Redox-induced umpolung of transition metal carbenes†

Peng Cui and Vlad M. Iluc*

Metal carbene complexes have been at the forefront of organic and organometallic synthesis and are instrumental in guiding future sustainable chemistry efforts. While classical Fischer and Schrock type carbenes have been intensely studied, compounds that do not fall within one of these categories have attracted attention only recently. In addition, applications of carbene complexes rarely take advantage of redox processes, which could open up a new dimension for their use in practical processes. Herein, we report an umpolung of a nucleophilic palladium carbene complex, \([\{\text{PC}(sp^2)\text{P}\}_\text{tBuPd(PMe}_3\}]\) (1), realized by successive one-electron oxidations that generated a cationic carbene complex, \([\{\text{PC}(sp^2)\text{P}\}_\text{tBuPdI}\]^+. An EPR spectroscopic study of \([\{\text{PC}(sp^2)\text{P}\}_\text{tBuPdI}\] indicated the presence of a ligand-centered radical, also supported by the results of reactions with 9,10-dihydroanthracene and PhSSPh. The cationic carbene complex shows electrophilic behavior toward nucleophiles such as NaH, t-BuNHLi, PhONa, and PMe3, resulting from an inversion of the electronic character of the Pd–C carbene bond in \([\{\text{PC}(sp^2)\text{P}\}_\text{tBuPd(PMe}_3\}]\). The redox induced umpolung is reversible and unprecedented.

Introduction

Transition metal carbene complexes, usually classified as Fischer and Schrock type according to the polarity of the M–C carbene bond,1 are among the most extensively studied organometallic species.2 While the reactivity of the M–C carbene fragment is generally governed by the electronic properties of the metal center and the substituents of the carbene moiety,3 its behavior in response to redox reactions has not been studied in detail.4 For example, although the one-electron reduction of a Fischer-type carbene leading to a carbene radical anion, which upon a second one-electron reduction generates a dianion, is known,5 the corresponding oxidation processes that could be applied to Schrock-type carbenes (Fig. 1) have not been reported so far. These electron transfer processes cause an umpolung of the original carbene’s character, namely the inversion of the M–C carbene bond polarity,6 and could open up new applications for these compounds in synthesis.

The development of redox chemistry of transition metal carbenes and reactivity studies of the species generated under redox conditions are still in their infancy,7 with only a few examples reported exclusively for Fischer carbenes.8 Interestingly, Fischer

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**Fig. 1** Top: Umpolung of transition metal carbenes by redox reactions. Bottom: Illustration of umpolung of palladium carbene’s character by redox processes described in this work.

**Notes:**

† Electronic supplementary information (ESI) available: Characterization data for all new compounds, computational results, single crystal X-ray structure analysis of complexes 4–6, 8–12. CCDC 1404570–1404575, 1416513–1416514. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc02859k
type carbenes of group 9 metals in the +2 oxidation state exhibited a remarkable radical character, their redox non-innocent behavior being considered crucial to the asymmetric cyclopropanation of olefins catalyzed by Co(II)porphyrins.6,7 Pioneering work by Casey and later by Cooper et al. showed that Fischer type carbene complexes could be reduced to the corresponding radical and dianionic entities.5 The latter reacted with CO2 to form a malonate, indicating an umpolung from the electrophilic character of the Fischer type carbene to nucleophilic.5b

As mentioned above, the redox behavior of Schrock type carbenes has not been explored. We reasoned that palladium nucleophilic carbenes5 represent good candidates for such a study given the higher stability of late transition metal carbene complexes when compared to that of their early metal counterparts. In addition, the combination between palladium, which can undergo two-electron processes (oxidative addition/reductive elimination), and a redox active ligand, which can undergo sequential one electron processes, has only recently been investigated.4b No examples in which a carbene carbon is the site of redox activity are known.

On the other hand, although it is known that palladium carbene species generated from diazo compounds show unique properties and undergo novel transformations, their isolation and characterization is still challenging due to their highly reactive nature.14 We previously reported the nucleophilic Pd(d) carbene complexes [PC(sp²)P]H[Pd(PR₃)] (1: R = Me; 2: R = Ph) [PC(sp²)P]H⁺ = bis[2-(di-iso-propylphosphino)phenyl]-methyl-ene] were12 and [PC(sp²)P]²Ru[Pd(PMe₃)] (3), [PC(sp²)P]²Ru = bis[2-(di-iso-propylphosphino)-4-tert-butylphenylmethylene],6b in which the Pd-C(carbene) bonds are best described as ylide-like, M-C⁺ type, as demonstrated by the reactivity of 1 toward MeI, HCl, MeOH and para-toluidine and also by C-H activation reactions.15 The strong nucleophilic character of 1 and 3 was also demonstrated by the rapid Lewis acid/base “quenching” reactions with B(C₆F₅)₃.16 As indicated by DFT calculations, the HOMO of 1 is largely localized on the carbene carbon atom, therefore, an oxidation process to induce the loss of electrons might occur from that orbital. Consequently, the one-electron oxidation of 1 with 0.5 equivalents of I₂ afforded a stable radical complex, [PC(sp²)P]²Pd], which persisted in solution but dimerized in the solid state. Interestingly, the chloride and bromide congeners are monomers in both phases.14

These results prompted us to study the oxidation of the radical species further to the corresponding cations, and therefore to realize an umpolung of a nucleophilic carbene. In order to prevent dimerization and also simplify the synthetic procedure, carbene complex 3 bearing bulky tert-butyl groups was employed instead of 1.14 The good solubility provided by the t-Bu groups also facilitated reactivity studies. Herein, we report the successive one-electron oxidation of 3 leading to a cationic carbene complex, [PC(sp²)P]²RuPdI][BAR]⁺ (5), via a monomeric radical species [PC(sp²)P]²RuPdI] (4). Reactivity studies on both complexes are consistent with their unique electronic properties, and the umpolung of carbene complex 3 was undoubtedly demonstrated by the reactions of 5 with various nucleophiles. Notably, the electron transfer processes to generate the carbene, radical, and cationic species are reversible.

Results and discussion

Synthesis and characterization of palladium radical and cationic carbene complexes

Slow addition of 0.5 equivalents of I₂ to the dark-brown solution of [PC(sp²)P]²RuPdI][BAR]⁺ (3) in THF at −35 °C instantly generated a dark-green solution, from which dark-green crystals of [PC(sp²)P]²RuPdI] (4) were isolated in 97% yield (Scheme 1). Complex 4 is silent by both H and ²H NMR spectroscopy. The magnetic susceptibility measurement at 298 K using the Evans method gave an effective magnetic moment μeff of 1.85 μB, thus indicating an S = 1/2 ground state. The X-band EPR spectrum recorded at 298 K revealed an isotropic signal typical for a carbon center radical complex with a g value of 2; no hyperfine coupling was observed (Fig. S1†). Complex 4 is stable toward water but highly sensitive toward oxygen. Upon exposing the dark-green solution of 4 to air, the color changed immediately to yellow. However, attempting to react 4 with a stoichiometric amount (1 or 0.5 equivalents) of pure oxygen only led to complicated mixtures of products. Interestingly, in contrast to radicals generated in situ from Fischer type carbenes,15 complex 4 is thermally robust: no significant decomposition was observed after heating 4 in C₆D₆ at 80 °C for a week, likely a consequence of the radical delocalization over both phenyl rings and of the steric protection from the two tert-butyl groups present in 4.

Cyclovoltammetry studies of 4 performed in a THF solution (Fig. 2) showed a quasi-reversible event at E½ = −0.38 V, assigned to [PC(sp²)P]²RuPdI][PC(sp²)P]²RuPdI] and an irreversible reduction event at E = −2.03 V (vs. Fc/Fc*), assigned to the reduction to [PC(sp²)P]²RuPdI].

Treatment of the dark-green solution of 4 with an equivalent of [Cp₂Fe][BAR]⁺ in diethyl ether at −35 °C instantly formed a dark-red solution, and the dark-red crystalline complex [PC(sp²)P]²RuPdI][BAR]⁺ (5) was isolated in 94% yield (Scheme 1). To the best of our knowledge, only two examples of nonheteratom-stabilized cationic Pd(d) carbene complexes are known: complex A (Fig. 3) was prepared from a cationic precursor by triflate abstraction with di-p-tolylidiazomethane,15 while compound B was synthesized by hydride abstraction from a PCHP pincer complex16 reactivity studies have not been reported for these species. In addition, cationic alkylidene complexes of other late transition metals are also rare.17

Scheme 1 Synthesis of radical and cationic carbene complexes: (1) 0.5 I₂, −35 °C, THF, 30 min; (2) [Cp₂Fe][BAR]⁺, −35 °C, diethyl ether, 15 min; (3) KC₈, PME₃, THF, 5 min; (4) K₅C₈, THF, 5 min.
The structures of 4 and 5 were unambiguously determined by single crystal X-ray diffraction studies. As shown in Fig. 4 and 5, both complexes contain square-planar palladium centers bound to the sp² hybridized backbone carbons (the sum of the angles at C is 359.8° for 4 and 359.7° for 5). The Pd-C_carbene distance of 2.076(3) Å in 3 contracts to 2.022(3) Å in 4 and further to 1.968(3) Å in 5. The Pd–C_carbene distance of 1.968(3) Å in 5 is comparable to that of 1.999(4) Å in [P,C==PdCl][PF6] (B, Fig. 3). Although the Pd–C_carbene bond in 3 is better described as a single bond,[94,101,14,20] the contraction observed for 4 and 5 can be attributed to the increased bond order between the metal center and the carbene carbon, achieved by the sequential removal of electrons from the π* antibonding orbital (vide infra). This trend also indicated a change of the electronic property of this atom from an anion in 3 to a cation in 5 via the radical in 4. Therefore, the isolation of 4 and 5 is remarkable and represents the first example of successive oxidations of a transition metal nucleophilic carbene leading to a well-defined radical and cation, with all three complexes characterized by X-ray crystallography.

**DFT calculations**

DFT calculations were performed on a model of the cationic carbene 5 (Fig. 6). In contrast to the antibonding character of HOMO observed for 3, a similar antibonding π type interaction was found for the LUMO of 5 and the SOMO of 4, resulting from the successive removal of electrons from the HOMO of 3 that is largely localized on the carbene carbon. The bonding component of this π bond was found in HOMO–11 for 5. Therefore, consistent with the observed contraction of the Pd–C_carbene distances from 3 (2.076(3) Å) to 5 (1.968(3) Å), the frontier molecular orbital analysis also indicates an increase of the Pd–

![Chemical structure diagram](image-url)
of carbene 3 in diethyl ether immediately generated a dark green solution containing carbene radical 4 and the cationic radical complex \([\{\text{PC}(\text{sp}^3)\text{HP}\}\text{BuPdCl}\}^+\text{[BArF}_4^-]\) (Fig. S41†), which were confirmed by their hydrogen atom abstraction reactions with 9,10-dihydroanthracene (vide infra).

Reactivity of palladium carbene radical complex

The carbene radical complex 4 is expected to undergo ligand centered radical-type reactions, such as hydrogen atom abstraction. Despite this prediction, heating a \(\text{CsD}_{6}\) solution of 4 with \(\text{^8Bu}_3\text{SnH}\) at 80 °C for one week did not produce the hydrogen atom abstraction product, and the color of the solution remained dark green. However, 4 reacted slowly reacted with 0.5 equivalents of 9,10-dihydroanthracene under similar conditions to generate a bright yellow solution, from which the expected hydrogen abstraction product \([\{\text{PC}(\text{sp}^3)\text{HP}\}\text{BuPdCl}\}^+\text{[BArF}_4^-]\) 6 was isolated as an orange crystalline solid in 81% yield, after recrystallization from \(n\)-pentane (Scheme 2). The formation of the by-product anthracene was also confirmed by NMR spectroscopy.

The \(^1\text{H}\) NMR spectrum of 6 in \(\text{CsD}_{6}\) showed \(\text{C}_{6}\) symmetry as observed for its chloride analogue \([\{\text{PC}(\text{sp}^3)\text{HP}\}\text{BuPdCl}\}^+\text{[BArF}_4^-]\). The benzylic proton of 6 was observed at \(\delta = 6.41 \text{ ppm}\) as a singlet, while the benzylic carbon was observed at \(\delta = 58.35 \text{ ppm}\) as a triplet (\(J_{\text{PC}} = 4.4 \text{ Hz}\)) in the corresponding \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum. Both values are slightly downfield shifted compared to those of the chloride analogue (\(\delta = 6.21 \text{ and } 50.59 \text{ ppm}\) for the \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra, respectively). In the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum, only one sharp singlet at \(\delta = 51.25 \text{ ppm}\) was observed. The crystal structure of 6 is analogous to that of \([\{\text{PC}(\text{sp}^3)\text{HP}\}\text{BuPdCl}\}^+\text{[BArF}_4^-]\) (Fig. 7), in that both contain an \(\text{sp}^3\) hybridized backbone carbon atom. The Pd–C_{backbone} distance of

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Fig. 5 Molecular structure of 5 with displacement parameters at 50% probability level. Hydrogen atoms and the counter anion are omitted for clarity. Selected distances (Å) and angles (degree): Pd–C = 1.968(3), Pd–P(1) = 2.3161(7), Pd–P(2) = 2.2884(7), Pd–I = 2.6255(5), P(1)–Pd–P(2) = 164.98(3), Pd–C–C(11) = 117.59(19), Pd–C–C(21) = 121.2(2), C(11)–C–C(21) = 120.9(2).

Fig. 6 Molecular orbitals for the Pd–C π interaction for 5. Left: HOMO–11, right: LUMO.
Coupling of the radical in 4 with a thyl radical occurs in the reaction with diphenyl disulfide (Scheme 2). Albeit slow, heating 4 with 0.5 equivalents of PhSSPh in C₆D₆ at 80 °C for 7 days formed [[PC(sp³)(SPh)P]²⁺[PdCl]₄]₁₆₅.₄₀(2), Pd–C(carbene) distance of 2.094(2) Å is also close to that of 2.078(2) Å in [[PC(sp³)HP]²⁺[PdCl]₄]₁₆₅.₄₀ but longer than the Pd–C(carbene) distance of 2.022(3) Å for 4.

According to the standard redox potential of PhSSPh (−1.7 V vs. SCE, −2.1 V vs. Fe(FeC)₃) and the observed value for the [[PC(sp³)(SPh)P]²⁺[PdCl]₄]/[[PC(sp³)HP]²⁺[PdCl]₄] redox couple (−0.38 V vs. Fe(FeC)), it is less likely that the carbene radical 4 was oxidized by PhSSPh to the carbene cation [[PC(sp³)(SPh)P⁺[PdCl]₄] which reacted with the [PhS]⁻ anion to form 7. Therefore, compound 7 was probably formed by direct radical coupling between the carbene radical and [PhS⁻] generated by the homolysis of PhSSPh.

It is also interesting to note that the carbene complex 3 can be readily oxidized by PhSSPh. Treatment of 3 with an equivalent of PhSSPh in C₆H₆ immediately generated a bright yellow solution at room temperature, from which the yellow crystalline solid of [[PC(sp³)(SPh)P⁺[Pd(SPh)]]₁₉₈.₄₀(6), Pd–O(O(61)] = 2.1895(17), S–C = 1.840(2), P(2)Pd–P(2) = 154.14(2).}

**Scheme 3** Reaction of carbene 3 with PhS-SPh.

Fig. 7 Molecular structure of 6 with displacement parameters at 50% probability level. Most hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (degree): Pd–C = 2.094(2), Pd–P(1) = 2.3123(7), Pd–P(2) = 2.2698(7), Pd–I = 2.6763(3), P(1)–Pd–P(2) = 165.40(2), Pd–C–C(11) = 109.32(16), Pd–C–C(21) = 115.91(16), C(11)–C–C(21) = 116.7(2).

Fig. 8 Molecular structure of 8 with displacement parameters at 50% probability level. Most hydrogen atoms and the solvent molecule are omitted for clarity. Selected distances (Å) and angles (degree): Pd–C = 2.051(2), Pd–P(1) = 2.2745(6), Pd–P(2) = 2.3554(6), Pd–O(O(61)] = 2.1895(17), S–C = 1.840(2), P(1)–Pd–P(2) = 154.14(2).
When carbene 3 was treated with only 0.5 equivalents of PhSSPd in C₆D₆, compound 9 and unreacted 3 were observed by ¹H and ³¹P NMR spectra; upon which the addition of another 0.5 equivalents of PhSSPd, the mixture led to 9. It is worth noting that a radical complex [PC(sp³)P]⁺⁺(PdPPh)⁻ (C) was not formed under these conditions, but it could be an intermediate species that generates 9 by rapid coupling with the [PhS⁺] radical. This intermediate, C, can be generated by an one-electron transfer from carbene 3 to PhSSPd, however, direct addition of PhSSPd across Pd⁺⁻C⁺⁺* carbene moiety or oxidative addition to palladium followed by the migration of the PhS⁻ moiety to the carbene carbon to form 9, cannot be ruled out.

Reactivity of palladium cationic carbene complex

The cationic carbene complex 5 is expected to be electrophilic, therefore its reactivity toward various nucleophiles was studied. We had previously isolated complex 6 from a hydrogen atom abstraction reaction with the carbene radical 4, and thus assumed that a nucleophilic attack on the cationic carbene 5 by a H⁻ nucleophile would also produce 6. Treatment of a dark-red solution of 5 with an equivalent of NaH in THF at room temperature gradually generated a bright yellow solution within 24 hours. Both ¹H and ³¹P{¹H} NMR spectra showed that the 6 was formed in quantitative yield together with the by-product Na[BF₄]⁻ (Scheme 4). Since the cationic Ir(η)[II] metallocyclic alkylidene complex was reported to react with LiAlH₄ even at low temperature, the slow reaction with 5 was attributed to the poor nucleophilicity of NaH, but also to its poor solubility in THF.

We then studied the reaction the cationic carbene 5 with nucleophiles. LiNHTol and PhONa, since both salts are readily soluble in THF. Slow addition of a THF solution of LiNHTol to the dark-red solution of 5 at −35 °C immediately formed a brownish-green solution. Similarly, the addition of PhONa to 5 resulted in the formation of a bright-yellow solution. The expected products [[PC(sp³)(NH)Tol]⁺⁺(PdI)⁻] (10) and [[PC(sp³)(OPh)P]⁺⁺(PdI)⁻] (11) were isolated in moderate yields (Scheme 4) as yellow crystalline solids, which are soluble in aliphatic solvents. Multiple recrystallizations were performed to remove the Na[BF₄]⁻ salt. The structures of 10 and 11 were confirmed by X-ray diffraction studies. As shown in Fig. 10 and 11, both contain a square planar palladium center anchored with the sp³ hybridized carbon. The hydrogen atom of the NH group was located in the electron density map. The short N−C(sp³) distance of 1.378(4) Å indicated a delocalization of the lone pair of the nitrogen atom to the phenyl ring of the para-toluidine group and the geometry at the nitrogen atom is essentially trigonal planar (sum of the angles of 360°). Interestingly, both phenyl rings of the NHPOl and OPh groups point somewhat toward palladium, with the corresponding dihedral angles between the planes of the phenyl rings and the planes defined by I, Pd, C backbone and X (X = N or O) being 64.05° and 58.91°, respectively, which are smaller than that of 73.49° in 8.

As expected, the ¹H NMR spectra of 10 and 11 in C₆D₆ showed C₆ symmetry. The proton of the NH group in 10 was observed at δ = 4.22 ppm as a triplet (J₁HH = 2.8 Hz). Interestingly, the ³¹P{¹H} NMR spectra of 10 and 11 at 298 K showed only broad singlets at δ = 49.89 (Δν₁/₂ ≈ 909 Hz) and 51.09
not observed for NMR spectra at 338 K. Since a similarly dynamic behavior was

\[ \text{selected distances (Å) and angles (degree): } Pd-C = 2.116(3), Pd-P(1) = 2.3206(7), Pd-P(2) = 2.2609(8), Pd-I = 2.6903(3), C-N = 1.461(3), P(1)-Pd-P(2) = 155.81(3). \]

The activation parameters obtained from Eyring plots for 10 are: \( \Delta G^\ddagger = 11.1 \pm 0.2 \text{ kcal mol}^{-1} \) (298 K), \( \Delta H^\ddagger = 13.9 \pm 0.4 \text{ kcal mol}^{-1} \) and \( \Delta S^\ddagger = 10 \pm 2 \text{ cal (mol}^{-1} \text{ K}) \); and for 11 are: \( \Delta G^\ddagger = 10.7 \pm 0.4 \text{ kcal mol}^{-1} \) (298 K), \( \Delta H^\ddagger = 11.8 \pm 0.4 \text{ kcal mol}^{-1} \) and \( \Delta S^\ddagger = 4 \pm 2 \text{ cal (mol}^{-1} \text{ K}) \).

Although the nucleophiles \( H^- \), \( Ph^0 \), and \( PhO^- \) afforded the expected products 6, 10, and 11, respectively, the reaction of 5 with PhCH2K did not lead to an isolable product. Also, the lithium salts MeOLi and PhOLi did not react with 5, probably due to their weaker nucleophilic character compared to that of the sodium salt PhONa.

A neutral nucleophile such as PMe3 also reacts instantly with 5 in diethyl ether to form a bright-yellow solution; yellow crystals of \([\text{PC}(\text{sp}^3)\text{PMe}_3]\text{PdI}\) [BArF4] (12) were isolated in quantitative yield by the diffusion of \( n \)-pentane into a fluoro-benzene solution at room temperature. Compound 12 is only soluble in ethereal and chlorinated solvents. Its 1H NMR spectrum in CDCl3 showed \( C_s \) symmetry as was also observed for compounds 6–11. The protons of the PMe3 group were observed at \( \delta = 1.31 \text{ ppm as a doublet (2J}_{HH} = 11.5 \text{ Hz}) \), which correlates with a doublet at \( \delta = 13.86 \text{ ppm (1J}_{CP} = 54.3 \text{ Hz}) \) in the \( ^{31} \text{C}(1) \text{H} \) NMR spectrum. In the \( ^{31} \text{P}(1) \text{H} \) NMR, two sharp singlets at \( \delta = 42.17 \text{ and } 31.01 \text{ ppm were observed for the two } ^{2} \text{P} \text{P phosphines and the PMe3 on the backbone carbon, respectively. Both signals remain sharp when the temperature was lowered to 248 K, indicating a lower energy barrier for the rotation of PMe3 group compared to those for } ^{2} \text{ToNH and PhO groups in 10 and 11. In the } ^{13} \text{C}(1) \text{H} \) NMR spectrum, the backbone carbon resonance was observed at \( \delta = 63.65 \text{ (dt, } 1J_{CP} = 21.5 \text{ Hz, } 2J_{CP} = 2.4 \text{ Hz}) \text{ ppm which is significantly shifted to higher field compared to } 284.47 \text{ ppm observed for 5, and close to the value of } 58.35 \text{ ppm in 6. Thus, the strong donation from PMe3 to the carbenium carbon effectively offsets the charge on this atom.} \)
The exclusive formation of 12 is consistent with its strong electrophilic character. Heating this compound at 60 °C in CDCl₃ for 24 h did not lead to any decomposition. However, the cationic Ir[IV] alkylidene hydride species \( [(C₅Me₅)H₂Ir\text{Pd}(PMe₃)] \) \( (1.854(2) \text{ Å}) \) and PMe₃ occurred upon mixing, but a complicated mixture was obtained by Pd-Pd coupling reactions. A broad peak at \( 78.9 \text{ °C} \) was observed in the \( 2.5 \text{ ppm} \) region of deuterated solvents for proton and carbon nuclear magnetic resonance (NMR) signals.

**Conclusions**

In conclusion, the one-electron oxidation of the palladium carbene complex \( \{[(PC(sp²)P)_{2}Pd(PMe₃)]\} \) \( (3) \) with \( I₂ \) generated a mononeric radical carbene complex \( \{[(PC(sp²)P)_{2}Pd(PMe₃)]\} \) \( (4) \), which upon a second one-electron oxidation with \( \text{Cp₂Fe}[\text{BArF}_4] \) formed a cationic carbene complex, \( \{[(PC(sp²)P)_{2}Pd(PMe₃)]\} \) \( (5) \). We were able to isolate and characterize for the first time a whole series of anionic carbene (3), a carbene radical (4), and a cationic carbene (5). Our studies show that: (1) transition metal carbene complexes possess a rich redox chemistry that allows the tuning of the electronic properties of the carbene backbone; (2) an umpolung of the \( M-C \text{ carbene} \) bond can be accomplished by successive electron transfer processes; and (3) the electron transfers among the carbene, radical, and cationic species are reversible.

**Experimental**

All experiments are performed under an inert atmosphere of \( N₂ \) using standard glovebox techniques. Solvents hexanes, \( n \)-pentane, diethyl ether, and \( CH₂Cl₂ \) were dried by passing through a column of activated alumina and stored in the glovebox. THF was dried over LiAlH₄ followed by vacuum transfer and stored in the glovebox. CDCl₃ was dried over 4 Å molecular sieves under \( N₂ \), while d₅D₅O was dried over CaH₂ followed by vacuum transfer, and stored in the glovebox. Complex \( 3, [\text{Cp₂Fe}] [\text{BArF}_4] \) and \( \text{KC₈} \) were prepared according to literature procedures. \( 30, 31 \) PolNHIL was prepared by deprotonation of \( p \)-toluidine with \( " \text{BuLi} \), while PhONa was prepared from NaH and phenol. \( 1H, 3C \{[\text{H}],[31P,11B,19F] \} \) and \( 11B \{[\text{H}] \} \) 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 \( H₂PO₄ \), BF₃·OEt₂, and CFCI₃ for \( 31P, 11B \), and \( 19F \) chemical shifts, respectively. Magnetic moments were determined by the Evans method \( 29 \) by using a capillary containing 1,3,5-trimethoxybenzene in \( C₅D₅N \) as a reference. EPR spectrum of compound 4 was recorded on a Bruker EMXplus EPR spectrometer with a standard X-band EMXplus resonator and an EMX premium microwave bridge. Cyclic voltammetry was performed on a Metrohm Autolab PGSTAT-128N instrument. 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 \( \{[(PC(sp²)P)_{2}Pd(PMe₃)]\} \) (4)**

Iodine (11 mg, 0.043 mmol) in 1 mL of THF was slowly added to a dark-brown solution of 3 (60 mg, 0.087 mmol) in 1 mL of THF at \( -35 \) °C. Upon addition, a dark-green solution was formed immediately and stirred at ambient temperature for 30 min. All volatiles were removed under reduced pressure and the dark-green residue was extracted with \( n \)-pentane (2 × 4 mL). After reducing the volume of the pentane solution to about 1 mL, the solution was stored at \( -35 \) °C to give 4 as a dark-green crystalline solid; yield 62 mg (97%). Compound 4 is paramagnetic. Magnetic moment (Evans method, 298 K); \( \mu_{eff} = 1.85 \mu_B \); EPR: \( g = 2.0000 \). Anal. calcd for \( C_{33}H_{52}IP_2Pd \): C, 53.27; H, 7.04. Found: C, 53.05; H, 7.24.

**Reduction of 4 with \( \text{KC₈} \)**

\( \text{KC₈} \) (2.3 mg, 0.016 mmol) was mixed with 4 (12 mg, 0.016 mmol) and PMe₃ (32 μL, 0.032 mmol, 1 M in THF) in 1 mL THF at room temperature.
temperature. The mixture turned dark-brown immediately. After stirring the reaction mixture for about 5 min, the volatiles were removed under reduced pressure and the residue was extracted with 1 mL of n-pentane. The solution was filtered through Celite. Compound 3 was obtained as dark brown crystalline solid from this n-pentane solution at −35 °C. 1H and 31P (1H) NMR spectra were identical with the previously reported data.26 Yield 9 mg (80%).

Synthesis of [PC(sp3)2P]4Pd[BAr4] (5) [Cp2Fe][BAr4] (83.2 mg, 0.079 mmol) in 3 mL of diethyl ether was slowly added to a dark-green solution of 4 (59 mg, 0.079 mmol) in 2 mL of diethyl ether at −35 °C. Upon addition, a dark-red solution was formed immediately that was stirred at room temperature for 15 min. After reducing the volume of the ether solution to about 1 mL, n-pentane (about 8 mL) was layered and the mixture was stored at −35 °C overnight to afford compound 5 as a dark-red crystalline solid, which was washed with n-pentane and dried under vacuum; yield 119 mg (94%). 1H NMR (500 MHz, CDCl3, 25 °C): δ = 7.93 (td, JHH = 3.8 Hz, JHP = 1.5 Hz, 2H, ArH), 7.73 (m, 4H, ArH), 7.64 (s, ArH, ortho-ArH), 7.46 (s, 4, para-ArH), 2.99 (m, 4H, CH(CH3)2), 1.39 (s, 18H, CH(CH3)3), 1.36 (dt, JHH = 9.0 Hz, JHP = 9.5 Hz, 12H, CH(CH3)2), 1.26 (dt, JHH = 9.0 Hz, JHP = 8.0 Hz, 12H, CH(CH3)2) ppm; 13C (1H) NMR (126 MHz, CDCl3, 25 °C): δ = 284.47 (s, Cbarrene), 169.05 (s, CAr), 161.81 (q, JCP = 49.94 Hz, ipso-ArCH), 156.24 (t, JCP = 15.0 Hz, ArC), 148.03 (t, JCP = 14.6 Hz, ArC), 136.30 (t, JCP = 7.0 Hz, ArC), 134.89 (s, ortho-ArC), 132.11 (s, ArC), 131.50 (s, ArC), 129.00 (q, JFC = 30.3 Hz, meta-ArC), 124.58 (q, JFC = 273.1 Hz, CF3), 117.55 (s, para-ArC), 37.26 (s, C(CH3)3), 30.36 (s, C(CH3)3), 26.66 (d, JCP = 11.6 Hz, CH(CH3)2), 26.57 (d, JCP = 11.5 Hz, CH(CH3)2), 19.34 (s, CH(CH3)2), 18.62 (s, CH(CH3)2) ppm; 31P (1H) NMR (202 MHz, CDCl3, 25 °C): δ = 72.04 (s) ppm; 11B (1H) NMR (160 MHz, CDCl3, 25 °C): δ = −6.62 (s) ppm; 19F (1H) NMR (170 MHz, CDCl3, 25 °C): δ = −65.79 (s) ppm. Anal. calc. for C65H64BF24IP2Pd: C, 48.59; H, 4.02; F, 6.62 (s) ppm; 19F{1H} NMR (170 MHz, CDCl3, 25 °C): δ = 58.35 (t, JFP = 127.68 Hz, ArF) ppm; 31P (1H) NMR (745.05 MHz, CDCl3, 25 °C): δ = 155.62 (t, JCP = 14.7 Hz, ArC); 148.28 (t, JCP = 3.0 Hz, ArC), 134.78 (t, JCP = 16.6 Hz, ArC), 128.71 (s, ArC), 126.68 (s, ArC), 120.84 (t, JCP = 9.6 Hz, ArC), 58.53 (t, JCP = 4.4 Hz, CH backbone), 34.44 (s, C(CH3)3), 31.48 (s, C(CH3)3), 26.91 (d, JCP = 9.1 Hz, C(CH3)2), 26.82 (d, JCP = 7.2 Hz, C(CH3)2), 26.73 (d, JCP = 5.2 Hz, C(CH3)2), 19.95 (t, JCP = 2.6 Hz, C(CH3)2), 19.42 (t, JCP = 1.8 Hz, C(CH3)2), 18.67 (s, C(CH3)2), 18.50 (s, C(CH3)2) ppm; 31P (1H) NMR (202 MHz, CDCl3, 25 °C): δ = 51.25 (s) ppm. Anal. calc. for C63H53IP2Pd: C, 53.20; H, 7.17. Found: C, 53.04; H, 7.23.

Synthesis of [PC(sp3)3(SPh)]4Pd (7) PhSSPh (4.4 mg, 0.020 mmol) and 4 (30 mg, 0.040 mmol) were mixed in 0.6 mL of C6D6 and heated at 80 °C for 7 d, during which time the dark-green solution slowly turned to bright yellow. The volatiles were removed under reduced pressure and the residue was extracted with 5 mL of n-pentane and filtered. Removal of the volatiles under reduced pressure gave an yellow waxy solid; yield 32 mg (94%). 1H NMR (500 MHz, CDCl3, 25 °C): δ = 7.52 (m, 2H, ArH), 7.27 (d, JHH = 8.5 Hz, 2H, ArH), 7.07 (dm, JHH = 8.5 Hz, 2H, ArH), 7.01 (d, JHH = 8.0 Hz, 2H, ArH), 6.97 (tt, JHH = 7.3 Hz, JHP = 1.3 Hz, 1H, ArH), 6.91 (tt, JHH = 7.0 Hz, JHP = 1.2 Hz, 2H, ArH), 3.11 (m, 2H, CH(CH3)2), 2.76 (m, 2H, CH(CH3)2), 1.51 (dt, JHH = 7.5 Hz, JHP = 7.5 Hz, 6H, CH(CH3)2), 1.44 (m, 12H, CH(CH3)2), 1.21 (s, 18H, C(CH3)3), 1.06 (dt, JHH = 7.5 Hz, JHP = 7.0 Hz, 6H, CH(CH3)2) ppm; 13C (1H) NMR (126 MHz, C6D6, 25 °C): δ = 156.63 (t, JCP = 12.7 Hz, ArC), 149.44 (t, JCP = 2.9 Hz, ArC), 136.58 (t, JCP = 3.2 Hz, ArC), 136.34 (s, ArC), 136.23 (t, JCP = 16.1 Hz, ArC), 129.60 (s, ArC), 128.84 (t, JCP = 9.0 Hz, ArC), 128.57 (s, ArC), 128.52 (s, ArC), 126.41 (s, ArC), 79.58 (t, JCP = 6.1 Hz, CH backbone), 34.46 (s, C(CH3)3), 31.41 (s, C(CH3)3), 28.19 (t, JCP = 11.7 Hz, CH(CH3)2), 27.36 (d, JCP = 11.1 Hz, CH(CH3)2), 20.00 (s, CH(CH3)2), 19.90 (s, CH(CH3)2), 19.20 (s, CH(CH3)2) ppm; 31P (1H) NMR (202 MHz, C6D6, 25 °C): δ = 48.59 (s) ppm. Anal. calc. for C63H52SP2Pd2 (853.21 g mol−1): C, 54.90; H, 6.73. Found: C, 54.82; H, 6.65.

Synthesis of [PC(sp3)3(SPh)]4PdOTf (8) AgOTf (9.6 mg, 0.038 mmol) in 1 mL of THF was added to 7 (32 mg, 0.038 mmol) in 1 mL of THF at room temperature. The resulting orange slurry was stirred for 4 h, slowly turning to a pale yellow slurry. The volatiles were removed under reduced pressure and the residue was extracted with 5 mL of benzene.
and filtered. Removal of volatiles under reduced pressure led to a yellow solid, which was recrystallized from diethyl ether at −35 °C to give 8 as yellow blocks; yield 20 mg (61%). 1H NMR (500 MHz, C6D6, 25 °C): δ = 7.89 (dd, JHH = 8.0 Hz, JCP = 1.3 Hz, 2H, ArH), 7.55 (d, JHH = 8.5 Hz, 2H, ArH), 7.37 (m, 2H, ArH), 7.11 (m, 4H, ArH), 6.94 (t, JHH = 7.5 Hz, 7H, 1H, ArH), 3.09 (m, 2H, CH(CH3)2), 2.35 (m, 2H, CH(CH3)2), 1.37 (dt, JHH = 7.5 Hz, JCP = 8.0 Hz, 2H, CH2(CH3)2), 1.31 (dt, JHH = 7.5 Hz, JCP = 8.0 Hz, 2H, CH2(CH3)2), 1.16 (s, C(CH3)2), 1.12 (dt, JHH = 7.5 Hz, JCP = 7.5 Hz, 6H, CH(CH3)2), 0.93 (dt, JHH = 8.0 Hz, 6H, CH2(CH3)2) ppm; 13C{1H} NMR (126 MHz, C6D6, 25 °C): δ = 154.67 (t, JCP = 13.5 Hz, ArC), 150.66 (t, JCP = 2.5 Hz, ArC), 137.07 (s, ArC), 134.85 (s, ArC), 134.08 (t, JCP = 16.9 Hz, ArC), 129.64 (s, ArC), 129.55 (s, ArC), 129.97 (s, ArC), 128.82 (t, JCP = 8.6 Hz, ArC), 127.03 (s, ArC), 121.24 (q, JFC = 320.3 Hz, CF3), 76.10 (t, JCP = 6.6 Hz, Cbackbone), 34.52 (s, C(CH3)2), 31.22 (s, C(CH3)2), 26.52 (t, JCP = 9.6 Hz, CH2(CH3)2), 25.88 (t, JCP = 10.2 Hz, CH2(CH3)2), 19.71 (s, CH(CH3)2), 19.19 (s, CH(CH3)2), 18.70 (t, JCP = 3.0 Hz, CH2(CH3)2), 18.29 (s, CH(CH3)2) ppm; 31P{1H} NMR (202 MHz, C6D6, 25 °C): δ = 49.44 (s) ppm; 31P{13C} NMR (470 MHz, C6D6, 25 °C): δ = −80.11 (s) ppm. Caled. for C45H62P2PdS2: C, 54.88; H, 6.56. Found: C, 54.97; H, 6.67.

**Synthesis of [{PC(sp3)(OPh)P}BuPd] (10)**

TolNH2I (3.3 mg, 0.029 mmol) in 1 mL of THF was slowly added to a dark-red solution of 5 (46 mg, 0.029 mmol) in 1 mL of THF at −35 °C. The resulting brownish-green solution was then stirred at room temperature for 15 min. The volatiles were removed under reduced pressure and the residue was extracted with 5 mL of benzene and filtered. Removal of volatiles under reduced pressure gave a greenish-yellow residue, which was extracted with n-pentane (8 mL), filtered, and the volume of the pentane solution reduced to about 1 mL. Storing this solution at −35 °C gave compound 10 as yellow crystals; yield 12 mg (49%). 1H NMR (500 MHz, C6D6, 25 °C): δ = 7.52 (m, 2H, ArH), 7.14 (d, JHH = 8.5 Hz, 2H, ArH), 7.10 (d, JHH = 8.0 Hz, 2H, ArH), 7.03 (d, JHH = 8.0 Hz, 2H, ArH), 6.79 (d, JHH = 8.0 Hz, 2H, ArH), 4.22 (t, JCP = 2.8 Hz, 1H, ArNH), 2.98 (m, 2H, CH(CH3)2), 2.55 (m, 2H, CH(CH3)2), 1.95 (s, 3H, ArCH3), 1.53 (dt, JHH = 8.0 Hz, JCP = 7.8 Hz, 6H, CH(CH3)2), 1.47 (dt, JHH = 7.5 Hz, JCP = 7.5 Hz, 6H, CH(CH3)2), 1.34 (dt, JHH = 8.0 Hz, JCP = 7.8 Hz, 6H, CH(CH3)2), 1.17 (s, 18H, C(CH3)2), 1.09 (dt, JHH = 7.5 Hz, JCP = 7.3 Hz, 7H, CH(CH3)2) ppm; 13C{1H} NMR (126 MHz, C6D6, 25 °C): δ = 157.90 (t, JCP = 14.6 Hz, ArC), 150.08 (s, ArC), 143.11 (s, ArC), 138.33 (m, ArC), 129.64 (s, ArC), 128.73 (s, ArC), 128.35 (s, ArC), 127.16 (s, ArC), 126.85 (br s, ArC), 116.76 (s, ArC), 87.41 (t, JCP = 9.5 Hz, Cbackbone), 34.55 (s, C(CH3)2), 31.37 (s, C(CH3)2), 27.28 (d, JCP = 10.7 Hz, CH(CH3)2), 27.19 (d, JCP = 10.7 Hz, CH(CH3)2), 27.11 (d, JCP = 10.2 Hz, CH(CH3)2), 27.03 (d, JCP = 10.2 Hz, CH(CH3)2), 20.54 (s, CH(CH3)2), 20.09 (s, CH(CH3)2), 19.90 (s, ArCH3), 19.60 (s, CH(CH3)2), 19.08 (s, CH(CH3)2) ppm; 31P{1H} NMR (202 MHz, C6D6, 25 °C): δ = 49.89 (br s) ppm. Anal. calc. for C57H82nP2Pd (850.18 g mol−1): C, 56.51; H, 7.11; N, 1.65. Found: C, 56.42; H, 7.10; N, 1.61.

**Synthesis of [{PC(sp3)(NH2Tol)P}BuPd] (11)**

PhONa (5.4 mg, 0.046 mmol) in 1 mL of THF was slowly added to a dark-red solution of 5 (71 mg, 0.044 mmol) in 1 mL of THF at −35 °C. The resulting bright yellow solution was then stirred at room temperature for 15 min. All volatiles were removed under reduced pressure and the residue was extracted with benzene (2 mL × 6) and filtered. Removal of volatiles under reduced pressure gave an yellow residue, which was then extracted with n-pentane (6 × 5 mL) and filtered. The solution was reduced to about 1 mL and stored at −35 °C. An yellow oil was obtained that was discarded and the solution carefully transferred to another vial. Slow evaporation at room temperature affords compound 11 as yellow crystals; yield 19 mg (53%). 1H NMR (500 MHz, C6D6, 25 °C): δ = 7.95 (dd, JHH = 7.5 Hz, JCP = 1.0 Hz, 2H, ArH), 7.49 (m, 2H, ArH), 7.27 (d, JHH = 8.5 Hz, 2H, ArH), 7.10 (d, JHH = 8.5 Hz, 2H, ArH), 7.02 (dd, JHH = 8.5 Hz, JCP = 7.5 Hz, 2H, ArH), 6.66 (t, JHH = 7.5 Hz, JCP = 1.0 Hz, 1H, ArH), 3.03 (m, 2H, CH(CH3)2), 2.54 (m, 2H,
Synthesis of $[[PC(sp^3)PMe_3]PPiPdL][BaF_4]$ (12)

PMe$_3$ (3.6 mg, 0.047 mmol) in 1 mL of diethyl ether was added to a dark-red solution of 5 (50 mg, 0.031 mmol) in 2 mL of diethyl ether at room temperature. The resulting bright yellow solution was stirred for 5 min. The volatiles were removed under reduced pressure and the residue was crystallized by layering n-pentane to a fluoro benzene solution at room temperature, affording compound 12 as yellow blocks; yield 52 mg (100%). $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta = 7.81$ (d, $^3$J$_{HH}$ = 8.5 Hz, 2H, ArH), 7.66–7.63 (m, 13H, ArH and Ar$_F$H), 7.51 (s, 3H, ArH), 3.02 (m, 2H, CH$_{(CH_3)}$), 2.67 (m, 2H, CH$_{(CH_3)}$), 1.63 (dt, $^3$J$_{HH}$ = 7.5 Hz, 3J$_{HP}$ = 7.5 Hz, 12H, CH$_{(CH_3)}$), 1.36 (s, 18H, C$_{(CH_3)}$), 1.31 (d, $^3$J$_{HP}$ = 11.5 Hz, 9H, P(CH$_{(CH_3)}$)), 1.20 (dt, $^3$J$_{HP}$ = 8.5 Hz, 3J$_{HP}$ = 7.5 Hz, 8H, 5H, CH$_{(CH_3)}$), 0.92 (d, $^3$J$_{HH}$ = 8.0 Hz, $^3$J$_{HP}$ = 8.0 Hz, 8H, 5H, CH$_{(CH_3)}$) ppm; $^{31}$P $^1$H NMR (202 MHz, CDCl$_3$, 25 °C): $\delta = 51.09$ (br s) ppm. Anal. calc'd for C$_{58}$H$_{52}$OPiPd (837.14 g mol$^{-1}$): C, 55.95%; H, 6.86%. Found: C, 55.61%; H, 6.61.

Comproportionation reaction between 3 and 5

A solution of $[[PC(sp^3)P]PPiPMe_3$ (3, 16 mg, 0.022 mmol) in 2 mL of diethyl ether was added to a solution of $[[PC(sp^3)P]PPiPdL]$ [BaF$_4$] (5, 36 mg, 0.022 mmol) in 1 mL of diethyl ether at $-35$ °C, which immediately generated a dark green solution. After stirring the mixture at room temperature for 15 min, all volatiles were removed under reduced pressure to give a green oil, which was then mixed with 9,10-dihydroanthracene (4 mg, 0.022 mmol) in C$_2$H$_5$O with 10% of THF-d$_6$ and heated at 80 °C for 7 days. The $^1$H and $^{31}$P NMR spectra showed the clean transformation to compound 6 as well as the cationic complex $[[PC(sp^3)P]PPiPdL][PMe_3][BaF_4]$ in about 1 : 1 ratio.

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