Heterobimetallic Pd–K carbene complexes via one-electron reductions of palladium radical carbenes†

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Heterobimetallic Pd–K carbenes featuring Pd–C(carbene)–K moieties were synthesized via an unprecedented sequential substitution/reduction reaction from a radical precursor, [[PC'(sp²)P]₂BuPd][PC(sp³)P]₁Bu = bis-[2-(di-iso-propylphosphino)-4-tert-butylphenyl]methylene). Polymeric structures were observed in the solid state for the heterobimetallic compounds that can be interrupted in the presence of a donor solvent.

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,6–8 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 carboxyclic,35 and heteroatom stabilized carbene ligands36–38 have been extensively studied as a consequence; however, the corresponding non-heteroatom stabilized species, [M=C(RR')] (R, R' = alkyl or H), are less explored.39–43 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 CpH₂ moiety could be isolated by the thermolysis or photolysis of its diphenyldiazalcone precursor.44,45 The isolation of the corresponding Pd and Pt carbenes is, however, more challenging than that of nickel complexes,48–51 because of the highly reactive nature of the former.52,53 On the other hand, these species are crucial intermediates in a variety of catalytic transformations,57,58 such as palladium carbone mediated cyclopropanations, cross-coupling with diazo compounds, and migratory insertion reactions.59

It is worth mentioning that only two examples of cationic Pd(n) carbene complexes are known (Chart 1, type A), synthesized via triflate or hydride abstraction, and that their reactivity has not been studied.56,57 A salt metathesis strategy was also reported for the synthesis of methanediide-based Pd(n) carbone complexes.60,61 We have recently applied dehydrohalogenation reactions58 to synthesize Pd(n) carbene complexes, [[PC(sp²)-P]₂BuPd(PMe₃)] (R = H, [PC(sp³)P]₁Bu = bis-[2-(di-iso-propylphosphino)phenyl]methylene); R = Bu, [PC(sp³)P]₁Bu = bis-[2-(di-iso-propylphosphino)-4-tert-butylphenyl]methylene).62–63 Interestingly, the Pd=C(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),64 strong Lewis acids,62 C–H¢ and Si–H¢ bond activation reactions. Furthermore, our recent study on the redox-induced umpolung of palladium carbenes revealed that the radical carbene [[PC(sp³)P]₂BuPd] (1, Chart 1, type C) bridges cationic and anionic carbenes via reversible one-electron transfer processes.65,66

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 carbone species, which would

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**Chart 1** Illustration of known palladium carbone complexes: (A) cationic carbone; (B) ylide-like carbone; (C) radical carbone; (D) heterobimetallic carbone discussed in this work.
Results and discussion
Synthesis and characterization of metal complexes

Treatment of 1 with potassium amides, R1R2NK, in THF afforded new radical complexes, [[PC(sp^2)P]^{[105]PdNHR}]^+ [2: R^1 = H, R^2 = R^3 = Ph, Scheme 1], which were crystallized from n-pentane at −35 °C as dark-green crystals in high yield. As observed for 1,2 2 and 3 are silent by ^H and ^31P NMR spectroscopy and are thermally robust. The effective magnetic moments \( \mu_{eff} \) of 1.70 \( \mu_B \) and 1.54 \( \mu_B \) obtained using the Evans method\(^{26}\) 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 \(^{105}\)Pd nucleus. As the natural abundance of the magnetic \(^{105}\)Pd isotope is 22.33%, each spectrum exhibits contributions from the non-magnetic palladium isotope (strong, well-resolved central signal) and the \(^{105}\)Pd 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 sp^2 hybridized backbone carbons (\( \angle \text{angles at C}_{\text{carbene}} \) are 359.9° for 2 and 360.0° for 3). The Pd–C_{\text{carbene}} distances in 2 (2.019(2) Å) and 3 (2.024(2) Å) are comparable to each other and close to the value of 2.022(3) Å in 1.\(^{22}\) Trigonal planar geometries were observed for both amide nitrogen atoms in 2 and 3, with the amide planes roughly perpendicular to the planes defined by C_{\text{carbene}}, C(11), and C(21) for 2 and 85.8° for 3). A longer Pd–N distance of 2.149(2) Å was observed in 3 compared to 2.0787(18) Å for 2, attributed to steric reasons.

Both radical complexes were subsequently treated with an equivalent of KC_8 in benzene, and the corresponding diamagnetic heterobimetallic complexes \([\text{K(OEt}_2]_2[\text{PC(sp}^2)\text{P}^{[105]PdNHR}]^+] (4: R^1 = H, R^2 = R^3 = \text{Tol}, n = 0; 5: R^1 = R^2 = \text{Ph}, n = 1)\) 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 \([\text{PC(sp}^2)\text{P}^{[105]PdNPh}_2]\) 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 Å vs. 3.17 Å). The coordination sphere of potassium was further completed by an additional diethyl ether molecule. The C_{\text{carbene}} carbon

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**Fig. 1** Experimental (black) and simulated (red) X-band EPR spectra of 10^{-1} M toluene solutions of radicals 2 (a) and 3 (b) at 298 K. Simulation parameters for 2: a1(2H) = 0.32 mT, a2(2H) = 0.13 mT, a3(2H) = 0.11 mT, a(N) = 0.09 mT, a^{[105]Pd} = 0.47 mT, g = 2.0088; for 3: a1(2H) = 0.31 mT, a2(2H) = 0.13 mT, a3(2H) = 0.10 mT, a(N) = 0.09 mT, a^{[105]Pd} = 0.51 mT, g = 2.0079. Contribution from the ^{105}Pd species is 22.33% for both radicals.

**Fig. 2** Thermal-ellipsoid (35% probability) representation of 2 (left) and 3 (right); most hydrogen atoms were removed for clarity. Selected distances [Å] and angles [°] 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) 1.1857(15), Pd–C–C(21) 1.1990(15), C(11)–C(–21) 1.2198(19); for 3: Pd–C 2.0242(2), Pd–P 2.3021(5), Pd–N 2.149(2), Pd–C–C(11) 1.1897(11), C(11)–C(–11) 1.221(2).

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**Scheme 1** Synthesis of heterobimetallic carbene complexes 4 and 5.
The polymeric structure of $5$ was studied in THF-$d_8$ and led to its displacement by the THF-$d_8$ ligand. Therefore, the polymeric chain can be proposed to be a similar one in the THF-$d_8$ spectrum. The 1H NMR spectrum of $5$ recorded at 298 K showed the peaks for the amide plane and the plane defined by $C_{\text{carbene}}$, $C(11)$ and $C(21)$ was much smaller than that in the 31P{1H} NMR spectrum, as well as three broad peaks at $d_8$ also exhibited a similar $C_2$ 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 $\delta = 7.23, 6.61$ and $6.54$ ppm in the 1H NMR spectrum. Only one sharp singlet at $\delta = 46.36$ ppm was observed in the 31P{1H} NMR spectrum. Therefore, a similar polymeric chain can be proposed for complex $4$ (vide infra).

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.

Heterobimetallic carbene complexes containing $K$–$C_{\text{carbene}}$–$M$ units, in which the carbene is not stabilized by adjacent heteroatoms, are rare; 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 PhCH$_2$K in THF led to a dark-brown diamagnetic complex, K[PC(sp$^3$)-P($^{\text{Bu}}$Pd(PMe$_3$)$_2$] (6), in 64% yield, instead of the expected benzyl substituted Pd[a] radical carbene [(PC(sp$^3$)-P($^{\text{Bu}}$Pd)CH$_2$Ph)] (7, Scheme 2). Using one equivalent of PhCH$_2$K 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(sp$^3$)-P($^{\text{Bu}}$Pd)CH$_2$Ph)] were bridged by potassium ions (Fig. 4). Although the $C_{\text{carbene}}$ carbon still retained its trigonal planar...
geometry (\(\Sigma_{\text{angles at C_{carbene}} = 359.8^\circ}\)), the Pd–C_{carbene} distance of 2.095(2) Å is slightly longer than that of 2.076(3) Å in \([\{\text{PC}(sp^3)P\}^{\mu}_6\text{Pd}2\text{PMe}_3]\)\(^{65}\) and of 2.043(2) Å in 5. Two different coordination modes were found for potassium ions: one is sandwiched between two \([\{\text{PC}(sp^3)P\}^{\mu}_6\text{Pd}2\text{CH}_2\text{Ph}]\) moieties in an \(\eta^3\) fashion, with K–C distances ranging from 3.000(2) to 3.137(3) Å, while the other is only \(\eta^1\) 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 \(\text{Ph}_2\text{N}\) amide group in 5 than the benzyl group in 6.

Similarly to 4 and 5, complex 6 is only soluble in etheral solvents and its \(^1\text{H}\) NMR spectrum recorded in THF-\(d_8\) is consistent with a \(C_2\) symmetric structure in solution. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum only shows a sharp singlet at \(\delta = 48.52\) ppm. A triplet at \(\delta = 2.45\) ppm \((2\text{P}_{\text{PC}} = 5.0\) Hz) was observed for the benzyl CH\(_2\) group in the \(^1\text{H}\) NMR spectrum that correlates with a triplet at \(\delta = 14.12\) ppm \((3\text{P}_{\text{PC}} = 9.0\) Hz) in the corresponding \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum. The peak corresponding to the carbene carbon could not be assigned unambiguously in the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum, a situation previously observed for \([\{\text{PC}(sp^3)P\}^{\mu}_6\text{Pd}2\text{PMe}_3]\)\(^{66}\) as well as for other palladium carbene complexes.\(^{60}\)

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 \(^1\text{H}\) 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 \(\text{NH}_2\text{Tol}\) groups have similar steric profiles, complexes 4 and 6 most likely possess similar solution structures. The \(^1\text{H}\) NMR spectrum of 6 in \(\text{C}_6\text{D}_6\) 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 \(\text{C}_6\text{D}_6\) 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 \([\text{PhCH}_2\text{}^\cdot]\), which dimerized to form \(\text{PhCH}_2\text{CH}_2\text{Ph}\). Analysis of the crude reaction mixture by \(^1\text{H}\) NMR spectroscopy indicated the formation of \(\text{PhCH}_2\text{CH}_2\text{Ph}\), 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 \(\text{CH}_4\) groups at \(\delta = 3.81\) (s) and 2.94 \((2\text{P}_{\text{PC}} = 5.5\) Hz) ppm in the \(^1\text{H}\) NMR spectrum, and a sharp singlet at \(\delta = 39.86\) ppm in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum. We tentatively assigned this species as complex \([\{\text{PC}(sp^3)\}^\mu\text{CH}_2\text{Ph}^\cdot\text{Pd}^\mu\text{Pd}^\mu\text{PCH}_2\text{Ph}]\), 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 \(\text{PhCH}_2\text{K}\) led directly to the formation of the heterobimetallic carbene complex 6, the subsequent one-electron oxidation of 6 with \([\text{Cp}_2\text{Fe}[\text{BAR}^\mu]^\cdot]\) afforded the radical complex 7 in quantitative yield (Scheme 2). The high solubility of 7 in aliphatic solvents prevented its separation from the byproduct, \(\text{CP}_2\text{Fe}\), but its EPR spectrum (in the presence of \(\text{CP}_2\text{Fe}\) in toluene at 298 K revealed a hyperfine splitting from four pairs of magnetically equivalent protons and a \(^{109}\text{Pd}\) nucleus (Fig. S5 and S6f). The smallest hyperfine constant was attributed to the \(\text{CH}_2\) 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...
with [CpFe][BARF] 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 CH3CN (5 equivalents) in THF quantitatively afforded [[PC(sp3)P]H2BuPd(Ph2CN)] (8, eqn (1)), which is the product of C–H activation, similarly to [[PC(sp3)P]H2Pd(PMe3)]. Given the presence of benzyl and amide ligands that could have been protonated by CH3CN, 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 [[PC(sp3)P]H2BuPd(PMe3)] with tBuNHK, Ph2NK and PhCH2K. Although the formation of the heterobimetallic complexes 4 and 6 was confirmed (5% TolNHK, Ph2NK and PhCH2K, 60% conversion) by 31P{1H} 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 Ph2NK does not react with [[PC(sp3)-P]H2BuPd(PMe3)] 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 PMe3 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.

**DFT calculations**

DFT calculations (B3LYP functional, LANL2DZ basis set) were performed on a model of the anion of 5, 5′, with the tBu and tPr groups replaced by H and methyl groups, respectively (Fig. 5). As was observed for [[PC(sp3)-P]H2BuPd(PMe3)], 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 [[PC(sp3)-P]H2Pd(PMe3)], as shown in eqn (1).

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 NPh2 group from a neighboring molecule was replaced with 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.27–31

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 carbene 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 [[PC(sp3)P]H2BuPd] (1) can be utilized to synthesize a series of heterobimetallic Pd–K carbene complexes [[PC(sp3)P]BuBuPdX][K(OEt2)2] (4: X = NH3, tol, n = 0; 5: X = NPh2, n = 1; 6: X = CH2Ph, n = 0) bearing functional groups on palladium. Polymeric structures were exhibited by these heterobimetallic Pd–K carbenes in the solid state, featuring unprecedented Pd–Ccarbene–K units that are not easily accessible by other synthetic strategies. The present carbenes 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 behavior 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.\(^2\) 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 were performed under an inert atmosphere of \(N_2\) using standard glove box 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 \(1^{17}\) \([Cp_2Fe][BF_4]\)\(^{-}\) and \(KC_8\)\(^{-}\) were prepared according to literature procedures. \(^{35}\)P{\(^1\)H} NMR spectra were recorded on a Bruker DRX 500 spectrometer. All chemical shifts are reported in \(\delta (ppm)\) 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\(^{18,22,23}\) 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^3)P]^\text{Bu}PdNHPol}\] (2)

\(^3\)TolNHK (10.2 mg, 0.071 mmol) in 1 mL of THF was slowly added to a dark-green solution of \(I\) (50 mg, 0.067 mmol) in 1 mL of THF at \(-35^\circ C\). 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 \(-35^\circ C\) to give compound 2 as green crystals. Yield 42 mg (87%). For 2: \([\{PC(sp^3)P]^\text{Bu}PdNHPol]\] (2) is paramagnetic. Magnetic moment (Evans method, 298 K): \(\mu_{\text{eff}} = 1.70 \mu_\text{B}\) EPR: \(g = 2.0088\). Anal. calcd for \(C_{10}H_{20}NP_2Pd\) (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^3)P]^\text{Bu}PdNPh_2\] (3)

\(Ph_2NK\) (19.5 mg, 0.094 mmol) and \(I\) (70 mg, 0.094 mmol) were mixed in 5 mL of THF and heated at 60 \(^\circ C\) 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 x 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 \(-35^\circ C\) to give compound 2 as green crystals. Yield 59 mg (80%). For 3: \([\{PC(sp^3)P]^\text{Bu}PdNPh_2\] (3) is paramagnetic. Magnetic moment (Evans method, 298 K): \(\mu_{\text{eff}} = 1.54 \mu_\text{B}\) EPR: \(g = 2.0079\). Anal. calcd for \(C_{14}H_{32}NP_2Pd\) (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^3)P]^\text{Bu}PdNHPol}\] \(K^+\) (4)

\(KC_8\) (10.3 mg, 0.076 mmol) and \(I\) (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: \(^1\)H NMR (500 MHz, 25 \(^\circ C\), 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, \(J_{HH} = 7.5\) Hz, \(2H, ArH\)), 6.10 (d, \(J_{HH} = 8.0\) Hz, \(2H, ArH\)), 2.36 (m, \(4H, CH(CH_3)_2\)), 1.98 (s, \(3H, (CH_3)_2\)), 1.33 (s, \(1H, NH\)), 1.24 (dt, \(J_{HP} = 7.5\) Hz, \(J_{HH} = 7.5\) Hz, \(J_{HP} = 7.0\) Hz, \(12H, CH(CH_3)_2\)), 1.16 (dt, \(J_{HH} = 7.5\) Hz, \(J_{HP} = 8.0\) Hz, \(12H, CH(CH_3)_2\)), 1.16 (s, \(18H, (CH_3)_3\)) ppm; \(^{13}\)C \(^1\)H) NMR (126 MHz, 25 \(^\circ C\), 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 (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, \(CH(CH_3)_3\)), 32.22 (br s, \(CH(CH_3)_3\)), 25.85 (br s, \(CH(CH_3)_3\)), 20.97 (s, \(^3\)TolCH), 19.25 (s, \(CH(CH_3)_3\)), 18.99 (s, \(CH(CH_3)_3\)) ppm. The peak for the carbonic carbon cannot be assigned in the 126–110 ppm region, but the total number of carbon peaks are correct. \(^{31}\)P \(^1\)H NMR (202 MHz, 25 \(^\circ C\), THF-\(d_8\)) \(\delta = 46.36\) (s) ppm. Anal. calcd for \(C_{40}H_{60}NP_2Pd\) (762.38 g mol\(^{-1}\)): C, 63.72; H, 8.42; N, 1.39. Found: C, 63.72; H, 8.42; N, 1.39.

#### Synthesis of \([\{PC(sp^3)P]^\text{Bu}PdNPh_2\] \(\text{KOE}_8\) (5)

\(KC_8\) (8.6 mg, 0.064 mmol) and \(I\) (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 x 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: ^1^H NMR (500 MHz, 25 °C, THF-d$_8$): δ = 7.35 (d, 3J$_{HH}$ = 7.5 Hz, 4H, ArH), 6.80 (t, 3J$_{HH}$ = 7.3 Hz, 4H, ArH), 6.18 (t, 3J$_{HH}$ = 7.0 Hz, 2H, ArH), 3.39 (q, 3J$_{HH}$ = 7.0 Hz, 4H, OCH$_2$CH$_3$), 1.98 (br s, 4H, C$_6$H$_4$(C$_3$H$_3$)$_2$), 1.14 (br s, 24H, CH(CH$_2$)$_3$), 1.12 (t, 4J$_{HH}$ = 7.0 Hz, 4H, OCH$_2$CH$_3$), 1.06 (br s, 18H, C(CH$_3$)$_3$) ppm; $^{31}$C{^1^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$_2$CH$_3$), 31.85 (s, C(CH$_3$)$_3$), 19.04 (br s, CH(CH$_2$)$_3$), 18.19 (br s, CH$_2$), 15.85 (s, OCH$_2$CH$_3$) ppm. The peaks for the phenyl of the [PC(sp$^2$)P] ligand backbone were not observed in the $^1$H and $^{31}$C{^1^H} NMR spectra (vide supra).

Oxidation of [{PC(sp$^2$)P}$_{14}$Pd(NH)$_2$]$_{12}$ (4)

$^{35}$P{^1^H} NMR (202 MHz, 25 °C, THF-d$_8$): δ = 48.64 (s) ppm. Ana. calcld for C$_{46}$H$_6$(P$_{12}$N$_4$)Pd$_{12}$ (1687.62 g mol$^{-1}$): C, 65.50; H, 8.08; N, 1.56. Found: C, 65.61; H, 8.12; N, 1.44.

Synthesis of [{PC(sp$^2$)P}$_{14}$PdCH$_2$Ph] $^+$ (6)

Ph$_4$CH$_2$K (7.5 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: $^1$H NMR (500 MHz, 25 °C, THF-d$_8$): δ = 7.20 (dt, 3J$_{HH}$ = 9.0 Hz, 3J$_{HP}$ = 4.5 Hz, 2H, ArH), 6.98 (d, 3J$_{HH}$ = 7.0 Hz, 2H, ArH), 6.81 (t, 3J$_{HH}$ = 7.5 Hz, 2H, ArH), 6.66 (td, 3J$_{HH}$ = 2.3 Hz, 3J$_{HP}$ = 4.8 Hz, 2H, ArH), 6.52 (dd, 3J$_{HH}$ = 9.0 Hz, 2J$_{HH}$ = 2.0 Hz, 2H, ArH), 6.46 (t, 3J$_{HH}$ = 7.3 Hz, 1H, ArH), 2.45 (t, 3J$_{HP}$ = 5.0 Hz, 2H, CH$_2$Ph), 2.26 (m, 4H, CH$_2$(CH$_3$)$_3$), 1.16 (dt, 3J$_{HH}$ = 7.0 Hz, 3J$_{HP}$ = 6.5 Hz, 12H, CH(CH$_3$)$_3$), 1.15 (s, 18H, C(CH$_3$)$_3$), 1.14 (3J$_{HH}$ = 6.0 Hz, 3J$_{HP}$ = 7.5 Hz, 12H, CH(CH$_3$)$_3$) ppm; $^{31}$C{^1^H} NMR (126 MHz, 25 °C, THF-d$_8$): δ = 161.56 (t, J$_{CP}$ = 18.6 Hz, ArC), 159.81 (t, J$_{CP}$ = 1.3 Hz, ArC), 130.35 (t, J$_{CP}$ = 3.0 Hz, ArC), 129.94 (s, ArC), 128.43 (s, ArC), 128.27 (s, ArC), 127.46 (s, ArC), 121.85 (s, J$_{CP}$ = 19.0 Hz, ArC), 118.62 (s, ArC), 115.38 (t, J$_{CP}$ = 10.3 Hz, ArC), 34.00 (s, C(CH$_3$)$_3$), 32.27 (s, C(CH$_3$)$_3$), 26.07 (t, J$_{CP}$ = 10.5 Hz, CH$_2$(CH$_3$)$_3$), 20.26 (t, J$_{CP}$ = 3.2 Hz, CH$_2$(CH$_3$)$_3$), 19.04 (s, CH(CH$_3$)$_3$), 14.12 (t, 3J$_{CP}$ = 9.0 Hz, CH$_2$Ph) ppm; $^{31}$P{^1^H} NMR (202 MHz, 25 °C, THF-d$_8$): δ = 48.52 (s) ppm. Ana. calcld for C$_{46}$H$_6$(P$_{12}$Pd)$^{14}$ (747.36 g mol$^{-1}$): C, 64.28; H, 7.96. Found: C, 64.81; H, 8.53.

Oxidation of [{PC(sp$^2$)P}$_{14}$Pd(NH)$_2$]$_{12}$ (4)

$[^35]$P{^1^H} NMR (126 MHz, 25 °C, C$_6$D$_6$): δ = 157.67 (t, J$_{CP}$ = 15.0 Hz, ArC), 155.51 (s, ArC), 146.47 (s, ArC), 136.23 (t, J$_{CP}$ = 17.3 Hz, ArC), 128.70 (s, ArC), 128.34 (s, ArC), 127.90 (s, ArC), 127.72 (t, J$_{CP}$ = 8.4 Hz, ArC), 127.00 (s, ArC), 120.48 (s, ArC), 56.26 (s, CH$_2$(backbone)), 34.36 (s, C(CH$_3$)$_3$), 31.65 (s, C(CH$_3$)$_3$), 25.62 (t, 3J$_{CP}$ = 11.2 Hz, CH(CH$_3$)$_3$), 25.52 (t, J$_{CP}$ = 9.3 Hz, CH(CH$_3$)$_3$), 19.87 (t, 2J$_{CP}$ = 3.6 Hz, CH(CH$_3$)$_3$), 19.32 (t, 3J$_{CP}$ = 2.5 Hz, CH(CH$_3$)$_3$), 19.17 (t, J$_{CP}$ = 2.1 Hz, CH(CH$_3$)$_3$), 18.00 (s, CH(CH$_3$)$_3$), 13.22 (t, 3J$_{CP}$ = 7.8 Hz, CH$_2$Ph); $^{31}$P{^1^H} NMR (202 MHz, 25 °C, C$_6$D$_6$): δ = 45.76 (s) ppm. Ana. calcld for C$_{46}$H$_6$(P$_{12}$Pd)$_{12}$ (709.27 g mol$^{-1}$): C, 67.74; H, 8.53. Found: C, 67.88; H, 8.62.

Substitution reactions of carbene [{PC(sp$^2$)P}$_{14}$Pd(PMe$_3$)$_3$] with Ph$_2$CH$_2$K, $^8$TOH and Ph$_2$N$_2$ nucleophiles

Ph$_2$CH$_2$K (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 Cd6 (with 2 drops of THF-d8) and monitored by $^1$H and $^{31}$P($^1$H) NMR spectra. Same procedures were applied for Ph2NK and Ph2NK. The reactions with PhCH2K and $^4$ToNH showed conversion to the heterobimetallic carbene 6 and 4 in 60% and 65% conversion, respectively, based on the $^{31}$P($^1$H) NMR spectra. No conversion was observed for Ph2NK.

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