole shows an additional potential utility of this methodology for the design of optically active NHC-phosphine ligands, which is currently under investigation in our group.

Experimental Section

General considerations

All manipulations were performed under nitrogen atmosphere using standard vacuum line and Schlenk tube techniques. Dry and deoxygenated organic solvents (THF, Et_2O , CH_2Cl_2 , toluene) were obtained using a LabSolv (Innovative Technology) solvent purification system. A liquid nitrogen/ethanol slush bath was used to maintain samples at the desired low temperature. Photochemical demetallation was performed in 125 mL reactor with an immersed Hg medium pressure lamp (150 W) cooled by Pyrex jacket with circulating water. Chromatographic purification of the phosphine-imidazolium salts was performed under inert atmosphere on silica (0.060–0.200 mm, 60 Å) obtained from Acros Organics using oxygen-free CH_2Cl_2 obtained by nitrogen bubbling for 10 min. Neutral alumina (Brockmann type III (4.7% water), 50–200 μm) obtained from Acros Organics was used for the synthesis of complex **6**. *N*-mesitylimidazole,^[62] *N*-2,6-diisopropylphenylimidazole,^[63] *N*-1-adamantylimidazole,^[64] *N*-(2-pyridyl)imidazole,^[65] *N*-[(methylthio)methyl]imidazole,^[66] 3-((1*H*-imidazol-1-yl)methyl)-1-methyl-1*H*-imidazolium iodide,^[67] *rac-trans*-2,5-diphenylphospholane^[51,52] as well as Mn(I) complexes $[1^R](BF_4)$ ^[44] and **3**^[50] were prepared according to previously described procedures. All other reagent-grade chemicals were purchased from commercial sources and used as received.

Solution IR spectra were recorded in 0.1 mm CaF_2 cells using a Perkin Elmer Frontier FT-IR spectrometer and given in cm^{-1} . 1H , ^{31}P , and ^{13}C NMR spectra were obtained on Bruker AV400 or NEO600 spectrometers. NMR chemical shifts δ are in ppm, with positive values to high frequency referenced against the residual signals of deuterated solvents (1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Deuterated benzene, CD_2Cl_2 and $CDCl_3$ for NMR

experiments were deoxygenated by three freeze-pump-thaw cycles and stored over 4 Å molecular sieves. MS spectra (ESI mode) were obtained in the mass spectrometry service of the "Institut de Chimie de Toulouse" using a Xevo G2 QToF (Waters) spectrometer.

Synthesis of 3-((1*H*-imidazol-1-yl)-methyl)-1-methyl-1*H*-imidazolium tetrafluoroborate

A solution of 3-((1*H*-imidazol-1-yl)-methyl)-1-methyl-1*H*-imidazolium iodide (0.60 g, 2.1 mmol) and NaBF₄ (0.68 g, 6.2 mmol) in MeCN (10 mL) was stirred at RT for 5 h. After addition of CH₂Cl₂ (10 mL), the solution was filtered through Celite and evaporated under vacuum. After washing with Et₂O (2 x 5 mL), the target salt was obtained as a white power (0.50 g, 96 %). ¹H-NMR (400 MHz, CD₃CN, 25°C): δ 9.31 (s, 1H, CH_{Im-2}), 8.11 (s, 1H, CH_{Ar}), 7.78 (s, 1H, CH_{Ar}), 7.51 (s, 1H, CH_{Ar}), 7.43 (s, 1H, CH_{Ar}), 7.00 (s, 1H, CH_{Ar}), 6.55 (s, 2H, CH₂), 3.85 (s, 3H, NCH₃); ¹³C{¹H}-NMR (101 MHz, CD₃CN, 25°C): 138.8 (s, CH_{Im-2}), 137.5, 130.6, 125.0, 122.3, 120.2 (s, CH_{Ar}), 58.0 (s, CH₂), 37.2 (s, CH₃). HR-MS (ES⁺): 163.0986 ([M]⁺, C₈H₁₁N₄⁺; calc. 163.0984).

Synthesis of η³-phosphinoketene Mn(I) complex 6.

To a solution of complex 3 (930 mg, 3.0 mmol) in hexane (60 mL), a 1.0 M solution of boron trichloride in hexane (6.6 mL, 6.6 mmol) was added rapidly via syringe at –60°C under vigorous stirring to form yellow-brown precipitate of [4]BCl₄. After stirring for an additional 15 min at –80°C, the supernatant was removed by means of a cannula tipped with filter paper. The resulting solid was washed with hexane (50 mL) and then dissolved in THF (100 mL) at –80°C. A solution of racemic *trans*-2,5-diphenylphospholane (720 mg, 3.0 mmol) and *i*Pr₂NEt (2.5 mL, 15 mmol) in THF (30 mL) was added dropwise at –80°C over ca. 1 h. The resulting orange-brown solution of phosphinocarbene intermediate 5 was stirred for additional 30 min and then was rapidly filtered at –80°C through an alumina column (4x8 cm) to remove [*i*Pr₂(Et)NH](BCl₄) using cold THF (ca. 50 mL) as an eluent to afford a deep red solution containing 6 as a major organometallic product according to IR data (ν_{CO} 1925 cm^{–1} (s), ν_{C=C=O} 1743–1650 cm^{–1} (m br.)). The volatiles were removed under vacuum to give a red waxy residue. Then toluene (200 mL) and nitrogen saturated 1M NaOH_{aq} (30 mL) were added and the resulting biphasic mixture was vigorously shaken until complete dissolution of the red precipitate of complex 6. Deep red organic layer was rapidly separated from yellow aqueous suspension and the latter was additionally extracted with toluene (3x30 mL). Combined toluene fractions were filtered consequently through a pad of Na₂SO₄ (2x10 cm) and Celite (2x2 cm), concentrated to ca. 70 mL and hexane (250 mL) was added slowly under stirring to induce the crystallization of the product, which was finished at –20°C overnight. The supernatant was removed using a cannula tipped with filter paper and the precipitate was washed with hexane (50 mL) and dried under vacuum to give complex 6 (0.787 g, 52%) as red crystals.

IR (CH₂Cl₂): ν_{CO} 1925 (s), ν_{C=C=O} 1740–1655 cm^{–1} (m br.). ¹H-NMR (400 MHz, CD₂Cl₂, 25°C): δ 7.30–7.39 (m, 5H, CH_{Ph}), 7.17–7.27 (m, 8H, CH_{Ph}), 7.10 (br. s, 1H, CH_{Ph}), 7.08 (br. s, 1H, CH_{Ph}), 4.18–4.28 (m, 1H, CH_{Phos}), 4.15 (s, 5H, CH_{CP}), 3.74–3.79 (m, 1H, CH_{Phos}), 2.70–2.88 (m, 2H, CH_{2Phos}), 2.32–2.48 (m, 2H,

CH_{2Phos}). ³¹P{¹H}-NMR (162 MHz, CD₂Cl₂, 25°C): δ 68.7 (s). ¹³C{¹H}-NMR (101 MHz, CD₂Cl₂, 25°C): δ 240.2 (d, ²J(P,C) = 23.6 Hz, P–C=C=O), 231.9 (d, ²J(P,C) = 32.2 Hz, Mn–CO), 141.9 (d, ²J(P,C) = 4.4 Hz, C_{Ph}), 138.1 (d, ²J(P,C) = 2.0 Hz, C_{Ph}), 136.8 (d, ²J(P,C) = 6.9 Hz, C_{Ph}), 132.4 (s, CH_{Ph}), 130.2 (d, ²J(P,C) = 6.0 Hz, CH_{Ph}), 129.5 (d, ²J(P,C) = 6.0 Hz, CH_{Ph}), 129.3 (d, ²J(P,C) = 2.0 Hz, CH_{Ph}), 128.8, 128.4, 127.5, 125.7 (s, CH_{Ph}), 85.7 (s, CH_{CP}), 47.5 (d, ²J(P,C) = 18.5 Hz, CH_{Phos}), 43.5 (d, ²J(P,C) = 16.0 Hz, CH_{Phos}), 38.7 (s, CH_{2Phos}), 35.0 (d, ²J(P,C) = 9.0 Hz, CH_{2Phos}), –30.7 (d, ²J(P,C) = 15.4 Hz, P–C=C=O). Anal. calc. for C₃₀H₂₆MnO₂P (M = 504.4): C 71.43, H 5.20; found: C 71.25, H 5.11.

Synthesis of η²-methylenephosphonium Mn(I) complex [7](BF₄).

To a solution of complex 6 (1.261 g, 2.5 mmol) in THF (40 mL), HBF₄·OEt₂ (345 μL, 2.5 mmol) was added dropwise at –80°C. The reaction mixture was allowed to reach slowly room temperature over ca. 3 h and the resulting yellow suspension was evaporated to dryness. The residue was dissolved in CH₂Cl₂ (20 mL) and the resulting solution was filtered through Celite, concentrated to a half of its volume and the product [7]BF₄ was precipitated by slow addition of diethyl ether (80 mL) under vigorous stirring. The supernatant was removed by decantation and the oily precipitate was washed with ether (30 mL) and dried under vacuum to give [7]BF₄ (1.377 mg, 94%) as air-stable non-hygroscopic yellow-brown powder. NMR assignment: ^a major isomer (53%), ^b minor isomer (47%).

IR (CH₂Cl₂): ν_{CO} 2032 (s), 1988 cm^{–1} (s). ¹H-NMR (600 MHz, CD₂Cl₂, –40°C): δ 7.58–7.70^{a,b} (m, 5.7H, CH_{Ph}), 7.28–7.55^{a,b} (m, 17.2H, CH_{Ph}), 7.18–7.26^b (m, 1.8H, CH_{Ph}), 6.95^b (br. d, J(H,H) = 6.0 Hz, 1.8H, CH_{Ph}), 6.86^a (br. d, J(H,H) = 6.1 Hz, 2H, CH_{Ph}), 5.01^a (s, 5H, Cp), 4.79–4.92^a (m, 1H, CH_{Phos}), 4.48–4.62^b (m, 0.9H, CH_{Phos}), 4.34^b (s, 4.5H, CH_{CP}), 4.15–4.26^b (m, 0.9H, CH_{Phos}), 3.61–3.75^a (m, 1H, CH_{Phos}), 3.32^a (s, 1H, P=CHPh), 3.00–3.18^b (m, 0.9H, CH_{2Phos}), 2.75–2.96^a (m, 3H, CH_{2Phos}), 2.72^b (s, 0.9H, P=CHPh), 2.38–2.56^b (m, 2.7H, CH_{2Phos}), 2.10–2.23 (m, 1H, CH_{2Phos}). ³¹P{¹H}-NMR (202 MHz, CD₂Cl₂, –40°C): δ 66.7^b (s), 45.5^a (s). ¹³C{¹H}-NMR (126 MHz, CD₂Cl₂, –40°C): δ 225.8^b (d overlapped with s, ²J(P,C) = 38.6 Hz, Mn–CO), 225.6^a (br. s, Mn–CO), 222.4^b (br. s, Mn–CO), 219.8^a (d, ²J(P,C) = 24.8 Hz, Mn–CO), 138.5^b (s, C_{Phos}), 138.0^a (s, C_{Phos}), 137.8^a (s, C_{Phos}), 137.4^b (s, C_{Phos}), 134.7^a (br. d, ²J(P,C) = 6.4 Hz, C_{Ph}), 131.3^b (br. d, ²J(P,C) = 5.5 Hz, C_{Ph}), 130.3^{a,b} (s, CH_{Ph}), 130.2^{a,b} (d, ²J(P,C) = 7.6 Hz, CH_{Ph}), 130.0, 129.9, 129.7, 129.4, 129.3^{a,b} (s, CH_{Ph}), 129.2^{a,b} (d, ²J(P,C) = 8.3 Hz, CH_{Ph}), 129.0^{a,b} (d, ²J(P,C) = 5.6 Hz, CH_{Ph}), 128.9^a (s, CH_{Ph}), 128.4^b (s, CH_{Ph}), 128.1^b (s, CH_{Ph}), 127.5^a (s, CH_{Ph}), 91.3^b (s, CH_{CP}), 88.2^a (s, CH_{CP}), 48.8^a (d, ²J(P,C) = 22.4 Hz, CH_{Phos}), 46.4^b (d, ²J(P,C) = 29.5 Hz, CH_{Phos}), 45.6^a (d, ²J(P,C) = 18.7 Hz, CH_{Phos}), 45.4^b (d, ²J(P,C) = 12.8 Hz, CH_{Phos}), 38.1^b (d overlapped with s, ²J(P,C) = 11.3 Hz, CH_{2Phos}), 38.0^a (s, CH_{2Phos}), 37.7^a (d, ²J(P,C) = 8.0 Hz, CH_{2Phos}), 34.2^b (br. s, CH_{2Phos}), 21.7^b (s, P=CHPh), 20.4 (d, ²J_{CP} = 9.3 Hz, P=CHPh). HR-MS (ES⁺): 505.1129 ([M]⁺, C₃₀H₂₇O₂PMn⁺; calc. 505.1129).

General procedure for the synthesis of NHC-phosphine pre-ligands

To a solution of the corresponding Mn(I) methylenephosphonium complex in CH₂Cl₂ (20 mL) solid imidazole derivative (1 equiv.) was added at room temperature and the reaction mixture was stirred for 5 min. After completion verified by IR spectrum of the aliquot, the resulting yellow

solution was transferred to a photochemical reactor, diluted with CH₂Cl₂ (100 mL) and HBF₄·OEt₂ (1 equiv.) was added. The solution was irradiated at RT with visible light under vigorous stirring until CO evolution ceased (ca. 15-30 min). The resulting suspension was filtered through Celite, the filtrate was vigorously shaken with deoxygenated saturated aqueous solution of NaHCO₃ (5-7 mL) until no CO₂ evolved. All volatiles were evaporated under vacuum and the residue was purified by column chromatography on silica using CH₂Cl₂/MeOH mixture as an eluent or by crystallization from CH₂Cl₂/Et₂O (compound **[12]**(BF₄)₂)

Phosphine-imidazolium salt **[2b]**(BF₄)

According to general procedure starting from **[1^{Ph}]**(BF₄) (1.12 g, 2 mmol) and *N*-2,6-diisopropylphenylimidazole (456 mg, 2 mmol) phosphine-imidazolium salt **[2b]**(BF₄) (792 mg, 67%) was isolated as light-yellow powder after column chromatography purification using 200:1 CH₂Cl₂/MeOH mixture.

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 9.12 (s, 1H, CH_{Im-2}), 8.10 (s, 1H, CH_{Ar}), 7.91-7.97 (m, 2H, CH_{Ar}), 7.83-7.87 (m, 2H, CH_{Ar}), 7.44-7.60 (m, 7H, CH_{Ar}), 7.34-7.41 (m, 3H, CH_{Ar}), 7.32 (br. s, 1H, CH_{Ar}), 7.27-7.30 (m, 3H, CH_{Ar}), 7.10-7.13 (m, 2H, CH_{Ar}), 1.95 (sept, ³J(H,H) = 6.8 Hz, 1H, CH_{IPr}), 1.64 (sept, ³J(H,H) = 6.8 Hz, 1H, CH_{IPr}), 1.07 (d overlapped with another d signal, ³J(H,H) = 6.3 Hz, 3H, CH_{3IPr}), 1.05 (d overlapped with another d signal, ³J(H,H) = 6.5 Hz, 6H, CH_{3IPr}), 0.99 (d, ³J_{HH} = 6.8 Hz, 3H, CH_{3IPr}). ³¹P{¹H}-NMR (162 MHz, CDCl₃, 25°C): δ -5.8 (s). ¹³C{¹H}-NMR (101 MHz, CDCl₃, 25°C): δ 145.4, 145.2 (s, C_{Ar}), 136.7 (d, ³J(P,C) = 4.2 Hz, C_{Ar}), 135.3 (d, ³J(P,C) = 15.1 Hz, C_{Ar}), 134.5 (d, ³J(P,C) = 22.1 Hz, CH_{Ar}), 133.7 (d, ³J(P,C) = 21.1 Hz, CH_{Ar}), 132.4 (d, ³J(P,C) = 12.1 Hz, CH_{Ar}), 132.1 (s, CH_{Ar}), 131.8 (d, ³J(P,C) = 8.0 Hz, CH_{Ar}), 131.0, 130.2 (s, CH_{Ar}), 130.0 (s, C_{Ar}), 129.7, 129.6 (s, CH_{Ar}), 129.5 (d, ³J(P,C) = 9.0 Hz, CH_{Ar}), 129.2 (d, ³J(P,C) = 9.0 Hz, CH_{Ar}), 128.9 (d, ³J(P,C) = 9.0 Hz, CH_{Ar}), 124.9 (s, CH_{Im-4,5}), 124.8 (s, CH_{Ar}), 121.9 (d, ³J(P,C) = 8.4 Hz, CH_{Im-4,5}), 63.1 (d, ³J(P,C) = 12.7 Hz, PC(H)Ph), 28.7, 28.5 (s, CH), 24.5, 24.2, 24.1, 24.0 (s, CH₃). HR-MS (ES⁺): 503.2621 ([M]⁺, C₃₄H₃₆N₂P⁺; calc. 503.2616).

Phosphine-imidazolium salt **[2c]**(BF₄)

According to general procedure starting from **[1^{Ph}]**(BF₄) (986 mg, 1.76 mmol) and *N*-1-adamantylimidazole (356 mg, 1.76 mmol) phosphine-imidazolium salt **[2c]**(BF₄) (720 mg, 64%) was isolated as white powder after column chromatography purification using 100:1 CH₂Cl₂/MeOH mixture.

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 8.65 (s, 1H, CH_{Im-2}), 7.87 (s, 1H, CH_{Im-4,5}), 7.85 (s, 1H, CH_{Im-4,5}), 7.48-7.57 (m, 6H, CH_{Ph}), 7.19-7.36 (m, 9H, CH_{Ph}), 6.76 (d, 1H, ³J(P,H) = 2.9 Hz, CHPh), 2.20 (br. s, 3H, CH_{Ad}), 1.80-1.86 (m, 6H, CH_{2Ad}), 1.62-1.72 (m, 6H, CH_{2Ad}). ³¹P{¹H}-NMR (162 MHz, CDCl₃, 25°C): δ -6.1 (s). ¹³C{¹H}-NMR (101 MHz, CDCl₃, 25°C): δ 134.7 (d, ³J(P,C) = 15.1 Hz, C_{Ph}), 134.3 (d, ³J(P,C) = 23.1 Hz, CH_{Ph}), 133.8 (d, ³J(P,C) = 14.1 Hz, C_{Ph}), 133.5 (d, ³J(P,C) = 20.1 Hz, CH_{Ph}), 130.7, 130.0 (s, CH_{Ph}), 129.9 (d, ³J(P,C) = 11.1 Hz, CH_{Ph}), 129.8, 129.6 (s, CH_{Ph}), 129.3 (d, ³J(P,C) = 8.0 Hz, CH_{Ph}), 129.0 (d, ³J(P,C) = 8.0 Hz, CH_{Ph}), 120.0 (br s, CH_{Im-4,5}), 118.6 (d, ³J(P,C) = 12.0 Hz, CH_{Im-4,5}), 63.3 (d, ³J(P,C) = 13.0 Hz, PC(H)Ph), 60.6 (s, C_{Ad}), 42.5, 35.3 (s, CH_{2Ad}), 29.4 (s, CH_{Ad}). HR-MS (ES⁺): 477.2456 ([M]⁺, C₃₂H₃₄N₂P⁺; calc. 477.2460).

Phosphine-imidazolium salt **[2d]**(BF₄)

According to general procedure starting from **[1^{Cy}]**(BF₄) (1.32 g, 2.0 mmol) and *N*-mesitylimidazole (372 mg, 2.0 mmol) phosphine-imidazolium salt **[2d]**(BF₄) (563 mg, 50%) was isolated as light-yellow powder after column chromatography purification using 100:1 CH₂Cl₂/MeOH mixture.

¹H NMR (400 MHz, CDCl₃, 25°C): δ 9.33 (s, 1H, CH_{Im-2}), 8.18 (br. s, 1H, CH_{Im-4,5}), 7.67-7.68 (m, 2H, CH_{Ph}), 7.36-7.43 (m, 3H, CH_{Ph}), 7.14 (s, 1H, CH_{Im-4,5}), 7.01 (s, 1H, CH_{Mes}), 6.97 (s, 1H, CH_{Mes}), 6.47 (d, ²J(P,H) = 3.1 Hz, 1H, CHPh), 2.33 (s, 3H, CH_{3Mes}), 2.04 (s, 3H, CH_{3Mes}), 1.93-1.98 (m, 2H, CH_{Cy}), 1.88 (s, 3H, CH_{3Mes}), 0.91-1.77 (m, 20H, CH_{2Cy}). ³¹P{¹H}-NMR (162 MHz, CDCl₃, 25°C): δ 13.8 (s). ¹³C{¹H}-NMR (101 MHz, CDCl₃, 25°C): δ 141.7 (s, C_{Mes}), 137.4 (d, ²J(P,C) = 9.0 Hz, C_{Ph}), 136.9 (d, ³J(P,C) = 4.9 Hz, CH_{Im-2}), 134.2, 134.1 (s, C_{Mes}), 130.1, 130.0 (s, CH_{Mes}), 129.9 (s, CH_{Ph}), 129.5 (s, CH_{Ph}), 128.5 (d, ³J(P,C) = 6.0 Hz, CH_{Ph}), 123.5 (s, CH_{Im-4,5}), 122.4 (d, ³J(P,C) = 9.0 Hz, CH_{Im-4,5}), 61.8 (d, ³J(P,C) = 22.9 Hz, PC(H)Ph), 33.8 (d, ³J(P,C) = 17.1 Hz, CH_{Cy}), 33.7 (d, ³J(P,C) = 14.1 Hz, CH_{Cy}), 31.0 (d, ³J(P,C) = 14.1 Hz, CH_{2Cy}), 30.7 (d, ³J(P,C) = 14.1 Hz, CH_{2Cy}), 30.2 (d, ³J(P,C) = 10.1 Hz, CH_{2Cy}), 29.3 (d, ³J(P,C) = 5.0 Hz, CH_{2Cy}), 27.9 (d, ³J(P,C) = 11.1 Hz, CH_{2Cy}), 27.7 (d, ³J(P,C) = 7.0 Hz, CH_{2Cy}), 27.1 (d, ³J(P,C) = 11.1 Hz, CH_{2Cy}), 26.9 (d, ³J(P,C) = 10.1 Hz, CH_{2Cy}), 26.2, 26.1 (s, CH_{2Cy}), 21.2, 17.4 (s, CH_{3Mes}). HR-MS (ES⁺): 473.3086 ([M]⁺, C₃₃H₄₂N₂P⁺; calc. 473.3086).

Phosphine-imidazolium salt **[8]**(BF₄)

According to general procedure starting from **[7]**(BF₄) (1.34 g, 1.94 mmol) and *N*-mesitylimidazole (360 mg, 1.94 mmol) phosphine-imidazolium salt **[8]**(BF₄) (0.94 g, 75%) was isolated as yellow-brown powder after column chromatography purification using 100:1 CH₂Cl₂/MeOH mixture.

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 9.14 (s, 1H, CH_{Im-2}), 7.63 (s, 1H, CH_{Im-4,5}), 7.19-7.24 (m, 6H, CH_{Ph}), 7.14 (s, 1H, CH_{Mes}), 7.12 (s, 1H, CH_{Mes}), 6.96-7.03 (m, 5H, CH_{Ph}), 6.87-6.91 (m, 3H, CH_{Ph+Im-4,5}), 6.78-6.81 (m, 2H, CH_{Ph}), 6.20 (d, ²J(P,H) = 3.2 Hz, 1H, CHPh) 3.85 (ddd, ³J(H,H) = 12.9 Hz, ³J(H,H) = 5.7 Hz, ²J(P,H) = 18.8 Hz, 1H, CH_{Phos}), 3.63 (dt, ³J(H,H) = 6.5 Hz, ²J(P,H) = 12.4 Hz, 1H, CH_{Phos}), 2.91-3.02 (m, 1H, CH_{2Phos}), 2.70-2.81 (m, 1H, CH_{2Phos}), 2.39-2.49 (m, 1H, CH_{2Phos}), 2.30 (s, 3H, CH_{3Mes}), 2.30 (s, 3H, CH_{3Mes}), 1.94 (s, 3H, CH_{3Mes}), 1.74-1.89 (m, 1H, CH_{2Phos}), 1.63 (s, 3H, CH_{3Mes}). ³¹P{¹H}-NMR (162 MHz, CDCl₃, 25°C): δ 16.7 (s). ¹³C{¹H}-NMR (101 MHz, CDCl₃, 25°C): δ 143.0 (d, ³J(P,C) = 17.6 Hz, C_{Ph}), 141.6, 139.1 (s, C_{Mes}), 136.5 (d, ³J(P,C) = 13.6 Hz, C_{Ph}), 136.3 (s, CH_{Im-2}), 136.3 (d, ³J(P,C) = 3.6 Hz, C_{Ar}), 134.0, 130.5 (s, CH_{Ph}), 130.0, 129.9 (br. s, CH_{Mes}), 129.2, 128.9 (s, CH_{Ph}), 128.8 (vt, ³J(P,C) = 4.9 Hz, CH_{Ph}), 128.5, 128.3 (s, CH_{Ph}), 128.1 (d, ³J(P,C) = 10.8 Hz, CH_{Ph}), 128.0 (s, CH_{Ph}), 126.5 (d, ³J(P,C) = 2.0 Hz, CH_{Ph}), 126.2 (br. s, CH_{Ar}), 123.6 (s, CH_{Im-4,5}), 121.8 (d, ³J(P,C) = 7.1 Hz, CH_{Im-4,5}), 62.1 (d, ³J(P,C) = 29.8 Hz, PC(H)Ph), 48.7 (d, ³J(P,C) = 16.6 Hz, CH_{Phos}), 47.2 (d, ³J(P,C) = 16.4 Hz, CH_{Phos}), 39.1 (d, ²J(P,C) = 2.5 Hz, CH_{2Phos}), 33.0 (d, ²J(P,C) = 4.0 Hz, CH_{2Phos}), 21.1, 17.4, 17.1 (s, CH_{3Mes}). HR-MS (ES⁺): 515.2618 ([M]⁺, C₃₅H₃₆N₂P⁺; calc. 515.2616).

Synthesis of phosphine oxide-imidazolium salt **[9]**(BF₄)

To a solution of **[8]**(BF₄) (30 mg, 0.05 mmol) in CH₂Cl₂ (2 mL) a 30% aqueous solution of H₂O₂ (50 µL, 0.5 mmol) was added and the reaction mixture was stirred overnight at room temperature. The reaction mixture was filtered

through Celite, the volatiles were removed under reduced pressure and the residue was washed with ether (2 mL) and dried under vacuum to afford [9](BF₄) (28 mg, 90%) as yellow powder. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane vapors to the solution of [9](BF₄) in CH₂Cl₂ at room temperature.

¹H-NMR (400 MHz, CD₃CN, 25°C): δ 8.76 (s, 1H, CH_{Im-2}), 7.84 (s, 1H, CH_{Im-4,5}), 7.21–7.30 (m, 7H, CH_{Ar}), 7.20 (s, 1H, CH_{Im-4,5}), 7.13–7.17 (m, 1H, CH_{Ar}), 6.99–7.08 (m, 9H, CH_{Ar}), 5.81 (d, ²J(P,H) = 4.0 Hz, 1H, CHPh) 3.81 (ddd, ³J(H,H) = 12.0 Hz, ³J(H,H) = 8.0 Hz, ²J(P,H) = 16.0 Hz, 1H, CH_{Phos}), 3.47–3.54 (m, 1H, CH_{Phos}), 2.32–2.70 (m, 4H, CH_{2Phos}), 2.28 (s, 3H, CH_{3Mes}), 1.76 (br. s, 3H, CH_{3Mes}), 1.48 (br. s, 3H, CH_{3Mes}). ³¹P{¹H}-NMR (162 MHz, CD₃CN, 25°C): δ 58.5 (s). ¹³C{¹H}-NMR (101 MHz, CD₃CN, 25°C): δ 142.3 (s, C_{Ar}), 137.7 (d, J(P,C) = 3.0 Hz, CH_{Ar}), 137.4 (d, J(P,C) = 5.0 Hz, C_{Ar}), 135.3, 135.2, 134.1, 131.7 (s, C_{Ar}), 130.3 (s, CH_{Ar}), 130.2 (d, J(P,C) = 5.0 Hz, CH_{Ar}), 130.1 (s, CH_{Ar}), 129.9 (d, J(P,C) = 5.0 Hz, CH_{Ar}), 129.8 (s, CH_{Ar}), 129.6 (d, J(P,C) = 2.0 Hz, CH_{Ar}), 129.5 (s, CH_{Ar}), 128.9 (d, J(P,C) = 4.0 Hz, CH_{Ar}), 128.2 (d, J(P,C) = 2.0 Hz, CH_{Ar}), 128.1 (d, J(P,C) = 3.0 Hz, CH_{Ar}), 125.0 (s, CH_{Im-4,5}), 124.3 (d, ³J(P,C) = 2.0 Hz, CH_{Im-4,5}), 63.1 (d, ¹J(P,C) = 53.3 Hz, PC(H)Ph), 50.8 (d, ¹J(P,C) = 60.4 Hz, CH_{Phos}), 47.2 (d, ¹J(P,C) = 60.4 Hz, CH_{Phos}), 34.7 (d, ²J(P,C) = 8.0 Hz, CH_{2Phos}), 28.9 (d, ²J(P,C) = 9.0 Hz, CH_{2Phos}), 21.0, 17.4 (s, CH_{3Mes}). HR-MS (ES⁺): 531.2568 ([M]⁺, C₃₅H₃₆N₂OP⁺; calc 531.2565).

Phosphine-imidazolium salt [10](BF₄)

According to general procedure starting from [1^{Cr}](BF₄) (1.40 g, 2.5 mmol) and *N*-(2-pyridyl)imidazole (363 mg, 2.5 mmol) phosphine-imidazolium salt [10](BF₄) (850 mg, 43%) was isolated as yellow powder after column chromatography purification using 98:2 CH₂Cl₂/MeOH mixture.

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 10.10 (s, 1H, CH_{Im-2}), 8.50 (br. d, J(H,H) = 4.8 Hz, 1H, CH_{Py}), 8.28 (t, J(H,H) = 2.0 Hz, 1H, CH_{Py}), 7.99–8.10 (m, 3H, CH_{Ar}), 7.66 (d, J_{HH} = 6.8 Hz, 2H, CH_{Ar}), 7.33–7.47 (m, 4H, CH_{Ar}), 6.37 (d, ²J(P,H) = 2.8 Hz, 1H, CHPh), 1.84–1.95 (m, 2H, CH_{2Cy}), 1.40–1.76 (m, 9H, CH_{2Cy}), 0.90–1.30 (m, 11H, CH_{2Cy}). ³¹P-NMR (162 MHz, CDCl₃, 25°C): δ 12.2 (s). ¹³C{¹H}-NMR (101 MHz, CDCl₃, 25°C): δ 149.2 (s, CH_{Py}), 145.9 (s, C_{Py}), 141.0 (s, CH_{Ar}), 137.0 (d, J(P,C) = 10.1 Hz, C_{Ar}), 133.5, 129.7 (s, CH_{Ar}), 128.6 (d, J(P,C) = 6.0 Hz, CH_{Ar}), 125.5 (s, CH_{Ar}), 122.0 (d, ³J(P,C) = 12.1 Hz, CH_{Im-4,5}), 119.4 (s, CH_{Im-4,5}), 114.5 (s, CH_{Py}), 62.3 (d, ¹J(P,C) = 24.5 Hz, CHPh), 33.8 (d, ¹J(P,C) = 18.1 Hz, CH_{2Cy}), 33.7 (d, ¹J(P,C) = 16.1 Hz, CH_{2Cy}), 31.0 (d, J(P,C) = 14.1 Hz, CH_{2Cy}), 30.7 (d, J(P,C) = 14.1 Hz, CH_{2Cy}), 30.1 (d, J(P,C) = 10.1 Hz, CH_{2Cy}), 29.4 (d, J(P,C) = 6.0 Hz, CH_{2Cy}), 27.8 (d, J(P,C) = 12.1 Hz, CH_{2Cy}), 27.6 (d, J(P,C) = 8.0 Hz, CH_{2Cy}), 27.1 (d, J(P,C) = 10.1 Hz, CH_{2Cy}), 27.0 (d, J(P,C) = 9.0 Hz, CH_{2Cy}), 26.1 (s, CH_{2Cy}). HR-MS (ES⁺): 432.2575 ([M]⁺, C₂₇H₃₅N₃P⁺; calc 432.2569).

Phosphine-imidazolium salt [11](BF₄)

According to general procedure starting from [1^{Ph}](BF₄) (1.53 g, 2.7 mmol) and *N*-[(methylthio)methyl]imidazole (350 mg, 2.7 mmol) phosphine-imidazolium salt [11](BF₄) (797 mg, 60%) was isolated as white powder after column chromatography purification using 100:1 CH₂Cl₂/MeOH mixture.

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 9.00 (s, 1H, CH_{Im-2}), 7.67–7.69 (m, 2H, CH_{Ar}), 7.57–7.63 (m, 3H, CH_{Ar}), 7.21–7.39 (m, 12H, CH_{Ar}), 6.48 (d, ²J(P,C) = 3.1 Hz, 1H, CHPh), 4.98 (d, ²J(H,H) = 12.0 Hz, 1H, CH₂), 4.90 (d, ²J(H,H) = 12.0 Hz,

1H, SCH₂), 1.81 (s, 3H, SCH₂). ³¹P{¹H}-NMR (162 MHz, CDCl₃, 25°C): δ –6.9 (s). ¹³C{¹H}-NMR (101 MHz, CDCl₃, 25°C): δ 136.1 (s, CH_{Ar}), 134.6 (d, J(P,C) = 15.1 Hz, C_{Ar}), 134.1 (d, J(P,C) = 22.1 Hz, CH_{Ar}), 133.4 (d, J(P,C) = 19.1 Hz, CH_{Ar}), 132.7 (d, J(P,C) = 14.1 Hz, C_{Ar}), 131.8 (d, J(P,C) = 9.0 Hz, C_{Ar}), 131.1, 130.2, 130.0, 129.7 (s, CH_{Ar}), 129.6 (d, J(P,C) = 9.0 Hz, CH_{Ar}), 129.4 (d, J(P,C) = 9.0 Hz, CH_{Ar}), 129.0 (d, J(P,C) = 8.0 Hz, CH_{Ar}), 121.8 (s, CH_{Im-4,5}), 121.1 (d, ³J(P,C) = 8.0 Hz, CH_{Im-4,5}), 64.1 (d, ¹J(P,C) = 15.3 Hz, PC(H)Ph), 53.2 (s, SCH₂), 14.4 (s, SCH₂). HR-MS (ES⁺): 403.1402 ([M]⁺, C₂₄H₂₄N₂SP⁺; calc 403.1398).

Phosphine-bisimidazolium salt [12](BF₄)₂

According to general procedure starting from [1^{Ph}](BF₄) (1.12 g, 2.0 mmol) and 3-((1H-imidazol-1-yl)-methyl)-1-methyl-1H-imidazolium tetrafluoroborate (500 mg, 2.0 mmol) phosphine-bisimidazolium salt [12](BF₄)₂ (428 mg, 35%) was isolated as white powder after precipitation of the crude product from CH₂Cl₂/Et₂O mixture.

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 8.93 (s, 1H, CH_{Im-2}), 8.82 (s, 1H, CH_{Im-2}), 7.72 (s, 1H, CH_{Im-4,5}), 7.61 (s, 1H, CH_{Im-4,5}), 7.59 (s, 1H, CH_{Im-4,5}), 7.49 (s, 1H, CH_{Im-4,5}), 7.39–7.43 (m, 3H, CH_{Ph}), 7.36 (s, 2H, CH_{Ph}), 7.16–7.30 (m, 10H, CH_{Ph}), 6.29 (d, ²J(H,H) = 16.0 Hz, 1H, CH₂), 6.24 (d, ²J(P,H) = 4.0 Hz, 1H, CHPh), 6.22 (d, ²J(H,H) = 16.0 Hz, 1H, CH₂), 3.73 (s, 3H, NCH₃). ³¹P{¹H}-NMR (162 MHz, CDCl₃, 25°C): δ –5.6 (s). ¹³C{¹H}-NMR (101 MHz, CDCl₃, 25°C): δ 138.2, 136.2 (s, CH_{Im-2}), 134.0 (d, ¹J(P,C) = 15.1 Hz, C_{Ph}), 133.8 (d, J(P,C) = 23.1 Hz, CH_{Ph}), 133.4 (d, J(P,C) = 20.1 Hz, CH_{Ph}), 132.7 (d, J(P,C) = 15.1 Hz, C_{Ph}), 131.9 (d, J(P,C) = 10.1 Hz, C_{Ph}), 131.0, 130.1, 129.7 (s, CH_{Ph}), 129.6 (d, J(P,C) = 9.1 Hz, CH_{Ph}), 129.5 (d, J(P,C) = 11.1 Hz, CH_{Ph}), 128.9 (d, J(P,C) = 7.0 Hz, CH_{Ph}), 124.8, 123.6, 121.8, 121.7 (s, CH_{Im-4,5}), 65.0 (d, ¹J(P,C) = 17.1 Hz, CHPh), 58.7 (s, NCH₃N), 36.6 (s, NCH₃). HR-MS (ES⁺): 525.2010 ([M+BF₄]⁺, C₂₇H₂₇BF₄N₄P⁺; calc 525.2003).

Generation of free carbenes 2d and 10 for NMR characterization

To a solution of phosphine-imidazolium salt ([2d](BF₄)) 42 mg, 0.075 mmol; [10](BF₄)) 39 mg, 0.075 mmol in dry toluene (1 mL) a 0.5 M solution of KHMDS in toluene (0.22 mL, 0.112 mmol) was added at room temperature. The resulting orange solution was sonicated for 2 min, stirred for 10 min and evaporated under vacuum. The residue was dissolved in dry C₆D₆ and the solution was filtered through a pad of Celite in a Pasteur pipette directly to NMR tube.

2d: ¹H-NMR (400 MHz, C₆D₆, 25°C): δ 7.70 (d, J(H,H) = 7.8 Hz, 2H, CH_{Ph}), 7.33 (br. d, ³J(H,H) = 1.2 Hz, 1H, CH_{Im-4,5}), 7.17–7.24 (m, 1H, CH_{Ph}), 7.13–7.15 (m overlapped with residual solvent protons, 2H, CH_{Ph}), 6.78 (br. s, 1H, CH_{Mes}), 6.71 (br. s, 1H, CH_{Mes}), 6.37 (br. d, ³J(H,H) = 1.2 Hz, 1H, CH_{Im-4,5}), 6.24 (d, ²J(P,H) = 4.1 Hz, 1H, CHPh), 2.15 (br. s, 3H, CH_{3Mes}), 2.11 (s overlapped with toluene signal, 3H, CH_{3Mes}), 1.90 (br. s, 3H, CH_{3Mes}), 1.78–1.86 (m, 2H, CH_{2Cy}), 1.70–1.76 (m, 2H, CH_{2Cy}), 1.42–1.65 (m, 2H, CH_{2Cy}), 0.92–1.32 (m, 10H, CH_{2Cy}). ³¹P{¹H}-NMR (162 MHz, C₆D₆, 25°C): δ 8.5 (s). ¹³C{¹H}-NMR (101 MHz, C₆D₆, 25°C): δ 216.2 (br. s, N₂C), 142.1 (d, J(P,C) = 13.0 Hz, C_{Ph}), 139.2, 137.2, 135.5, 135.2 (s, C_{Mes}), 129.1 (br. s, CH_{Mes}), 129.0 (d, J(P,C) = 7.3 Hz, CH_{Ph}), 128.9 (s, CH_{Ph}), 127.9 (s, CH_{Ph}), 121.2 (s, CH_{Im-4,5}), 118.4 (d, ³J(P,C) = 3.7 Hz, CH_{Im-4,5}), 62.0 (d, ¹J(P,C) = 17.3 Hz, CHPh), 34.2 (d, ¹J(P,C) = 19.9 Hz, CH_{2Cy}), 33.8 (d, ¹J(P,C) = 17.4 Hz, CH_{2Cy}), 31.4 (d, J(P,C) = 14.0 Hz, CH_{2Cy}), 31.1 (d, J(P,C) = 12.3

Hz, CH₂Cy), 30.6 (d, *J*(P,C) = 7.5 Hz, CH₂Cy), 30.5 (d, *J*(P,C) = 10.2 Hz, CH₂Cy), 28.2 (d, *J*(P,C) = 8.6 Hz, CH₂Cy), 28.1 (d, *J*(P,C) = 8.9 Hz, CH₂Cy), 28.0 (d, *J*(P,C) = 6.5 Hz, CH₂Cy), 27.9 (d, *J*(P,C) = 9.2 Hz, CH₂Cy), 26.8, 26.7 (s, CH₂Cy), 21.0 (s, CH₃Mes), 18.4, 18.1 (br. s, CH₃Mes).

10: ¹H-NMR (400 MHz, C₆D₆, 25°C): δ 8.71 (d, *J*(H,H) = 7.6 Hz, 1H, CH_{Py}), 8.23 (d, *J*_{HH} = 1.6 Hz, 1H, CH_{Im-4,5}), 8.14 (d, *J*(H,H) = 4.4 Hz, 1H, CH_{Py}), 7.67 (d, *J*(H,H) = 7.8 Hz, 2H, CH_{Ph}), 7.24 (d, *J*(H,H) = 1.6 Hz, 1H, CH_{Im-4,5}), 7.00–7.13 (m, 4H, CH_{Ph+Py}), 6.49 (t, *J*(H,H) = 7.4 Hz, 1H, CH_{Py}), 6.24 (d, ²*J*(P,H) = 4.0 Hz, 1H, CH_{Ph}), 1.76–1.82 (m, 2H, CH_{Cy}), 1.44–1.66 (m, 9H, CH₂Cy), 0.95–1.27 (m, 11H, CH₂Cy). ³¹P{¹H}-NMR (162 MHz, C₆D₆, 25°C): δ 7.8 (s). ¹³C{¹H}-NMR (101 MHz, C₆D₆, 25°C): δ 216.0 (d, ³*J*(P,C) = 7.0 Hz, N₂C), 154.3 (s, C_{Py}), 147.9 (s, C_{Py}), 141.4 (d, *J*(P,C) = 13.8 Hz, C_{Ph}), 137.9 (s, CH_{Ar}), 129.2 (d, *J*(P,C) = 7.0 Hz, CH_{Ar}), 128.9 (s, CH_{Ar}), 121.0 (s, CH_{Im-4,5}), 119.4 (d, ³*J*(P,C) = 8.0 Hz, CH_{Im-4,5}), 117.3 (s, CH_{Py}), 114.3 (s, CH_{Py}), 62.7 (d, ¹*J*(P,C) = 18.3 Hz, CH_{Ph}), 34.2 (d, ¹*J*(P,C) = 20.1 Hz, CH_{Cy}), 33.8 (d, ¹*J*(P,C) = 18.1 Hz, CH_{Cy}), 31.3 (d, *J*(P,C) = 14.1 Hz, CH₂Cy), 31.0 (d, *J*(P,C) = 12.1 Hz, CH₂Cy), 30.6 (d, *J*(P,C) = 8.0 Hz, CH₂Cy), 30.5 (d, *J*(P,C) = 10.6 Hz, CH₂Cy), 28.1 (d, *J*(P,C) = 10.1 Hz, CH₂Cy), 28.0 (d, *J*(P,C) = 5.0 Hz, CH₂Cy), 27.9 (d, *J*(P,C) = 8.0 Hz, CH₂Cy), 27.8 (d, *J*(P,C) = 9.1 Hz, CH₂Cy), 26.8, 26.6 (s, CH₂Cy).

X-ray diffraction study of compound [9](BF₄)

The single crystal was coated with paratone oil and mounted onto the goniometer. The X-ray crystallographic data were obtained at 100K from a Rigaku XtaLAB Synergy diffractometer (CuKα radiation source) equipped with an Oxford Cryosystem. The structure has been solved using ShelXT^[68] and refined by means of least-squares procedures on F² using the program CRYSTALS.^[69] The scattering factors for all the atoms were used as listed in the International Tables for X-ray Crystallography. Absorption correction was performed using a Multiscan procedure.^[70] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were set in idealized positions using riding model. Diffuse contribution of co-crystallized solvent molecules, which cannot be modelled in terms of atomic sites was removed using SQUEEZE procedure.^[71] The BF₄[−] anion was found to be disordered over two positions.

Crystal and refinement data for [9](BF₄): C₃₅H₃₆N₂OP₂BF₄, M = 618.46 g.mol^{−1}, monoclinic, C₂/c, Z = 8, a = 20.1235(1), b = 14.9989(1), c = 22.3181(1) Å, α = γ = 90°, β = 93.664(1)°, V = 6722.51(6) Å³, 82420 collected reflections, 7275 unique reflections (R_{int} = 0.032), R-factor = 0.0433, weighted R-factor = 0.0104 for 6794 contributing reflections [*I* > 2σ(*I*)]. Residual electron density 0.26/−0.40 e.Å^{−3}.

Supporting Information

Copies of original NMR spectra for all new compounds.

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Author Contribution Statement

N.L., Y.C. and D.A.V. planned and guided the research project. J.W. and S.F. carried out experimental work. C.D. performed single crystal X-ray diffraction analysis. Y.C. and D.A.V. prepared the initial draft of the manuscript. All authors have read and approved the final version of the manuscript.

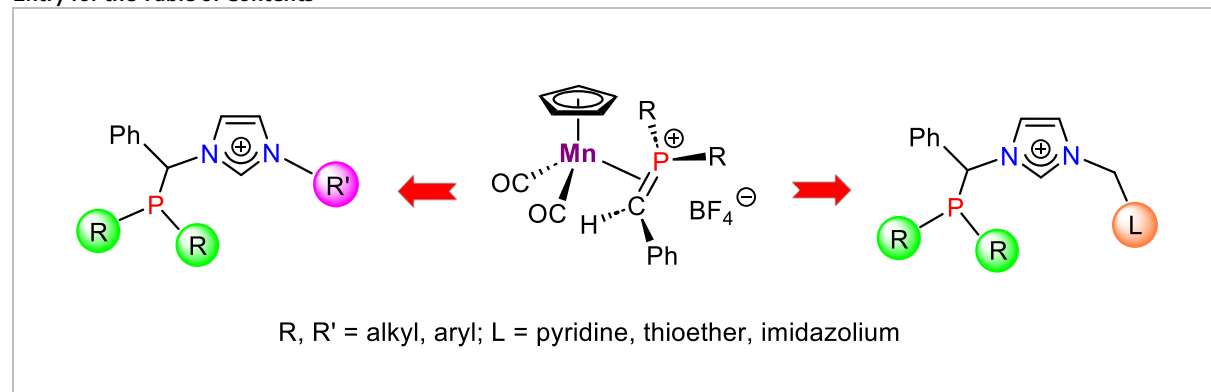
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