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Introduction

The influence of Lewis acids in catalysis cannot be underestimated. While most efforts have focused on using them as the sole mediators of chemical transformations,^{1–5} few examples have been reported that discuss the role of Lewis acids as co-activators in homogeneous catalysis.^{6–9} These are related to heterogeneous processes,^{10,11} with a singular example discussing the role of potassium ions on the hydrogenation of dinitrogen in the Haber–Bosch process,¹² and biological systems, with several examples reporting that Lewis acids are necessary cofactors that help modulate the redox properties of the oxygen-evolving complex's manganese cluster and likely its reactivity.^{13–17} In organic synthesis, Shibasaki's rare-earth alkali-metal heterobimetallic complexes¹⁸ are among the most enantioselective and broadly used catalysts to date,^{19–21} but few studies discuss the role of Lewis acids in applications of late transition metals, in general, and of carbene complexes, in particular.^{22–24}

Transition metal carbenes are of vital importance to science and have witnessed a tremendous progress in their applications in the past few decades.^{25–32} Late transition metal complexes with N-heterocyclic,^{33,34} carbocyclic,³⁵ and heteroatom stabilized carbene ligands^{36–38} have been extensively studied as a consequence; however, the corresponding non-heteroatom stabilized species, $[M=CRR']$ ($R, R' = \text{alkyl or H}$), are less explored.^{39–45} This situation is even more pronounced for group 10 metals, likely because these metals are too electron rich to stabilize the $M=C$ bond. Pioneering work by Hillhouse showed that a Ni(0) carbene containing a CPh_2 moiety could be isolated by the thermolysis or photolysis of its diphenyldiazoalkane precursor.^{46,47} The isolation

of the corresponding Pd and Pt carbenes is, however, more challenging than that of nickel complexes,^{48–54} because of the highly reactive nature of the former.^{55,56} On the other hand, these species are crucial intermediates in a variety of catalytic transformations,^{57,58} such as palladium carbene mediated cyclopropanations, cross-coupling with diazo compounds, and migratory insertion reactions.⁵⁹

It is worth mentioning that only two examples of cationic Pd(II) carbene complexes are known (Chart 1, type A), synthesized *via* triflate or hydride abstraction, and that their reactivity has not been studied.^{48,49} A salt metathesis strategy was also reported for the synthesis of methanediide-based Pd(II) carbene complexes.^{50,51} We have recently applied dehydrohalogenation reactions⁶⁰ to synthesize Pd(II) carbene complexes, $[\{PC(sp^2)-P\}^R Pd(PMe_3)]$ ($R = H$, $[PC(sp^2)P]^H = \text{bis}[2-(\text{di-iso-propylphosphino})\text{phenyl}]\text{methylene}$; $R = {^t\text{Bu}}$, $[\{PC(sp^2)P\}^{{^t\text{Bu}}} = \text{bis}[2-(\text{di-iso-propylphosphino})-4-\text{tert-butylphenyl}]\text{methylene}$).^{61–63} Interestingly, the $Pd-C_{\text{carbene}}$ bonds in these compounds are best described as ylide-like (Chart 1, type B), as demonstrated by their strong nucleophilic reactivity toward polar substrates (MeI, HCl, MeOH, *para*-toluidine),⁶¹ strong Lewis acids,⁶² C–H⁶⁴ and Si–H⁶⁵ bond activation reactions. Furthermore, our recent study on the redox-induced umpolung of palladium carbenes revealed that the radical carbene $[\{PC(sp^2)P\}^{{^t\text{Bu}}} PdI]$ (1, Chart 1, type C) bridges cationic and anionic carbenes *via* reversible one-electron transfer processes.^{66,67}

We reasoned that the presence of iodide as a leaving group in 1 would facilitate its substitution with various anionic nucleophiles to afford new radical carbene species, which would

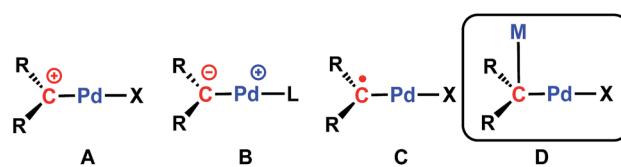


Chart 1 Illustration of known palladium carbene complexes: (A) cationic carbene; (B) ylide-like carbene; (C) radical carbene; (D) heterobimetallic carbene discussed in this work.

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generate Pd(II) carbenes with functional groups when subsequent one-electron reductions are applied. Herein, we report a sequential substitution/reduction reaction of the radical carbene **1** to form heterobimetallic Pd–K carbene complexes featuring amides or benzyl ligands that represent rare examples of late transition metal complexes containing Pd–C_{carbene}–M units (Chart 1, type D). Such bonding motifs were recently proposed to be instrumental in the hydroarylation of dienes catalysed by rhodium carbodicarbene complexes, but structural characterization was not available.²²

Results and discussion

Synthesis and characterization of metal complexes

Treatment of **1** with potassium amides, R¹R²NK, in THF afforded new radical complexes, $[\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{PdNR}^1\text{R}^2]$ (**2**: R¹ = H, R² = ^pTol; **3**: R¹ = R² = Ph, Scheme 1), which were crystallized from *n*-pentane at -35°C as dark-green crystals in high yield. As observed for **1**,⁶⁷ **2** and **3** are silent by ¹H and ³¹P NMR spectroscopy and are thermally robust. The effective magnetic moments μ_{eff} of $1.70\ \mu_{\text{B}}$ and $1.54\ \mu_{\text{B}}$ obtained using the Evans method⁶⁸ indicated an *S* = 1/2 ground state for both compounds. EPR spectra of radicals **2** and **3** (Fig. 1) exhibit similar hyperfine patterns arising from an interaction of the unpaired electron with three pairs of magnetically equivalent protons, one nitrogen nucleus, and a ¹⁰⁵Pd nucleus. As the natural abundance of the magnetic ¹⁰⁵Pd isotope is 22.33%, each spectrum exhibits contributions from the non-magnetic palladium isotope (strong, well-resolved central signal) and the ¹⁰⁵Pd isotope (broad wings). Proton hyperfine couplings were assigned to protons of the phenyl rings adjacent to the radical center.

The solid state molecular structures of **2** and **3** are consistent with their radical carbene nature (Fig. 2): both contain square-planar palladium centers bound to sp² hybridized backbone carbons (Σ_{angles} at C_{carbene} are 359.9° for **2** and 360.0° for **3**). The Pd–C_{carbene} distances in **2** ($2.019(2)\ \text{\AA}$) and **3** ($2.024(2)\ \text{\AA}$) are comparable to each other and close to the value of $2.022(3)\ \text{\AA}$ in **1**.⁶⁷ Trigonal planar geometries were observed for both amide nitrogen atoms in **2** and **3**, with the amide planes roughly

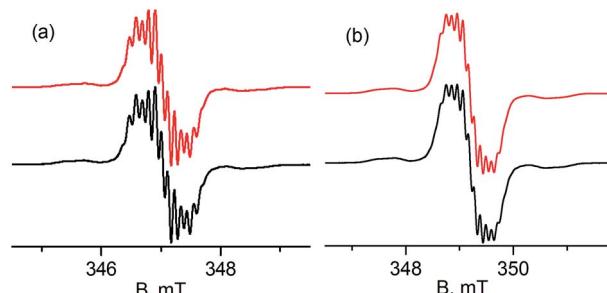
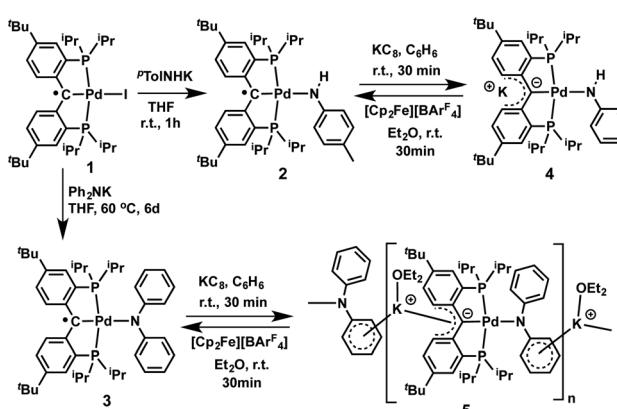


Fig. 1 Experimental (black) and simulated (red) X-band EPR spectra of $10^{-4}\ \text{M}$ toluene solutions of radicals **2** (a) and **3** (b) at $298\ \text{K}$. Simulation parameters for **2**: $a_1(2\text{H}) = 0.32\ \text{mT}$, $a_2(2\text{H}) = 0.13\ \text{mT}$, $a_3(2\text{H}) = 0.11\ \text{mT}$, $a(\text{N}) = 0.09\ \text{mT}$, $a^{105}\text{Pd} = 0.47\ \text{mT}$, $g = 2.0088$; for **3**: $a_1(2\text{H}) = 0.31\ \text{mT}$, $a_2(2\text{H}) = 0.13\ \text{mT}$, $a_3(2\text{H}) = 0.10\ \text{mT}$, $a(\text{N}) = 0.09\ \text{mT}$, $a^{105}\text{Pd} = 0.51\ \text{mT}$, $g = 2.0079$. Contribution from the ¹⁰⁵Pd species is 22.33% for both radicals.

perpendicular to the planes defined by C_{carbene}, C(11), and C(21) or C(11)[#] (80.6° for **2** and 85.8° for **3**). A longer Pd–N distance of $2.149(2)\ \text{\AA}$ was observed in **3** compared to $2.0787(18)\ \text{\AA}$ for **2**, attributed to steric reasons.

Both radical complexes were subsequently treated with an equivalent of KC₈ in benzene, and the corresponding diamagnetic heterobimetallic complexes $[\text{K}(\text{OEt}_2)_n]\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{PdNR}^1\text{R}^2]$ (**4**: R¹ = H, R² = ^pTol, n = 0; **5**: R¹ = R² = Ph, n = 1) were obtained in high yield (Scheme 1). Both compounds are only soluble in ethereal solvents and were recrystallized by diethyl ether/*n*-pentane diffusion at ambient temperature. The solid state molecular structure of **5** was determined by X-ray diffraction studies (Fig. 3). Compound **5** exists as a notable polymer in which the anionic $[\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{PdNPh}_2]$ moieties are bridged by potassium ions through the carbene units and one phenyl ring of the amide group. The average K–C distances are slightly shorter when potassium binds the phenyl ring of the amide group rather than the carbene moiety ($3.08\ \text{\AA}$ vs. $3.17\ \text{\AA}$). The coordination sphere of potassium was further completed by an additional diethyl ether molecule. The C_{carbene} carbon



Scheme 1 Synthesis of heterobimetallic carbene complexes **4** and **5**.

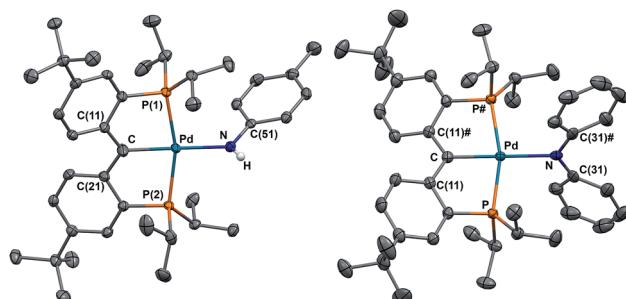


Fig. 2 Thermal-ellipsoid (35% probability) representation of **2** (left) and **3** (right); most hydrogen atoms were removed for clarity. Selected distances [\AA] and angles [$^\circ$] for **2**: Pd–C 2.019(2), Pd–P(1) 2.2983(5), Pd–P(2) 2.2841(5), Pd–N 2.0787(18), Pd–C–C(11) 118.57(15), Pd–C–C(21) 119.30(15), C(11)–C–(21) 121.98(19); for **3**: Pd–C 2.024(2), Pd–P 2.3021(5), Pd–N 2.149(2), Pd–C–C(11) 118.97(11), C(11)–C–(11)[#] 122.1(2).



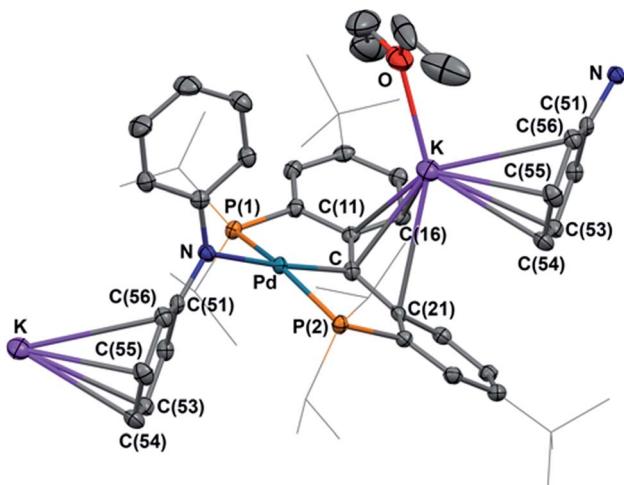


Fig. 3 Thermal-ellipsoid (35% probability) representation of 5; most hydrogen atoms were removed for clarity. Selected distances [Å] and angles [°]: Pd–C 2.043(2), Pd–P(1) 2.2827(5), Pd–P(2) 2.3064(5), Pd–N 2.1445(16), K–C 2.939(2), K–C(11) 3.047(2), K–C(21) 3.292(2), K–C(16) 3.069(2), K–C(53) 3.240(2), K–C(54) 3.004(2), K–C(55) 3.062(2), K–C(56) 3.372(2), Pd–C–C(11) 118.45(14), Pd–C–C(21) 118.31(14), C(11)–C(21) 123.14(18).

retains its trigonal planar geometry (Σ angles at C_{carbene} are 359.9°) with a Pd–C_{carbene} distance of 2.043(2) Å, which is shorter than the corresponding value of 2.076(3) Å in $[\{PC(sp^2)-P\}^{tBu}Pd(PMe_3)]$.⁶² The trigonal planar geometry at the amide nitrogen was also retained, but the dihedral angle between the amide plane and the plane defined by C_{carbene}, C(11) and C(21) was much smaller than that in 3 (59.4° vs. 85.8°), probably due to the more congested environment found in the polymer.

Due to its poor solubility in non-coordinating solvents, the solution behaviour of 5 was studied in THF-*d*₈. The ¹H NMR spectrum in THF-*d*₈ recorded at 298 K showed the peaks for the free Et₂O at δ = 3.39 (q) and 1.12 (t) ppm, thus indicating its labile coordination that led to its displacement by the THF-*d*₈ molecules. Unlike the polymeric structure observed in the solid state, 5 exhibited a C₂ symmetry in the THF-*d*₈ solution, as evidenced by only a broad peak at δ = 48.64 ppm ($\Delta\nu^{1/2} \approx 870$ Hz) in the ³¹P{¹H} NMR spectrum, as well as three broad peaks for the ¹Pr (δ = 1.98 and 1.14 ppm) and ¹Bu (δ = 1.06 ppm) groups. Therefore, the polymeric structure of 5 is disrupted in the donor solvent and even in the presence of a small amount of THF-*d*₈ since the ¹H NMR spectrum of 5 in C₆D₆ with 2 drops of THF-*d*₈ also showed C₂ symmetry.

Interestingly, the NPh₂ group on palladium exhibited three well-resolved peaks at δ = 7.35 (d), 6.80 (t), and 6.18 (t) ppm in the ¹H NMR spectrum of 5 in THF-*d*₈, however, no resonances were observed from the phenyl rings of the supporting ligand in both ¹H and ¹³C{¹H} NMR spectra. The variable temperature NMR spectra recorded in the temperature range of 208 to 323 K in THF-*d*₈ did not show any changes for these resonances. Only broadening of all the other peaks was observed in the ¹H NMR spectrum at 208 K, while a relatively sharp ($\Delta\nu^{1/2} \approx 320$ Hz) peak was found in the ³¹P{¹H} NMR spectrum (see Fig. S35 and

S36†). The phenyl rings of the supporting ligand are NMR silent in this whole temperature range. It is known that larger alkali metals such as potassium prefer anionic units that can delocalize the electron density, thus shifting the coordination of potassium away from the carbanion to the peripheral phenyl rings, leading to an η^6 -coordination mode.^{69,70} Therefore, the observed solution behaviour might be explained by a fast motion of the potassium ions between the two phenyl rings of the supporting ligand that cannot be frozen out at 208 K, causing a C₂ symmetry on the NMR time scale. A comparable system has been reported for arene complexes of yttrium supported by a macrocyclic [P₂N₂] ligand ([P₂N₂] = [PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh]).⁷¹ However, since all the signals from the phenyl rings of the supporting ligand could not be observed in the whole temperature range, a non-dynamic process caused by the formation of other polymers or oligomers containing bridging potassium ions cannot be ruled out.⁷²

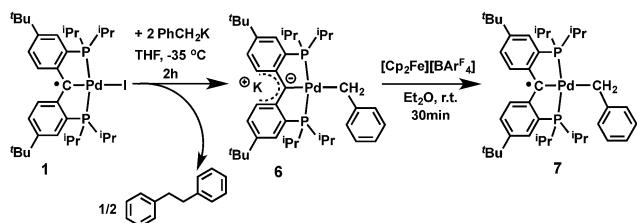
The ¹H NMR spectrum of 4 in THF-*d*₈ also exhibited a similar C₂ symmetry as observed for 5. No coordination of diethyl ether was observed, even though 4 was crystallized from a diethyl ether/n-pentane mixture, indicating a slightly different bonding mode of potassium in 4, caused by the different amide substituent on palladium. Unlike those in 5, the phenyl groups from the supporting ligand in 4 exhibited three broad singlets at δ = 7.23, 6.61 and 6.54 ppm in the ¹H NMR spectrum. Only one sharp singlet at δ = 46.36 ppm was observed in the ³¹P{¹H} NMR spectrum. Therefore, a similar polymeric chain can be proposed for complex 4 (*vide infra*). Notably, the proton of the NH group appears as a singlet at δ = 1.33 ppm, thus the formation of a possible [Pd=N^pTol] or [Pd–N^pTol–Pd] imido species is excluded.

Our study of the solution behavior of 4 and 5 shows that not only the polymeric structure can be disrupted by donor solvents such as THF, but that the mobility of the potassium cation increases as well. These findings support the proposal by Meek and coworkers that the interaction of a rhodium catalyst for the hydroarylation of dienes with a Lewis acid has to be reversible in order to observe an increased activation of the substrate.²²

Heterobimetallic carbene complexes^{73,74} containing K–C_{carbene}–M units, in which the carbene is not stabilized by adjacent heteroatoms, are rare;^{23,75} to the best of our knowledge, complexes 4 and 5 represent the only known characterized heterobimetallic carbene species possessing such binding motifs. The successful synthesis of amide substituted carbene complexes 4 and 5 from the radical precursor 1 prompted us to investigate other nucleophiles, especially those featuring an alkyl group. Interestingly, the reaction of 1 with two equivalents of PhCH₂K in THF led to a dark-brown diamagnetic complex, K[PC(sp²)P]^{tBu}Pd(CH₂Ph)] (6), in 64% yield, instead of the expected benzyl substituted Pd(II) radical carbene [PC(sp²)P]^{tBu}Pd(CH₂Ph)] (7, Scheme 2). Using one equivalent of PhCH₂K also led to 6, albeit with a lower conversion.

As observed for 5, X-ray diffraction studies on single crystals of 6 grown from a diethyl ether solution also showed a polymeric structure, where the anionic carbene moieties [PC(sp²)P]^{tBu}PdCH₂Ph] were bridged by potassium ions (Fig. 4). Although the C_{carbene} carbon still retained its trigonal planar





Scheme 2 Synthesis of 6 and 7.

geometry (Σ angles at C_{carbene} are 359.8°), the Pd–C_{carbene} distance of $2.095(2)$ Å is slightly longer than that of $2.076(3)$ Å in $[\{PC(sp^2)-P\}^{tBu}Pd(PMe_3)]$,⁶² and of $2.043(2)$ Å in 5. Two different coordination modes were found for potassium ions: one is sandwiched between two $[\{PC(sp^2)P\}^{tBu}PdCH_2Ph]$ moieties in an η^4 fashion, with K–C distances ranging from $2.998(2)$ to $3.176(3)$ Å, while the other is only η^1 coordinated to the carbene carbons of two anionic carbene moieties, with a K–C distance of $3.040(2)$ Å. The K–C_{carbene}–K–C_{carbene} chain is not strictly linear, with the K–C_{carbene}–K and C_{carbene}–K–C_{carbene} angles being $163.40(8)^\circ$ and $173.86(9)^\circ$, respectively. The different bridging modes observed for potassium in 5 and 6 are largely attributed to the bulkier Ph₂N amide group in 5 than the benzyl group in 6.

Similarly to 4 and 5, complex 6 is only soluble in ethereal solvents and its ¹H NMR spectrum recorded in THF-*d*₈ is consistent with a *C*₂ symmetric structure in solution. The ³¹P{¹H} NMR spectrum only shows a sharp singlet at $\delta = 48.52$ ppm. A triplet at $\delta = 2.45$ ppm ($^3J_{PH} = 5.0$ Hz) was observed for the benzyl CH₂ group in the ¹H NMR spectrum that correlates with a triplet at $\delta = 14.12$ ppm ($^2J_{PC} = 9.0$ Hz) in the

corresponding ¹³C{¹H} NMR spectrum. The peak corresponding to the carbene carbon could not be assigned unambiguously in the ¹³C{¹H} NMR spectrum, a situation previously observed for $[\{PC(sp^2)P\}^H Pd(PMe_3)]$,⁶¹ as well as for other palladium carbene complexes.⁵⁰

As observed for 4 and 5, a discrepancy between the solid state and THF-*d*₈ solution structures of 6 exists that suggests a disruption of the polymeric chain by the donor solvent. In the ¹H NMR spectrum, three well-resolved peaks at $\delta = 7.20$ (dt), 6.66 (td) and 6.52 (dd) ppm were assigned to the signals from the phenyl groups of the supporting ligand, which are very close to those of 4. Considering that benzyl and NH⁺Tol groups have similar steric profiles, complexes 4 and 6 most likely possess similar solution structures. The ¹H NMR spectrum of 6 in C₆D₆ with 2 drops of THF-*d*₈ also showed a *C*₂ symmetric structure. Notably, resonances of the phenyl groups of the supporting ligand are significantly shifted upfield in THF-*d*₈ compared to those in C₆D₆ with only a small amount of THF-*d*₈ (from 7.61, 6.94, and 6.86 ppm to 7.20, 6.66, and 6.52 ppm, respectively), consistent with the generation in THF-*d*₈ of a monomer, in which the potassium ion interacts with only one carbene moiety and not with two, as observed in the solid state or in a non-donor solvent.⁷⁶

The formation of 6 is a combined substitution and reduction of radical complex 1: the benzyl group on palladium was introduced by substitution of iodide by a benzyl anion. Due to the reductive nature of the benzyl anion, the loss of an electron from it also reduced the radical species to an anionic carbene. This process is accompanied by the formation of the benzyl radical [PhCH₂·], which dimerized to form PhCH₂CH₂Ph. Analysis of the crude reaction mixture by ¹H NMR spectroscopy indicated the formation of PhCH₂CH₂Ph, which was confirmed by comparison with an authentic sample. A minor palladium containing species was also observed, which showed two sets of peaks for the benzylic CH₂ groups at $\delta = 3.81$ (s) and 2.94 ($^3J_{PH} = 5.5$ Hz) ppm in the ¹H NMR spectrum, and a sharp singlet at $\delta = 39.86$ ppm in the ³¹P{¹H} NMR spectrum. We tentatively assigned this species as complex $[\{PC(sp^3)(CH_2Ph)-P\}^{tBu}Pd(CH_2Ph)]$, containing another benzyl group on the backbone carbon *via* radical coupling. Attempts to isolate this compound were hampered by its high solubility in aliphatic solvents.

Although the substitution reaction of 1 with PhCH₂K led directly to the formation of the heterobimetallic carbene complex 6, the subsequent one-electron oxidation of 6 with [Cp₂Fe][BAr₄^F] afforded the radical complex 7 in quantitative yield (Scheme 2). The high solubility of 7 in aliphatic solvents prevented its separation from the byproduct, Cp₂Fe, but its EPR spectrum (in the presence of Cp₂Fe) in toluene at 298 K revealed a hyperfine splitting from four pairs of magnetically equivalent protons and a ¹⁰⁵Pd nucleus (Fig. S5 and S6†). The smallest hyperfine constant was attributed to the CH₂ group protons (0.08 mT), while the remaining proton hyperfine constants (0.32, 0.19 and 0.12 mT) were assigned to the six phenyl ring protons of the supporting ligand, which are close to the corresponding values for 2 and 3. Accordingly, the one-electron oxidations of the heterobimetallic carbene complexes 4 and 5

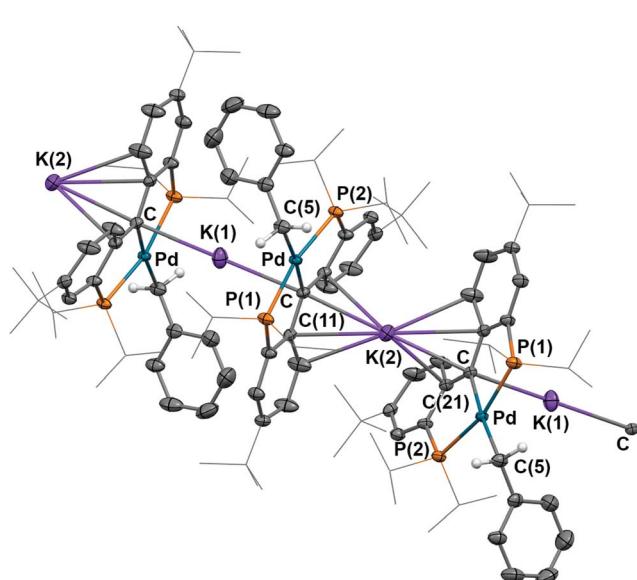
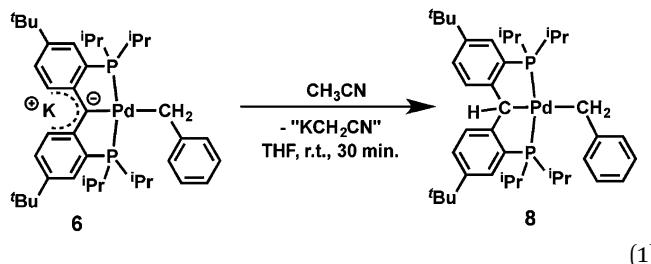


Fig. 4 Thermal-ellipsoid (35% probability) representation of 6; most hydrogen atoms were removed for clarity. Selected distances [Å] and angles [°]: Pd–C 2.095(2), Pd–P(1) 2.2695(6), Pd–P(2) 2.2868(6), Pd–C(5) 2.163(2), K(1)–C 3.040(2), K(2)–C 3.028(2), K(2)–C(11) 3.162(2), K(2)–C(16) 3.176(3), K(2)–C(21) 2.998(2), Pd–C–C(11) 118.76(15), Pd–C–C(21) 118.06(15), C(11)–C–(21) 123.02(19).



with $[\text{Cp}_2\text{Fe}][\text{BAr}^F_4]$ also regenerated the radical complexes **2** and **3**, respectively (Scheme 1), as confirmed by EPR spectroscopy (Fig. S1 and S3[†]).

Preliminary reactivity studies showed that the reaction of **6** with CH_3CN (5 equivalents) in THF quantitatively afforded $[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{tBu}}\text{Pd}(\text{CH}_2\text{Ph})]$ (**8**, eqn (1)), which is the product of C–H activation, similarly to $[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{H}}\text{Pd}(\text{PMe}_3)]$.^{61,62} Given the presence of benzyl and amide ligands that could have been protonated by CH_3CN , it is interesting to note that the former carbene carbon is more nucleophilic than these ligands, consistent with a localized negative charge on that carbon.



We also tested the direct nucleophilic substitutions of the parent carbene complex $[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{tBu}}\text{Pd}(\text{PMe}_3)]$ with $^p\text{TolNH}_2\text{K}$, Ph_2NK and PhCH_2K . Although the formation of the heterobimetallic complexes **4** and **6** was confirmed ($^p\text{TolNH}_2\text{K}$, 65% and PhCH_2K , 60% conversion) by $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, some unknown species as well as unreacted starting material were also observed after 24 h. Attempts to isolate pure **4** and **6** from these mixtures met with difficulty and were inefficient. The bulky nucleophile Ph_2NK does not react with $[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{tBu}}\text{Pd}(\text{PMe}_3)]$ under similar conditions, probably due to its steric hindrance. The sluggish substitution reactions observed for these nucleophiles could also be attributed to the relatively strong coordination of PMe_3 to palladium, therefore, the substitution/reduction strategy presented herein is preferable because it takes advantage of a facile redox process that provides a relatively easier access to heterobimetallic Pd–K carbene complexes.^{77–79}

DFT calculations

DFT calculations (B3LYP functional, LANL2DZ basis set) were performed on a model of the anion of **5**, **5'**, with the ^tBu and ^iPr groups replaced by H and methyl groups, respectively (Fig. 5). As was observed for $[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{H}}\text{Pd}(\text{PMe}_3)]$,^{61,62} the HOMO of **5'** shows a π type interaction between the carbene carbon p orbital and the appropriate symmetry d orbital of Pd, while the LUMO shows the corresponding σ interaction, with both molecular orbitals having antibonding character. Thus the carbene moiety in these heterobimetallic carbene complexes is predicted to show some similar reactivity to that observed for $[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{H}}\text{Pd}(\text{PMe}_3)]$, as was shown in eqn (1).^{62,64,66}

In order to study the influence of the potassium cation on the Pd–C interaction, another simplified model, **5''**, was considered, in which the interaction between potassium and a NPh_2 group from a neighboring molecule was replaced with

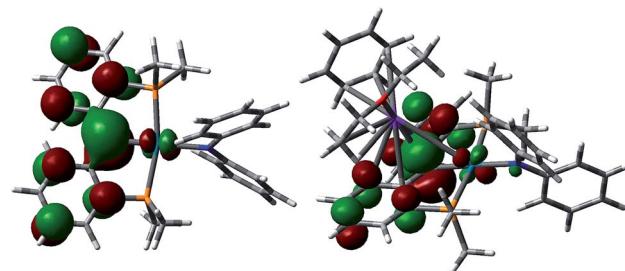


Fig. 5 HOMO for $[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{Me}}\text{PdNPh}_2]^-$ (**5'**, left) and $[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{Me}}\text{PdNPh}_2\text{K}(\text{OEt}_2)(\text{C}_6\text{H}_5\text{P})]^-$ (**5''**, right).

a potassium benzene interaction. The HOMO of **5''** (Fig. 5) resembles that calculated for **5'**, in agreement with an electrostatic interaction between the potassium cation and the anionic carbon, while the LUMO is localized on the benzene ring coordinated to the potassium atom. The interaction between the cation and the carbene ligand observed in both the solid state structure and the computed model involves the delocalized π orbital of the two phenyl rings attached to the carbene atom. That carbon maintains its planar geometry in both **5** and **6**, similarly to other delocalized π systems coordinated to potassium.^{77–79}

A similar situation was observed for **6**. We studied the electronic structure of the free anion (**6'**) and a model of the heterobimetallic carbene (**6''**). In both, the iso-propyl groups and the *tert*-butyl groups were replaced by hydrogen atoms. For **6''**, in order to simulate the coordination environments of both potassium atoms, we reduced the polymer to a dimer (Fig. S24 and S25[†]). Both HOMO and HOMO–1 for **6''** are comprised of the lone pair on the carbenic carbon; LUMO and LUMO+1 are localized on the benzene rings coordinated to the terminal potassium cations. The planarity of the carbene carbons can be attributed to the symmetric donation from the lone pair on these atoms to the two potassium atoms.

Conclusions

In conclusion, we showed that a substitution/reduction strategy employing the radical carbene $[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{tBu}}\text{PdI}]$ (**1**) can be utilized to synthesize a series of heterobimetallic Pd–K carbene complexes $\{[\{\text{PC}(\text{sp}^2)\text{P}\}^{\text{tBu}}\text{PdX}]_n\}$ (**4**: $\text{X} = \text{NH}^p\text{Tol}$, $n = 0$; **5**: $\text{X} = \text{NPh}_2$, $n = 1$; **6**: $\text{X} = \text{CH}_2\text{Ph}$, $n = 0$) bearing functional groups on palladium. Polymeric structures were exhibited by these heterobimetallic Pd–K carbene in the solid state, featuring unprecedented Pd–C_{carbene}–K units that are not easily accessible by other synthetic strategies. The present carbene complete the palladium carbene series containing a cationic (Chart 1, type A), an ylide-like (type B), a radical (type C), and a heterobimetallic (type D) carbene. The isolation of these novel species not only provides a fundamental understanding of their bonding and structural features, but also sheds some light on the role of alkalis in transition metal catalysis. Notably, the solution behaviour of these complexes showed that the interaction of the potassium ion with the carbene moiety is highly



influenced by the donating ability of the solvent, which led to a lower aggregation state of the complex; this may better represent species related to transition metal catalytic systems with alkali metals in polar solvents. More importantly, the flexible interaction of potassium might also be crucial in terms of substrate activation, as proposed recently in the rhodium catalyzed hydroarylation of dienes, that a reversible interaction with Lewis acids enhance the reactivity.²² Finally, the facile redox properties exhibited by these palladium carbenes also indicate their potential non-innocent ligand-based reactivity, and, therefore, future studies can lead to new and useful transformations in synthesis.

Experimental

All experiments are performed under an inert atmosphere of N_2 using standard glovebox techniques. Solvents hexanes, *n*-pentane, diethyl ether, and CH_2Cl_2 were dried by passing through a column of activated alumina and stored in the glovebox. THF and $THF-d_8$ were dried over $LiAlH_4$ followed by vacuum transfer and stored in the glovebox, while C_6D_6 was dried over CaH_2 followed by vacuum transfer, and stored in the glovebox. Complex **1**,⁶⁷ $[Cp_2Fe][BAr^F_4]$,⁸⁰ and KC_8 ⁸¹ were prepared according to literature procedures. pTolNH , pTolNH K and Ph_2NK were prepared by deprotonation of amines with nBuLi and KH , respectively. 1H , $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DRX 500 spectrometer. All chemical shifts are reported in δ (ppm) with reference to the residual solvent resonance of deuterated solvents for proton and carbon chemical shifts, and to external H_3PO_4 , for ^{31}P chemical shifts, respectively. Magnetic moments were determined by the Evans method^{68,82,83} by using a capillary containing 1,3,5-trimethoxybenzene in C_6D_6 as a reference. EPR spectra were recorded on a Bruker EMXplus EPR spectrometer with a standard X-band EMXplus resonator and an EMX premium microwave bridge, at microwave power of 2 mW, modulation frequency 100 kHz and amplitude 0.01 mT. Elemental analyses were performed on a CE-440 Elemental analyzer, or by Midwest Microlab. Gaussian 03 (revision D.02) was used for all reported calculations. The B3LYP (DFT) method was used to carry out the geometry optimizations on model compounds specified in text using the LANL2DZ basis set. The validity of the true minima was checked by the absence of negative frequencies in the energy Hessian.

Synthesis of $[\{PC(sp^2)P\}^{tBu}PdNH^pTol]$ (2)

pTolNH (10.2 mg, 0.071 mmol) in 1 mL of THF was slowly added to a dark-green solution of **1** (50 mg, 0.067 mmol) in 1 mL of THF at -35 °C. The resulted greenish slurry was allowed to stir at room temperature for 1 h. All volatiles were removed under reduced pressure and the residue was extracted with 6 mL of *n*-pentane, and filtered to give a dark-green solution. The volume of this *n*-pentane solution was reduced to about 0.5 mL under reduced pressure and stored at -35 °C to give compound **2** as green crystals. Yield 42 mg (87%). For **2**: $[\{PC(sp^2)P\}^{tBu}PdNH^pTol]$ (2) is paramagnetic. Magnetic moment (Evans

method, 298 K): $\mu_{eff} = 1.70 \mu_B$; EPR: $g = 2.0088$. Anal. calcd for $C_{40}H_{60}NP_2Pd$ (723.28 g mol $^{-1}$): C, 66.42; H, 8.36; N, 1.94. Found: C, 66.52; H, 8.31; N, 1.68.

Synthesis of $[\{PC(sp^2)P\}^{tBu}PdNPh_2]$ (3)

Ph_2NK (19.5 mg, 0.094 mmol) and **1** (70 mg, 0.094 mmol) were mixed in 5 mL of THF and heated at 60 °C for 6 days, during which time a greenish slurry was formed. All volatiles were removed under reduced pressure and the residue was extracted with *n*-pentane (3×4 mL), and filtered to give a dark-green solution. The volume of the *n*-pentane solution was reduced to about 1 mL under reduced pressure and stored at -35 °C to give compound **2** as green crystals. Yield 59 mg (80%). For **3**: $[\{PC(sp^2)P\}^{tBu}PdNPh_2]$ (3) is paramagnetic. Magnetic moment (Evans method, 298 K): $\mu_{eff} = 1.54 \mu_B$; EPR: $g = 2.0079$. Anal. calcd for $C_{45}H_{62}NP_2Pd$ (785.35 g mol $^{-1}$): C, 68.82; H, 7.96; N, 1.78. Found: C, 68.91; H, 7.55; N, 1.40.

Synthesis of $[\{PC(sp^2)P\}^{tBu}PdNH^pTol]^-K^+$ (4)

KC_8 (10.3 mg, 0.076 mmol) and **2** (55 mg, 0.076 mmol) were mixed in 3 mL of C_6H_6 at room temperature. The resulted dark-brown reaction mixture was stirred at room temperature for 30 min. All volatiles were removed under reduced pressure and the residue was extracted with 4 mL of diethyl ether and filtered to give a dark-brown solution. The volume of this solution was reduced to about 1.5 mL under reduced pressure and layered with 7 mL of *n*-pentane at room temperature. Compound **4** crystallized from this solution as dark-brown crystals. Yield 48 mg (83%). For **4**: 1H NMR (500 MHz, 25 °C, $THF-d_8$): $\delta = 7.23$ (br s, 2H, ArH), 6.61 (br s, 2H, ArH), 6.54 (br s, 2H, ArH), 6.35 (d, $^3J_{HH} = 7.5$ Hz, 2H, ArH), 6.10 (d, $^3J_{HH} = 8.0$ Hz, 2H, ArH), 2.36 (m, 4H, $CH(CH_3)_2$), 1.98 (s, 3H, pTolCH_3), 1.33 (s, 1H, NH), 1.24 (dt, $^3J_{HH} = 7.5$ Hz, $^3J_{HP} = 7.0$ Hz, 12H, $CH(CH_3)_2$), 1.16 (dt, $^3J_{HH} = 7.5$ Hz, $^3J_{HP} = 8.0$ Hz, 12H, $CH(CH_3)_2$), 1.16 (s, 18H, $C(CH_3)_3$) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, 25 °C, $THF-d_8$): $\delta = 162.42$ (s, ArC), 161.98 (m, ArC), 130.91 (br s, ArC), 129.56 (br s, ArC), 129.40 (s, ArC), 128.50 (br s, ArC), 119.08 (br s, ArC), 115.73 (s, ArC), 115.53 (br s, ArC), 112.95 (s, ArC), 110.35 (br s, ArC), 34.03 (s, $C(CH_3)_3$), 32.22 (br s, $C(CH_3)_3$), 25.85 (br s, $CH(CH_3)_2$), 20.97 (s, pTolCH_3), 19.25 (s, $CH(CH_3)_2$), 18.99 (s, $CH(CH_3)_2$) ppm. The peak for the carbenic carbon cannot be assigned in the 162–110 ppm region, but the total number of carbon peaks are correct. $^{31}P\{^1H\}$ NMR (202 MHz, 25 °C, $THF-d_8$): $\delta = 46.36$ (s) ppm. Anal. calcd for $C_{40}H_{60}KNP_2Pd$ (762.38 g mol $^{-1}$): C, 63.02; H, 7.93; N, 1.84. Found: C, 63.72; H, 8.42; N, 1.39.

Synthesis of $[\{PC(sp^2)P\}^{tBu}PdNPh_2]^-[KOEt_2]^+$ (5)

KC_8 (8.6 mg, 0.064 mmol) and **3** (50 mg, 0.064 mmol) were mixed in 2 mL of C_6H_6 at room temperature. The resulted greenish-brown reaction mixture was stirred at room temperature for 30 min. All volatiles were removed under reduced pressure and the residue was extracted with ether (3×5 mL) and filtered to give a greenish-brown solution. The volume of this solution was reduced to about 3 mL under reduced pressure and layered with 9 mL of *n*-pentane at room temperature. Compound **5** crystallized from this solution as greenish brown



crystals. Yield 41 mg (71%). For **5**: ^1H NMR (500 MHz, 25 °C, THF- d_8): δ = 7.35 (d, $^3J_{\text{HH}} = 7.5$ Hz, 4H, ArH), 6.80 (t, $^3J_{\text{HH}} = 7.3$ Hz, 4H, ArH), 6.18 (t, $^3J_{\text{HH}} = 7.0$ Hz, 2H, ArH), 3.39 (q, $^3J_{\text{HH}} = 7.0$ Hz, 4H, OCH_2CH_3), 1.98 (br s, 4H, $\text{CH}(\text{CH}_3)_2$), 1.14 (br s, 24H, $\text{CH}(\text{CH}_3)_2$), 1.12 (t, $^3J_{\text{HH}} = 7.0$ Hz, 4H, OCH_2CH_3), 1.06 (br s, 18H, $\text{C}(\text{CH}_3)_3$) ppm; $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, 25 °C, THF- d_8): δ = 158.82 (s, ArC), 128.14 (s, ArC), 121.73 (s, ArC), 113.63 (s, ArC), 66.47 (s, OCH_2CH_3), 31.85 (s, $\text{C}(\text{CH}_3)_3$), 19.04 (br s, $\text{CH}(\text{CH}_3)_2$), 18.19 (br s, $\text{CH}(\text{CH}_3)_2$), 15.85 (s, OCH_2CH_3) ppm. The peaks for the phenyl of the $\{\text{PC}(\text{sp}^2)\text{P}\}$ ligand backbone were not observed in the ^1H and $^{13}\text{C}\{\text{H}\}$ NMR spectra (*vide supra*). $^{31}\text{P}\{\text{H}\}$ NMR (202 MHz, 25 °C, THF- d_8): δ = 48.64 (s) ppm. Anal. calcd for $\text{C}_{49}\text{H}_{72}\text{KNOP}_2\text{Pd}$ (898.57 g mol $^{-1}$): C, 65.50; H, 8.08; N, 1.56. Found: C, 65.61; H, 8.12; N, 1.44.

Synthesis of $[\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{PdCH}_2\text{Ph}]^-\text{K}^+$ (6)

PhCH_2K (17.5 mg, 0.134 mmol) in 1 mL of THF was slowly added to **1** (50 mg, 0.067 mmol) in 1 mL of THF at -35 °C. The dark-red reaction mixture was stirred at room temperature for 2 hours. Volatiles were removed under reduced pressure and the residue was extracted with 8 mL of diethyl ether and filtered to give a dark-brown solution. The volume of this solution was reduced to about 1.5 mL under reduced pressure and layered with 7 mL of *n*-pentane. Compound **6** crystallized from this solution at -35 °C as dark-brown solid. Yield 32 mg (64%). For **6**: ^1H NMR (500 MHz, 25 °C, THF- d_8): δ = 7.20 (dt, $^3J_{\text{HH}} = 9.0$ Hz, $^3J_{\text{HP}} = 4.5$ Hz, 2H, ArH), 6.98 (d, $^3J_{\text{HH}} = 7.0$ Hz, 2H, ArH), 6.81 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H, ArH); 6.66 (td, $^4J_{\text{HH}} = 2.3$ Hz, $^3J_{\text{HP}} = 4.8$ Hz, 2H, ArH), 6.52 (dd, $^3J_{\text{HH}} = 9.0$ Hz, $^4J_{\text{HH}} = 2.0$ Hz, 2H, ArH), 6.46 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H, ArH), 2.45 (t, $^3J_{\text{HP}} = 5.0$ Hz, 2H, CH_2Ph), 2.26 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 1.16 (dt, $^3J_{\text{HH}} = 7.0$ Hz, $^3J_{\text{HP}} = 6.5$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.15 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.14 ($^3J_{\text{HH}} = 6.0$ Hz, $^3J_{\text{HP}} = 7.5$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm; $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, 25 °C, THF- d_8): δ = 161.56 (t, $J_{\text{CP}} = 18.6$ Hz, ArC), 159.81 (t, $J_{\text{CP}} = 1.3$ Hz, ArC), 130.35 (t, $J_{\text{CP}} = 3.0$ Hz, ArC), 129.94 (s, ArC), 128.43 (s, ArC), 128.27 (s, ArC), 127.46 (s, ArC), 121.85 (t, $J_{\text{CP}} = 19.0$ Hz, ArC), 118.62 (s, ArC), 115.38 (t, $J_{\text{CP}} = 10.3$ Hz, ArC), 34.00 (s, $\text{C}(\text{CH}_3)_3$), 32.27 (s, $\text{C}(\text{CH}_3)_3$), 26.07 (t, $^1J_{\text{CP}} = 10.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 20.26 (t, $^2J_{\text{CP}} = 3.2$ Hz, $\text{CH}(\text{CH}_3)_2$), 19.04 (s, $\text{CH}(\text{CH}_3)_2$), 14.12 (t, $^2J_{\text{CP}} = 9.0$ Hz, CH_2Ph) ppm; $^{31}\text{P}\{\text{H}\}$ NMR (202 MHz, 25 °C, THF- d_8): δ = 48.52 (s) ppm. Anal. calcd for $\text{C}_{40}\text{H}_{59}\text{KP}_2\text{Pd}$ (747.36 g mol $^{-1}$): C, 64.28; H, 7.96. Found: C, 64.81; H, 8.53.

Synthesis of $[\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{PdCH}_2\text{Ph}]$ (7)

$[\text{Cp}_2\text{Fe}][\text{BAr}^{\text{F}}_4]$ (32 mg, 0.031 mmol) in 1 mL of THF was slowly added to **6** (23 mg, 0.031 mmol) in 1 mL of THF at -35 °C. The dark-red reaction mixture was stirred at room temperature for 30 min. All volatiles were removed under reduced pressure and the residue was extracted with 4 mL of *n*-pentane and filtered to give a red solution. The volatiles were removed under reduced pressure to give a red oily mixture of **7** and Cp_2Fe , which are not separable due to similar solubilities in common solvents. For **7**: $[\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{PdCH}_2\text{Ph}]$ (7) is paramagnetic. EPR: $g = 2.0086$.

Oxidation of $[\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{PdNH}^p\text{Tol}]^-\text{K}^+$ (4)

$[\text{Cp}_2\text{Fe}][\text{BAr}^{\text{F}}_4]$ (6.9 mg, 0.007 mmol) in 1 mL of diethyl ether was added to $[\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{PdNH}^p\text{Tol}]^-\text{K}^+$ (4) (5 mg, 0.007 mmol) in 1 mL of diethyl ether at -35 °C. The resulted brownish-green solution was allowed to stir at room temperature for 30 min. The volatiles were removed under reduced pressure and the residue was extracted with *n*-pentane. This solution was filtered and the volatiles were removed under reduced pressure to give a green solid. The EPR spectrum measured in toluene at 298 K is identical to that of a pure sample of **2** isolated by a different method (*vide supra*).

Oxidation of $[\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{PdNPh}_2]^-[\text{KOEt}_2]^+$ (5)

$[\text{Cp}_2\text{Fe}][\text{BAr}^{\text{F}}_4]$ (5.8 mg, 0.006 mmol) in 1 mL of diethyl ether was added to **5** (5 mg, 0.006 mmol) in 1 mL of diethyl ether at -35 °C. The resulted green solution was allowed to stir at room temperature for 30 min. The volatiles were removed under reduced pressure and the residue was extracted with *n*-pentane and filtered. The volatiles were removed under reduced pressure to give a green solid. The EPR spectrum measured in toluene at 298 K is identical to that of a pure sample of **3** isolated by a different method (*vide supra*).

Synthesis of $[\{\text{PCHP}\}^{t\text{Bu}}\text{PdCH}_2\text{Ph}]$ (8)

CH_3CN (4 mg, 0.1 mmol) in 0.5 mL of THF was added to a solution of **6** (15 mg, 0.02 mmol) in 1 mL of THF at room temperature. The dark-red solution immediately turned to orange, which was stirred for another 30 min. Volatiles were removed under vacuum to give an yellow oil, which was extracted into 3 mL of pentane, filtered and removal of all volatiles under reduced pressure afforded **8** as an yellow foam. Yield 14 mg (quantitative). For **8**: ^1H NMR (500 MHz, 25 °C, C_6D_6): δ = 7.51 (d, $^3J_{\text{HH}} = 7.0$ Hz, 2H, ArH); 7.46-7.44 (m, 4H, ArH); 7.26 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, ArH); 7.21 (dd, $^3J_{\text{HH}} = 8.5$ Hz, $^4J_{\text{HH}} = 2.0$ Hz, 2H, ArH); 6.96 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H, ArH), 5.65 (s, 1H, $\text{CH}_{\text{backbone}}$), 3.00 (t, $^3J_{\text{HP}} = 5.3$ Hz, 2H, CH_2Ph), 2.41 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 2.27 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 1.28 (dt, 6H, $^3J_{\text{HH}} = 8.0$ Hz, $^3J_{\text{HP}} = 7.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.27 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.17 (dt, $^3J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{HP}} = 6.5$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.06 (m, 12H, $\text{CH}(\text{CH}_3)_2$) ppm; $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, 25 °C, C_6D_6): δ = 157.67 (t, $J_{\text{CP}} = 15.0$ Hz, ArC), 155.51 (s, ArC), 146.47 (s, ArC), 136.23 (t, $J_{\text{CP}} = 17.3$ Hz, ArC), 128.70 (s, ArC), 128.34 (s, ArC), 127.90 (s, ArC), 127.72 (t, $J_{\text{CP}} = 8.4$ Hz, ArC), 127.00 (s, ArC), 120.48 (s, ArC), 56.26 (s, $\text{CH}_{\text{backbone}}$), 34.36 (s, $\text{C}(\text{CH}_3)_3$), 31.65 (s, $\text{C}(\text{CH}_3)_3$), 25.62 (t, $^1J_{\text{PC}} = 11.2$ Hz, $\text{CH}(\text{CH}_3)_2$), 25.52 (t, $J_{\text{PC}} = 9.3$ Hz, $\text{CH}(\text{CH}_3)_2$), 19.87 (t, $^2J_{\text{PC}} = 3.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 19.32 (t, $^2J_{\text{PC}} = 2.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 19.17 (t, $^2J_{\text{PC}} = 2.1$ Hz, $\text{CH}(\text{CH}_3)_2$), 18.00 (s, $\text{CH}(\text{CH}_3)_2$), 13.22 (t, $^2J_{\text{PC}} = 7.8$ Hz, CH_2Ph); $^{31}\text{P}\{\text{H}\}$ NMR (202 MHz, 25 °C, C_6D_6): δ = 45.76 (s) ppm. Anal. calcd for $\text{C}_{40}\text{H}_{60}\text{P}_2\text{Pd}$ (709.27 g mol $^{-1}$): C, 67.74; H, 8.53. Found: C, 67.88; H, 8.62.

Substitution reactions of carbene $[\{\text{PC}(\text{sp}^2)\text{P}\}^{t\text{Bu}}\text{Pd}(\text{PMe}_3)]$ with PhCH_2K , $^p\text{TolNH}_2$ and Ph_2NK nucleophiles

PhCH_2K (2.8 mg, 0.022 mmol) in 1 mL of THF was added to carbene (15 mg, 0.022 mol) in 0.5 mL of THF at -35 °C. The



dark-red solution was then stirred at room temperature for 24 h. Volatiles were removed under reduced pressure and the residues were dissolved in C₆D₆ (with 2 drops of THF-d₈) and monitored by ¹H and ³¹P{¹H} NMR spectra. Same procedures were applied for ^pTolNHK and Ph₂NK. The reactions with PhCH₂K and ^pTolNHK showed conversion to the heterobimetallic carbene **6** and **4** in 60% and 65% conversion, respectively, based on the ³¹P{¹H} NMR spectra. No conversion was observed for Ph₂NK.

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