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A Pd(II) Complex Exhibiting Tetradentate NHC-Phosphine Ligand: On Route to Unconventional Phosponium Ylide Derivatives

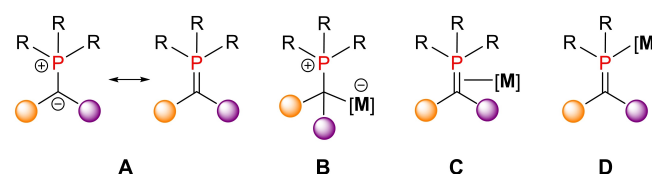
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Unusual open-chain tetradentate NHC-phosphine pre-ligand [Ph₂PCH(Ph)ImCH₂ImC(H)PhPPH₂](BF₄)₂ was prepared in a good yield by metal-mediated approach starting from Mn(I) complex [Cp(CO)₂Mn(η²-Ph₂P=C(H)Ph)](BF₄) and bis(imidazole) derivative ImCH₂Im. Its reaction with Pd(OAc)₂ afforded dicationic Pd(II) complex of bis(NHC)bis(phosphine) ligand adopting κ⁴PĈĈP

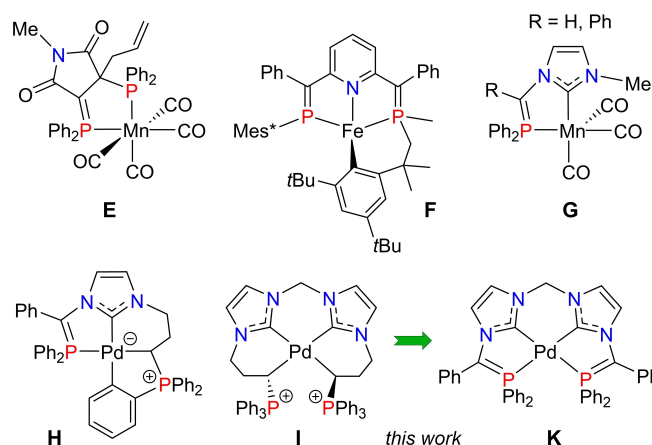
coordination mode as a mixture of two diastereomers. The deprotonation of the C(H)Ph ligand bridge in the latter using KN(SiMe₃)₂ as base provided stable complex exhibiting unconventional phosponium ylide moiety, whereas all attempts to detect the corresponding bis(ylide) derivative failed.

Introduction

Beyond traditional application in organic synthesis,^[1] phosphonium ylides (Scheme 1, A) have also been recently used in organocatalysis^[2] and as molecular bricks in the design of highly electron-rich phosphine ligands.^[3] In transition metal organometallic chemistry, phosphonium ylides typically exhibit η¹-C coordination mode^[4] (Scheme 1, B) and behave as strong σ-donor ligands. It was demonstrated that their electron-donating character is even more pronounced than that of *N*-heterocyclic carbenes (NHCs),^[5] thus motivating the association of both donor fragments within chelating scaffolds.^[6] In sharp contrast, an only precedent of η²-C,P ylide binding to the metal (Scheme 1, C) was proposed by Streubel and coll. based on NMR spectroscopy data.^[7] The last option concerns very few examples of so-called unconventional phosphonium ylides (Scheme 1, D), in which the metal fragment represents one of phosphonium substituents formally accounting for η¹-P coordination mode. The first representative example of such compounds, the Mn(I) complex E (Scheme 2) featuring stabilized ylide was described by Fenske and coll. in 1981.^[8] Later on, complex F was isolated in low yield upon the reaction of the corresponding Fe(II) bromide precursor bearing



Scheme 1. General representation of phosphonium ylides and their possible coordination modes in transition metal complexes.



Scheme 2. Known examples of transition metal complexes incorporating unconventional phosphonium ylide moieties (E-H) and Pd(II) complex K based on *P*-coordinated bis(NHC)bis(ylide) ligand targeted in this work.

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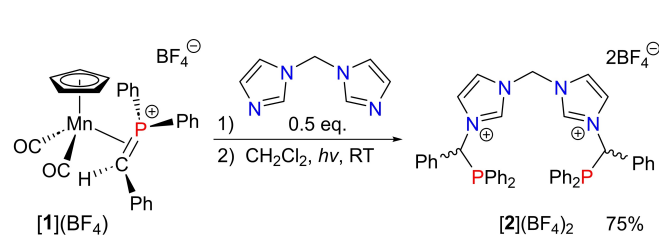
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bis(phosphaalcene)pyridine pincer ligand with [Me₂Mg(THF)₂].^[9] More recently, we have shown by DFT calculations that the 16-electron Mn(I) species G were directly involved in cooperative dihydrogen activation^[10] thus constituting the first evidence for the implication of formally pentavalent phosphorus species in metal-ligand cooperation.^[11] In continuation of our research on the design of bidentate^[12] and pincer-type^[13] ligands combining NHCs and phosphonium ylides, we have succeeded to generate and fully characterize the Pd(II) complex H (Scheme 2) by

deprotonation of the NHC–C(H)Ph–PPh₂ fragment in the corresponding cyclometallated precursor using LDA as a base.^[14] This complex incorporating both *C*- and *P*-coordinated ylides in the same structure allowed us to perform for the first time the direct comparison of their spectroscopic and bonding properties. Importantly, it was found that the presence of the phenyl substituent at the carbon atom of the unconventional ylide was essential for the stabilization of such species being persistent in solution for several hours around 0 °C. Inspired by these results and previous synthesis of Pd(II) complex **I** based on bis(NHC)bis(ylide) scaffold,^[15] we considered accessing the structurally related analogue **K** now exhibiting two unconventional ylide moieties instead of regular *C*-coordinated ones (Scheme 2). In this contribution, we report the preparation of original tetradentate bis(NHC)bis(phosphine) pre-ligand, its complexation with palladium(II) metal center and subsequent studies of *P*-coordinated phosphonium ylide derivatives.

Results and Discussion

The synthesis of the tetradentate pre-ligand **[2](BF₄)₂** (Scheme 3) incorporating two C(H)Ph units between phosphine and imidazolium moieties was carried out following the same metal-mediated approach previously used for the preparation of related bidentate and pincer NHC-phosphine architectures.^[14,16] The quaternization of the bis-imidazole derivative with two equivalents of electrophilic Mn(I) methylenephosphonium complex **[1](BF₄)** followed by the removal of [Cp(CO)₂Mn] fragments by visible light irradiation led to the formation of the target product isolated in 75% yield by column chromatography on silica under inert atmosphere. According to ³¹P NMR spectroscopy **[2](BF₄)₂** exists as a quasi-equi-molar (*ca.* 47:53) mixture of *d,l*- and *meso*-isomers exhibiting the resonances at δ_p –5.90 and –5.95 ppm in the classical region for diaryl(alkyl)phosphines. The most pertinent ¹H NMR resonances namely the signals of N₂CH (δ_H 8.93 ppm) and C(H)Ph (δ_H 6.23 ppm) fragments for each of two diastereomers are barely differentiable with a notable exception of CH₂ bridge protons appearing as a singlet at δ_H 6.12 ppm and as AB spin system centered at 6.11 ppm (²*J*_{HH} = 14.4 Hz) for racemic and *meso*-forms, respectively (Figure S1). While pincer-type phosphine-NHC-phosphine^[17] and NHC-phosphine-NHC^[18] systems are quite common in literature, the only known example of bis(NHC)bis(phosphine) ligand with macrocyclic topology was obtained by template synthesis on a Pt(II) center.^[19]



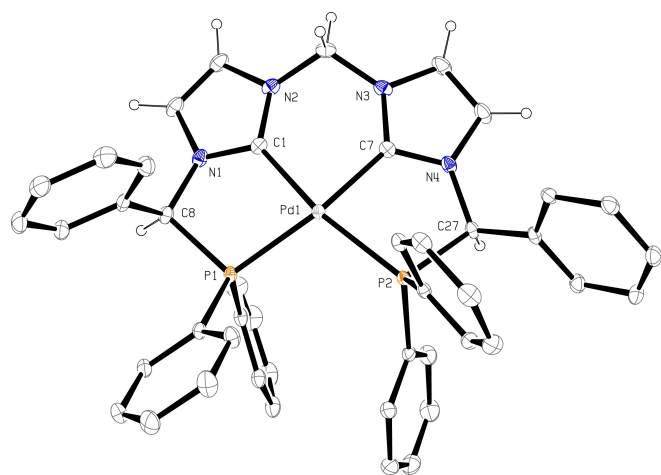
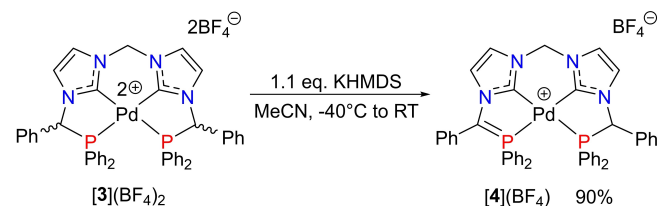


Figure 1. Molecular geometry of Pd(II) complex *meso*-[3](BF₄)₂ (the absolute configuration of the enantiomer shown is (*S*_{C8},*R*_{C27}), ellipsoids are set at 25% probability level, BF₄[−] and hydrogen atoms of phenyl groups are not shown for clarity). Selected bond distances (Å) and angles (°): Pd1–C1 1.991(2), Pd1–C7 1.980(2), Pd1–P1 2.2919(6), Pd1–P2 2.2974(6), C1–Pd1–C7 87.77(10), C1–Pd1–P1 81.77(7), C7–Pd1–P2 81.94(7), P1–Pd1–P2 107.49(2).

complexes exhibiting tetradentate L-NHC-CH₂-NHC-L ligands (L = pyridine,^[21c] 1,2,3-triazole^[21b]) are *ca.* 0.02–0.03 Å shorter than those in *meso*-[3](BF₄)₂ probably due to stronger *trans*-effect of phosphine moieties compared to those of nitrogen donor ligands.

We have attempted to generate the target Pd(II) bis(NHC)bis(ylide) derivative by double deprotonation of complex [3](BF₄)₂ under the same conditions as previously described for synthesis of **H** (Scheme 2), namely using 2.2 equivalents of LDA in THF at low temperature.^[14] Unfortunately, ³¹P NMR analysis showed the formation of intractable mixture of products accompanied by the formation of dark insoluble precipitate. Several combinations of different strong bases (LDA, KHMDS, *t*BuOK) and solvents (THF, MeCN, toluene) did not improve the situation. Considering that the expected neutral bis-ylide Pd(II) complex supported with four strongly donating ligands was probably too reactive, we next tried to obtain a cationic ylide product by single deprotonation. Gratifyingly, the treatment of [3](BF₄)₂ with 1.1 equivalents of KHMDS in acetonitrile at −40 °C smoothly afforded the complex [4](BF₄) (Scheme 5), which was isolated in *ca.* 90% yield as orange powder stable at room temperature.



Scheme 5. Synthesis of Pd(II) complex [4](BF₄) featuring unconventional phosphonium ylide ligand.

The structure of [4](BF₄) was elucidated from multi-nuclear NMR spectra. Its ³¹P spectrum showed a doublet at δ_p 53.8 ppm (²J_{pp} = 16.2 Hz) and a broad signal at δ_p 60.0 ppm, the latter being unambiguously attributed to the coordinated phosphine according to ¹H NMR spectrum with selective ³¹P decoupling. The chemical shift of the unconventional ylide in ³¹P NMR spectrum of [4](BF₄) was shifted downfield by *ca.* 24 ppm compared to that previously observed in the Pd(II) complex **H**.^[14] ¹H NMR spectrum of [4](BF₄) showed characteristic signals of the remaining C(H)Ph fragment at δ_H 6.25 ppm (d, ²J_{PH} = 10.1 Hz), while the methylene bridge between two NHC groups appeared as an AB spin system centered at δ_H 6.45 ppm (²J_{HH} = 12.8 Hz) being consistent with the presence of a chiral center in the close proximity. The loss of symmetry within bis(NHC) scaffold was additionally confirmed by the presence of four distinct CH imidazolylene resonances in ¹H and ¹³C NMR spectra. The characteristic carbenic signals were found as two doublets of doublets at δ_C 178.0 (²J_{PC} = 148.0 Hz, ²J_{PC} = 15.6 Hz) and 170.9 ppm (²J_{PC} = 134.8 Hz, ²J_{PC} = 2.8 Hz) revealing a *ca.* three-fold increase of the coupling constant with the phosphorus nuclei in *trans*-position compared to those in Pd(II) precursor [3](BF₄)₂. Finally, the ¹³C NMR resonances of C(H)Ph, CH₂ and ylide moieties were unambiguously attributed using JMOD and HSQC spectra being observed at δ_C 71.9 (dd, ¹J_{PC} = 36.3 Hz, ³J_{PC} = 2.8 Hz), 64.8 (s) and 54.6 ppm (d, ¹J_{PC} = 3.7 Hz), respectively. While the ¹³C chemical shift of the unconventional phosphonium ylide in complex [4](BF₄) was found to be quite similar to that in its Pd(II) analogue **H** (δ_H 68.0 ppm (d, ¹J_{PC} = 83.1 Hz)),^[14] the value of the ¹J_{PC} coupling constant was surprisingly small. Unfortunately, despite all efforts we were unable to grow single crystals of complex [4](BF₄) suitable for X-ray diffraction to get more information on its metrical features.

Conclusions

We have developed an efficient synthetic route to the linear phosphine-NHC-NHC-phosphine pre-ligand, which was until now a missing link in the family of tetradentate L₄-type ligands featuring bis(NHC) core and shown that this bis(imidazolium) salt can be easily coordinated to Pd(II) center in κ⁴P²C²P mode. The resulting dicationic complex can be selectively deprotonated at the C(H)Ph bridge between phosphine and NHC fragments to form stable product exhibiting nonconventional phosphonium ylide ligand thus demonstrating the potential generality of this approach towards such exotic organophosphorus species. Though in this case we failed to detect the complex bearing symmetric bis(NHC)bis(ylide) ligand due to its instability, we can expect that this challenge may be readily addressed in the future with more electron-deficient metal center.

Experimental Section

General considerations. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen.

Dry and oxygen-free organic solvents were obtained using LabSolv (Innovative Technology) solvent purification system. Complex [1](BF₄)^{16c} and bis(imidazol-1-yl)methane²⁵ⁱ were prepared according to previously described methods, all other reagents were used as received. Photochemical demetallation was performed in 125 mL reactor with an immersed 150 W/Hg medium pressure lamp cooled by Pyrex jacket with circulating water. Chromatographic purification was performed on silica (0.060–0.200 mm, 60 Å, Aldrich) or activated neutral alumina (Brockmann II, 0.050–0.200 mm Acros Organics) using solvents deoxygenated by nitrogen bubbling. Solution IR spectra were recorded in 0.1 mm CaF₂ cells using a Perkin Elmer Frontier FT-IR spectrometer and given in cm⁻¹ with relative intensity in parentheses. ¹H, ³¹P and ¹³C NMR spectra were obtained on Bruker Avance 400HD and Avance 400 Neo spectrometers and referenced to the residual signals of deuterated solvent (¹H and ¹³C) or to 85% H₃PO₄ (³¹P). When necessary, additional information on the signal attribution was obtained using ¹³C{¹H, ³¹P}, *J*-modulated spin-echo (JMOD) ¹³C{¹H} and ¹H-¹³C HSQC experiments. High-resolution MS spectra (ESI mode) were performed by the mass spectrometry service of the "Institut de Chimie de Toulouse" using a Xevo G2 QToF (Waters) spectrometer.

Synthesis of pre-ligand [2](BF₄)₂. To a solution of Mn(II) complex [1](BF₄)₂ (1.06 g, 2.0 mmol) in CH₂Cl₂ (50 mL) solid bis(imidazol-1-yl)methane (148 mg, 1.0 mmol) was added at room temperature under vigorous stirring. The color of the reaction mixture changed from orange to yellow and IR monitoring showed complete transformation of the starting [1](BF₄)₂ (ν_{CO} 2034, 1981 cm⁻¹) into the mixture of phosphine complexes [(CpMn(CO)₂](μ-Ph₂PC(H)Ph)MnCH₂ImC(H)PhPPH₂)](BF₄)₂ (ν_{CO} 1940, 1872 cm⁻¹). The resulting solution was transferred via canula to the photochemical reactor, diluted with CH₂Cl₂ (50 mL) and irradiated under vigorous stirring until CO evolution ceased (ca. 30 min). The resulting pale yellow suspension was filtered through pad of Celite, the filtrate was shaken with saturated aqueous solution of NaHCO₃ (2 mL) and evaporated under vacuum. The yellow residue was purified by column chromatography on silica (15×2 cm) under nitrogen atmosphere. Several yellow and orange bands (discarded) were first removed with pure CH₂Cl₂, followed by pale-yellow band of the desired product eluted with CH₂Cl₂/THF 95:5 mixture. After evaporation of the eluate and drying the residue under vacuum target pre-ligand [2](BF₄)₂ (650 mg, 75% yield) was obtained as pale-yellow powder. NMR assignment: ^ameso-isomer (53%), ^b*d,l*-isomer (47%), no adjustment of integration intensities in ¹H spectra between two isomers have been performed.

[2](BF₄)₂: ¹H NMR (400.1 MHz, CDCl₃, 25 °C): δ 8.93^{ab} (br. s, 4H, CH_{Im-2}), 7.71–7.63^{ab} (m, 12H, CH_{Im-4,5}+CH_{Ph}), 7.51^b (br. s, 2H, CH_{Im-4,5}), 7.48^a (br. s, 2H, CH_{Im-4,5}), 7.41–7.26^{ab} (m, 30H, CH_{Ph}), 7.24–7.07^{ab} (m, 22H, CH_{Ph}), 6.27^a (d, ²J_{HH} = 14.4 Hz, 1H, NCH₂N), 6.23^{ab} (br. s, 4H, PCHPh), 6.12^b (s, 2H, NCH₂N), 5.95^a ppm (d, ²J_{HH} = 14.4 Hz, 1H, NCH₂N); ³¹P{¹H} NMR (162.0 MHz, CDCl₃, 25 °C): δ -5.9^b, -5.95^a ppm; ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25 °C): δ 136.2^b (d, ²J_{PC} = 2.2 Hz, C_{ipso Ph}), 133.9^b (d overlapped with another d signal, ¹J_{PC} = 4.5 Hz, CH_{Ph}), 133.85^a (d, ¹J_{PC} = 14.0 Hz, C_{ipso PPH₂}), 133.8^b (d overlapped with another d signal, ¹J_{PC} = 14.8 Hz, C_{ipso PPH₂}), 133.6^a (d, ¹J_{PC} = 4.5 Hz, CH_{Ph}), 133.2^{ab} (d, ¹J_{PC} = 19.3 Hz, CH_{Ph}), 132.65^a (d, ¹J_{PC} = 14.7 Hz, C_{ipso PPH₂}), 132.60^b (d, ¹J_{PC} = 14.7 Hz, C_{ipso PPH₂}), 131.6^{ab} (d, ¹J_{PC} = 10.6 Hz, CH_{Ph}), 131.1^{ab} (s, CH_{Ph}), 130.3^b (s, CH_{Ph}), 130.2^a (s, CH_{Ph}), 129.95^b (s, CH_{Ph}), 129.9^a (s, CH_{Ph}), 129.6^b (d overlapped with another d signal, ¹J_{PC} = 7.6 Hz, CH_{Ph}), 129.55^b (d overlapped with another d signal, ¹J_{PC} = 6.9 Hz, CH_{Ph}), 129.45^a (d, ¹J_{PC} = 6.4 Hz, CH_{Ph}), 129.0^a (d, ¹J_{PC} = 7.4 Hz, CH_{Ph}), 123.5^{ab} (s, CH_{Im-4,5}), 121.85^a (br. d, ³J_{PC} = 5.0 Hz, CH_{Im-4,5}), 121.80^b (br. d, ³J_{PC} = 6.0 Hz, CH_{Im-4,5}), 65.4^b (d, ¹J_{PC} = 17.8 Hz, PCHPh), 65.35^a ppm (d, ¹J_{PC} = 18.0 Hz, PCHPh). HRMS (ES⁺): *m/z* 785.2758 [M-BF₄]⁺, calcd for C₄₅H₄₀BF₄N₄P₂ 785.2758 (ε_r = 0.1 ppm).

Synthesis of Pd(II) complex [3](BF₄)₂. To a solution of pre-ligand [2](BF₄)₂ (218 mg, 0.25 mmol) in MeCN (5 mL) solid Pd(OAc)₂ (56 mg, 0.25 mmol) was added at room temperature. The reaction mixture was stirred at 40 °C for 2 h and then filtered through a short alumina column (5×1 cm) using MeCN as eluent. The resulting orange solution was evaporated under vacuum and the residue was thoroughly washed with toluene (2×10 mL) and toluene/THF mixture (2×10 mL) to afford after drying under vacuum complex [3](BF₄)₂ (195 mg, 80%) as orange-brown powder. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of ether into the solution of complex [3](BF₄)₂ in MeCN at room temperature. NMR assignment: ^ameso-isomer (47%), ^b*d,l*-isomer (53%), no adjustment of integration intensities in ¹H spectra between two isomers have been performed.

[3](BF₄)₂: ¹H NMR (400.1 MHz, CD₃CN, 25 °C): δ 7.82^a (br. s, 2H, CH_{Im-4,5}), 7.80^b (br. s, 2H, CH_{Im-4,5}), 7.63–7.49^{ab} (m, 9H, CH_{Ph}), 7.44–7.19^{ab} (m, 24H, CH_{Ph}+CH_{Im-4,5}), 7.14^{ab} (t, ¹J_{HH} = 7.7 Hz, 6H, CH_{Ph}), 7.08–7.00^{ab} (m, 11H, CH_{Ph}), 6.96^b (d, ²J_{PH} = 6.4 Hz, 2H, PCHPh), 6.92^{ab} (d, ¹J_{HH} = 7.8 Hz, 4H, CH_{Ph}), 6.88–6.81^{ab} (m, 6H, PCHPh+CH_{Ph}), 6.80–6.71^{ab} (m, 8H, NCH₂N+CH_{Ph}), 6.68^b ppm (s, 2H, NCH₂N); ³¹P{¹H} NMR (162.0 MHz, CD₃CN, 25 °C): δ 60.1^b, 59.4^a ppm; ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 25 °C): δ 168.8^b (dd, ²J_{PC} = 49.2 Hz, ²J_{PC} = 15.2 Hz, Pd–CN₂), 167.5^a (dd, ²J_{PC} = 49.2 Hz, ²J_{PC} = 15.2 Hz, Pd–CN₂), 136.5^b (vt, ¹J_{PC} = 7.0 Hz, CH_{Ph}), 136.2^a (vt, ¹J_{PC} = 6.8 Hz, CH_{Ph}), 134.0^a (br. vt, ²J_{PC} = 1.5 Hz, C_{ipso Ph}), 133.9^b (br. vt, ²J_{PC} = 1.5 Hz, C_{ipso Ph}), 133.8^{ab} (br. s, CH_{Ph}), 133.4^a (s, CH_{Ph}), 133.35^{ab} (vt, ¹J_{PC} = 12.0 Hz, CH_{Ph}), 133.3^b (s, CH_{Ph}), 130.7^{ab} (vt, ¹J_{PC} = 5.0 Hz, CH_{Ph}), 130.3^a (s, CH_{Ph}), 130.1^b (s, CH_{Ph}), 129.9^b (s, CH_{Ph}), 129.7^a (s overlapped with vt signal, CH_{Ph}), 129.7^b (vt, ¹J_{PC} = 6.0 Hz, CH_{Ph}), 129.4^a (vt, ¹J_{PC} = 6.0 Hz, CH_{Ph}), 128.5^{ab} (br. s, CH_{Ph}), 126.7^b (dd, ¹J_{PC} = 47.3 Hz, ³J_{PC} = 3.5 Hz, C_{ipso PPH₂}), 125.8^a (dd, ¹J_{PC} = 47.3 Hz, ³J_{PC} = 3.5 Hz, C_{ipso PPH₂}), 125.1^{ab} (br. s overlapped with dd signal, CH_{Im-4,5}), 125.8^a (dd overlapped with singlet signal, ¹J_{PC} = 47.3 Hz, ³J_{PC} = 3.5 Hz, C_{ipso PPH₂}), 124.0^b (dd, ¹J_{PC} = 49.2 Hz, ³J_{PC} = 3.5 Hz, C_{ipso PPH₂}), 123.0^a (vt, ¹J_{PC} = 5.7 Hz, CH_{Im-4,5}), 122.8^b (vt, ¹J_{PC} = 6.0 Hz, CH_{Im-4,5}), 68.8–68.2^{ab} (m, PCHPh), 66.3^a (s, NCH₂N), 66.1^b ppm (s, NCH₂N). HRMS (ES⁺): 401.0809 [M]²⁺, calcd for C₄₅H₃₈N₄P₂Pd 401.0811 (ε_r = 0.5 ppm).

Synthesis of Pd(II) complex [4](BF₄)₂. To a solution of complex [3](BF₄)₂ (48 mg, 0.05 mmol) in MeCN (5 mL) cooled to –40 °C KHMDS (110 μL of 0.5 M solution in toluene, 0.055 mmol) was added dropwise under vigorous stirring. The reaction mixture was allowed to reach slowly room temperature and the resulting orange solution was filtered through Celite and evaporated under vacuum. The orange residue was washed with ether (5 mL) and thoroughly dried under vacuum to afford [4](BF₄)₂ (40 mg, 90% yield) as orange powder.

[4](BF₄)₂: ¹H NMR (400.1 MHz, CD₃CN, 25 °C): δ 7.93–7.77 (m, 2H, CH_{Ph}), 7.67 (t, ¹J_{HH} = 8.1 Hz, 2H, CH_{Ph}), 7.60 (s, 1H, CH_{Im-4,5}), 7.49 (s, 1H, CH_{Im-4,5}), 7.44 (br. d, ¹J_{HH} = 6.3 Hz, 4H, CH_{Ph}), 7.39–7.14 (m, 12H, CH_{Im-4,5}+CH_{Ph}), 7.12–7.04 (m, 4H, CH_{Im-4,5}+CH_{Ph}), 6.94 (t, ¹J_{HH} = 7.7 Hz, 2H, CH_{Ph}), 6.88 (t, ¹J_{HH} = 7.0 Hz, 1H, CH_{Ph}), 6.79–6.64 (m, 5H, CH_{Ph}), 6.45 (AB system, ²J_{HH} = 12.8 Hz, 2H, NCH₂N), 6.25 ppm (d, ²J_{PH} = 10.1 Hz, 1H, PCHPh); ³¹P{¹H} NMR (162.0 MHz, CD₃CN, 25 °C): δ 60.0 (br. s, PCHPh), 53.8 ppm (d, ²J_{PP} = 16.2 Hz, P=CPh); ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 25 °C): δ 178.0 (dd, ²J_{PC} = 148.0 Hz, ²J_{PC} = 15.6 Hz, Pd–CN₂), 170.9 (dd, ²J_{PC} = 134.8 Hz, ²J_{PC} = 2.8 Hz, Pd–CN₂), 149.1 (d, ¹J_{PC} = 40.0 Hz, C_{ipso PPH₂}), 147.5 (dd, ¹J_{PC} = 40.8 Hz, ³J_{PC} = 8.7 Hz, C_{ipso PPH₂}), 138.6 (s, C_{ipso Ph}), 137.4 (d, ¹J_{PC} = 12.9 Hz, CH_{Ph}), 133.5 (d, ¹J_{PC} = 2.4 Hz, CH_{Ph}), 132.7 (d, ¹J_{PC} = 10.5 Hz, CH_{Ph}), 132.1 (d, ¹J_{PC} = 2.3 Hz, CH_{Ph}), 130.3 (d, ¹J_{PC} = 11.7 Hz, CH_{Ph}), 130.1 (d, ¹J_{PC} = 10.1 Hz, CH_{Ph}), 129.9 (d overlapped with singlet signal, ¹J_{PC} = 5.0 Hz, CH_{Ph}), 129.9 (s overlapped with doublet signal, CH_{Ph}), 129.8 (d, ¹J_{PC} = 2.0 Hz, CH_{Ph}), 129.5 (br. s, CH_{Ph}), 129.4 (s, CH_{Ph}), 129.3 (d, ¹J_{PC} = 9.8 Hz, CH_{Ph}), 129.0 (br. d, ¹J_{PC} = 2.0 Hz, CH_{Ph}), 128.9 (s, CH_{Ph}), 128.4 (d, ¹J_{PC} = 9.6 Hz, CH_{Ph}), 128.3 (d, ¹J_{PC} = 9.6 Hz, CH_{Ph}), 125.0 (d, ³J_{PC} = 4.1 Hz, CH_{Im-4,5}), 124.8 (d,

$^3J_{PC}=3.4$ Hz, $CH_{lm-4,5}$), 122.9 (d, $^3J_{PC}=3.8$ Hz, $CH_{lm-4,5}$), 121.1 (dd, $^3J_{PC}=7.3$ Hz, $^4J_{PC}=3.1$ Hz, $CH_{lm-4,5}$), 71.9 (dd, $^1J_{PC}=36.3$ Hz, $^3J_{PC}=2.8$ Hz, PCHPh), 64.8 (s, NCH_2N), 54.6 ppm (d, $^1J_{PC}=3.7$ Hz, P=CPh). HRMS (ES⁺): m/z 819.1661 [M+H₂O]⁺, calcd for C₄₅H₃₉N₄OP₂Pd 819.1650 ($\epsilon_r=1.3$ ppm).

X-ray diffraction study. X-ray diffraction data were collected at 100 K on a Bruker Kappa Apex2 diffractometer using MoK α radiation ($\lambda=0.71073$ Å, graphite monochromator). The structure was solved using the by direct methods using SUPERFLIP program^[26] and refined by means of least-square procedures on F using CRYSTALS.^[27] Absorption correction was performed using a multi-scan procedure. All non-hydrogen atoms were allowed to vibrate anisotropically. The hydrogen atoms were set in idealized positions (R_3CH , C–H=0.96 Å; R_2CH_2 , C–H=0.97 Å; RCH_3 , C–H=0.98 Å; $C(sp^2)$ –H=0.93 Å; U_{iso} 1.2 or 1.5 times greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and their positions refined as “riding” atoms. Hydrogen atoms could not be located on the co-crystallized water molecules with partial occupancy.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

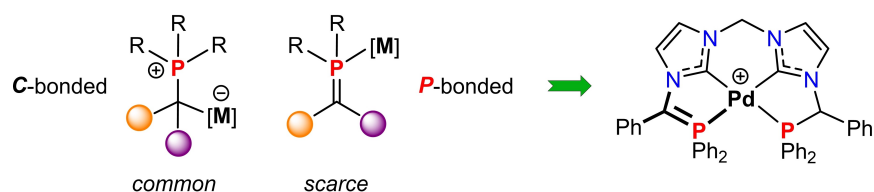
The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Phosphines · Phosphonium ylides · N-heterocyclic carbenes · Palladium · Polydentate ligands

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RESEARCH ARTICLE



Phosphonium ylides are typically coordinated to transition metals at the ylidic C-atom and only few examples of alternative P-bonding mode have been described so far. In this contribu-

tion we report an efficient synthesis of a stable Pd(II) complex incorporating a P-metalla-substituted phosphonium ylide moiety.

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A Pd(II) Complex Exhibiting Tetradentate NHC-Phosphine Ligand: On Route to Unconventional Phosphonium Ylide Derivatives

