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Oxidation Reactions of a Nucleophilic Palladium Carbene: Mono and Bi-radical Carbenes

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Abstract

Palladium(II) cationic carbene radical and neutral bi-radical complexes were synthesized from a previously reported Pd(II) carbene in the presence of one and two electron oxidants. When [{PC(sp^2)P}$^{t\text{Bu}}$Pd(PMe$_3$)] (**1**, [PC(sp^2)P]$^{t\text{Bu}}$ = (bis[2-(di-*iso*-propylphosphino)4-tertbutylphenyl]methylene)) was treated with [Cp$_2$Fe][X] (X = BAr$^F_4$, Ar^F =3,5-(CF$_3$)$_2$C$_6$H$_3$, or PF$_6$), the corresponding radical cationic complexes [{PC$^\bullet$(sp^2)P}$^{t\text{Bu}}$Pd(PMe$_3$)][X] (**2**: X = BAr$^F_4$, **3**: PF$_6$) were isolated and characterized. Magnetic moment measurements and EPR spectroscopy indicated the presence of a ligand centered unpaired electron. In the presence of two electron oxidants such as 1,8-naphthylene disulfide or 9,10-anthracenedione, **1** converts to [{PC$^\bullet$(sp^2)P}$^{t\text{Bu}}$PdS(C$_{10}$H$_6$)SPd{PC$^\bullet$(sp^2)P}$^{t\text{Bu}}$] (**4**) or [{PC$^\bullet$(sp^2)P}$^{t\text{Bu}}$PdO(C$_{14}$H$_{10}$)OPd{PC$^\bullet$(sp^2)P}$^{t\text{Bu}}$] (**5**), respectively. Single crystal X-ray diffraction and EPR spectroscopy confirmed the bi-radical nature of **4** and **5**.

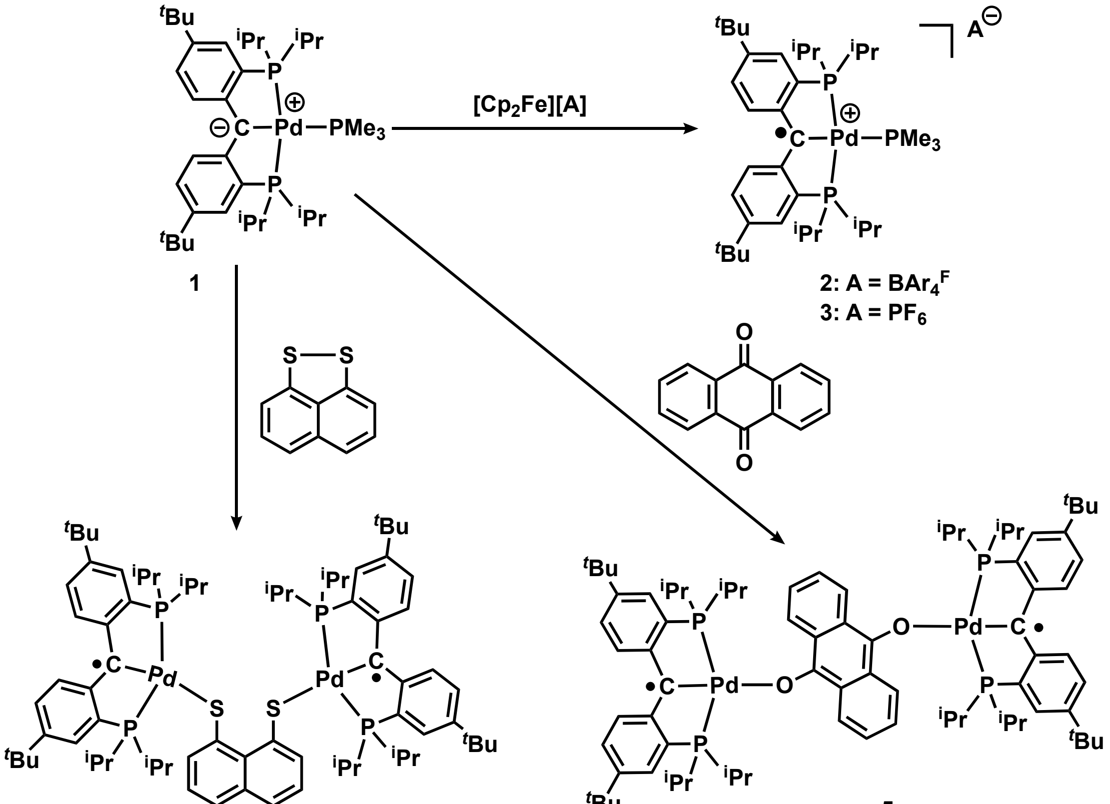
Introduction

Transition metal carbenes have been studied extensively in the last decades because of their catalytic applications in organic and polymer synthesis.[1-7] For example, late transition metal complexes supported by N-heterocyclic, carbocyclic, and heteroatom carbene ligands play important roles in versatile stoichiometric and catalytic transformations.[8-12] On the other hand, metal complexes bearing non-heteroatom stabilized carbenes are less explored, especially for the electron rich group 10 metals.[13-20]

Though typically classified as Fischer or Schrock type, metal carbene species that do not belong to these two distinct categories have exhibited unique structural features and remarkable reactivity.[21-26] Radical carbene complexes are particularly interesting due to their redox non-innocent feature,[27-29] which is crucial to the asymmetric cyclopropanation of olefins catalyzed by Co^{II}(porphyrin) complexes.[30-33] Generally, a one-electron reduction of a Fischer carbene or a one-electron oxidation of a Schrock carbene would generate the corresponding radical carbene, however, the isolation and characterization of such reactive species are still challenging.[34-37] We successfully synthesized a series of Pd(II) radical carbene complexes, $[\{PC^{\bullet}(sp^2)P\}^{R}PdX]$ (R = H, $[PC(sp^2)P]^{H}$ = bis[2-(di-*iso*-propylphosphino)phenyl]methylene, X = Cl, Br, I; R = ^{t}Bu, $[PC(sp^2)P]^{tBu}$ = bis[2-(di-*iso*-propylphosphino)-4-*tert*-butylphenyl]methylene, X = I, NH^{p}Tol, NPh_2, CH_2Ph), from their carbene precursors $[\{PC(sp^2)P\}^{R}Pd(PMe_3)]$ (R = H, ^{t}Bu).[38-40] The combined EPR spectroscopy, X-ray diffraction studies, and DFT calculations revealed that the unpaired spin in these complexes is largely localized on the carbene carbon. These previously reported Pd(II) radical carbene complexes are neutral and possess only one radical center. Herein, we report the expansion of this series by synthesizing a Pd(II) carbene radical cation, as well as bi-radicals via an oxidation of the corresponding carbene precursor.

Results and discussion

Treatment of $[\{PC(sp^2)P\}^{tBu}Pd(PMe_3)]$ (**1**) with an equivalent of $[Cp_2Fe][X]$ (X = BAr^F_4, Ar^F = 3,5-$(CF_3)_2C_6H_3$, or PF_6) in an ethereal solvent at -35 °C instantly afforded a green solution, from which the paramagnetic complexes [{PC$^{\bullet}$(sp^2)P}^{tBu}Pd(PMe$_3$)][X] (X = BAr$^F{}_4$, **2**, and PF$_6$, **3**) were isolated in 60% and 94% yield, respectively (Scheme 1). Both compounds are only soluble in THF and chlorinated solvents, and are highly air sensitive. As observed previously for the radical carbene complexes [{PC$^{\bullet}$(sp^2)P}^{tBu}PdX] (X = I, NH^{p}Tol, and NPh$_2$), only the resonances associated with the BAr$^F{}_4$ and PF$_6$ counterions are observed for **2** and **3** in their corresponding ^{1}H and ^{31}P{^{1}H} NMR spectra.[38, 39] The EPR spectrum of **2** (Figure 1) was recorded in dichloromethane at 298 K and exhibits a doublet centered at g = 2.020 (a(^{31}P$_{\text{trans}}$) = 12 G) with a well resolved hyperfine splitting attributed to 6 phenyl ring protons: a1(2H) = 3.4 G, a2(2H) = 2.0 G, a3(2H) = 1.9 G. Interestingly, no coupling to the *cis* phosphorus nuclei was observed for **2** or in the previously reported carbene radicals.[39] The effective magnetic moment, μ_{eff} = 2.03 μ_B, measured by the Evans method in solution is consistent with an unpaired electron present in **2**.



Scheme 1. Synthesis of compounds **2-5**.

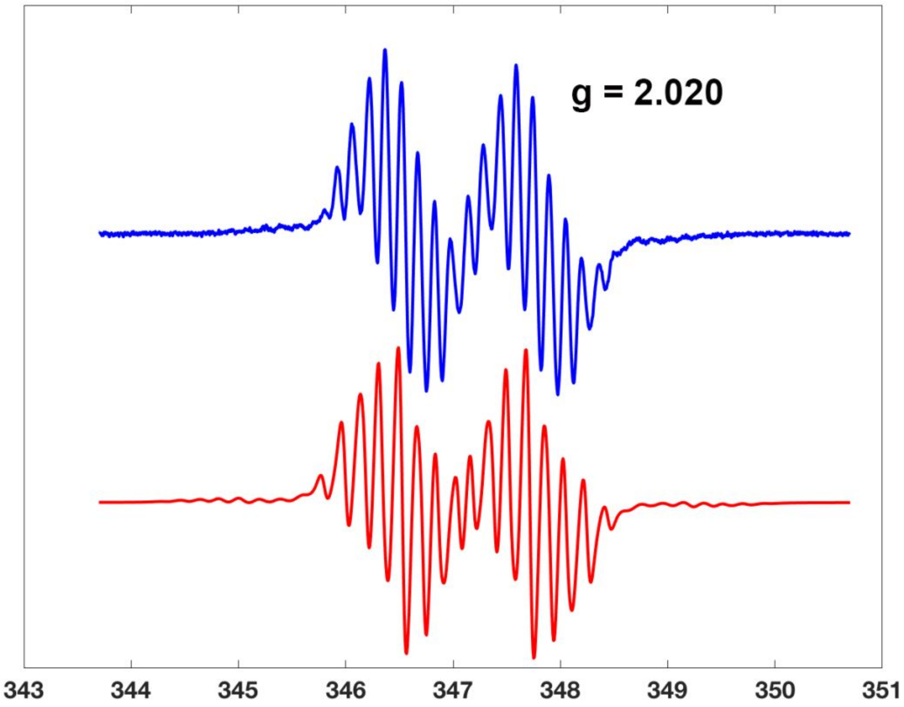


Figure 1. EPR spectrum of **2** (298 K, 4 mM solution in CH_2Cl_2, X-band). The blue line represents the experimental data and the red line the simulated spectrum.

Green needles of **2** suitable for X-ray diffraction studies were obtained by layering *n*-pentane onto a diethyl ether solution at -35 °C. As shown in Figure 2, **2** possesses a typical square-planar palladium center bound to a characteristic sp^2 hybridized backbone carbon (Σ_{angles} at $C_{carbene}$ is 359.9°). The Pd-$C_{carbene}$ distance of 2.064(3)Å is close to that of 2.076(3) Å in **1**, in contrast to the contraction observed in the oxidation of **1** with 0.5 equivalents of I_2 to form the neutral radical carbene $[\{PC^{\bullet}(sp^2)P\}^{tBu}PdI]$ (from 2.076(3) Å to 2.022(3) Å). This can be attributed to a stronger donation from PMe_3 than from the iodide anion. Therefore, the Pd-$C_{carbene}$ distance in **2** is longer than in the neutral radical carbene complexes $[\{PC^{\bullet}(sp^2)P\}^{tBu}PdX]$ (2.022(3), 2.019(2) and 2.024(2) Å for X = I, $NH^{p}Tol$, and NPh_2, respectively). The Pd-P distances (Pd-P(1) = 2.3256(9) Å, Pd-P(2) = 2.3208(8) Å, Pd-P(3) = 2.3704(9) Å) in **2** are close to those in **1** (Pd-P(1) = 2.3120(7) Å, Pd-P(2) = 2.3099(7) Å, Pd-P(3) = 2.3701(7) Å), also supporting a predominant change of the electronic properties of the carbene carbon instead of the palladium center, as previously illustrated in the reversible one-electron transfer between carbene **1**, the radical carbene [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$PdI], and the cationic carbene [{PC$^{\bullet}$(sp^2)P}$^{t\mathrm{Bu}}$Pd(PMe$_3$)][BAr$^{F}_4$].[39]

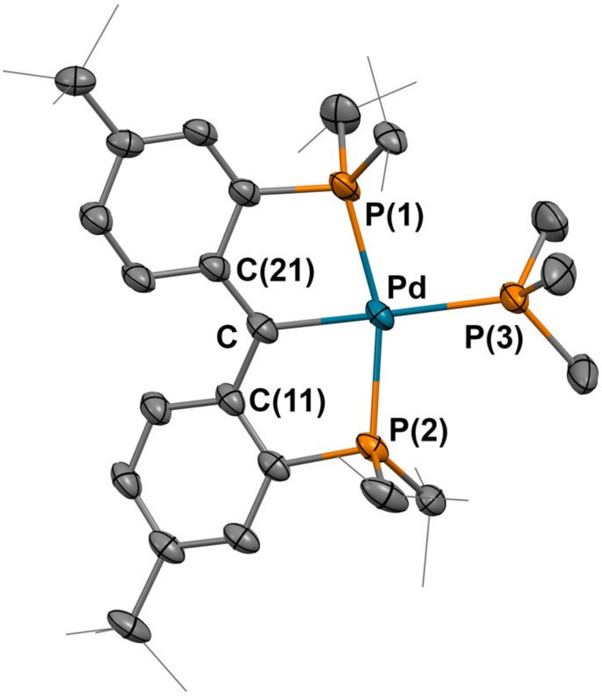


Figure 2. Thermal ellipsoid (50% probability level) representation of the cation in **2**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (º): Pd-C 2.064(3), Pd-P(1) 2.3256(9), Pd-P(2) 2.3208(8), Pd-P(3) 2.3704(9), C-Pd-P(3) 175.97(10), P(1)-Pd-P(2) 160.65, C(21)-C-C(11) 121.5(3), C(11)-C-Pd 119.1(2), C(21)-C-Pd 119.3(2).

We showed previously that alkyl halides can oxidize the carbene complex [{PC(sp^2)P}$^{\mathrm{H}}$Pd(PMe$_3$)] to the corresponding radical [{PC(sp^2)P}$^{\mathrm{H}}$PdX] (X = Cl, Br, I) with the concomitant generation of a side product.[40] To explore further the synthetic availability of radical carbene complexes bearing different functional groups from the oxidation of **1**, other mild oxidants were also investigated. Silver salts such as AgOTf and AgPF$_6$ did not afford any isolable products. However, the one-electron oxidation of **1** with PhSSPh quantitatively led to [{PC(sp^3)(SPh)P}$^{t\mathrm{Bu}}$Pd(SPh)], presumably via a radical coupling between [PhS$^{\bullet}$] and an unobserved radical carbene species

$[\{PC^{\bullet}(sp^2)P\}^{tBu}PdSPh]$.[39] It is therefore interesting to investigate a related oxidation reaction with 1,8-naphthylene disulfide, which contains a S-S bond in a rigid aromatic ring. Addition of the disulfide solution to a dark-brown solution of **1** in benzene at room temperature did not lead to any significant color change, but a brown crystalline product $[\{PC^{\bullet}(sp^2)P\}^{tBu}PdS(C_{10}H_6)SPd[\{PC^{\bullet}(sp^2)P\}^{tBu}]$ (**4**) was isolated in 60% yield, after its recrystallization from diethyl ether at -35 °C (Scheme 1). Compound **4** is silent by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, indicating the presence of a similar paramagnetic feature.

The structure of **4** was determined by single crystal X-ray diffraction studies (Figure 3), which revealed an unusual palladium bi-radical carbene featuring two isolated radicals with the two palladium metal centers bridged over an 1,8-naphthylene disulfide moiety. The two palladium planes of the $[\{PC^{\bullet}(sp^2)P\}^{tBu}Pd]$ units are twisted toward each other with the dihedral angle being 52.3°, therefore, the naphthylene plane is not perpendicular to both units. As expected, both carbene carbons exhibit a trigonal planar geometry (Σ_{angles} at $C_{carbene}$ are 359.9° and 359.9°), and the Pd-$C_{carbene}$ distances (2.031(3) and 2.033(3) Å) are close to those in $[\{PC^{\bullet}(sp^2)P\}^{tBu}PdX]$ (2.022(3), 2.019(2) and 2.024(2) Å for X = I, $NH^{p}Tol$, and NPh_2, respectively). The formation of **4** highlights the kinetic stability of the radical species. Moreover, unlike what was observed for the reaction with PhSSPh, the radical coupling within one carbene molecule was not favorable due to the rigid 1,8-naphthylene ring. It is worth mentioning that the oxidation of the Pd(II) center to form a high valent Pd(III) species bearing a S-Pd-S six-member ring was also not observed, likely because of the much lower redox potential of the disulfide (for PhSSPh: -1.7 V vs. SCE, -2.1 V vs. Fc/Fc^+).

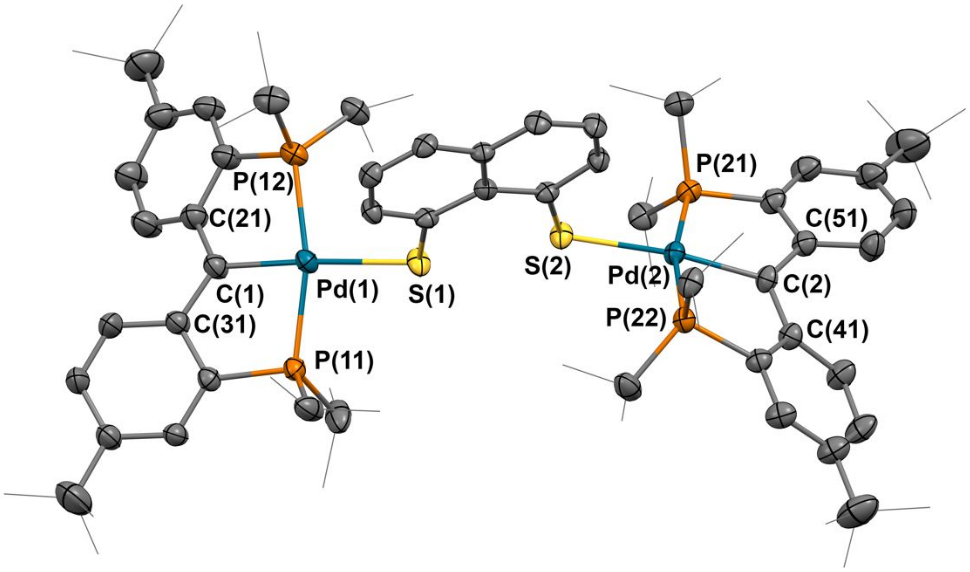


Figure 3. Thermal ellipsoid (50% probability level) representation of **4**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (º): C(1)-Pd(1) 2.031(3), Pd(1)-P(11) 2.273(9), Pd(1)-P(12) 2.308(9), Pd(1)-S(1) 2.389(8), P(12)-Pd(1)-P(11) 165.81(3), C(1)-Pd(1)-S(1) 170.65(10), C(21)-C(1)-C(31) 122.0(3), C(31)-C(1)-Pd(1) 119.4(2), C(21)-C(1)-Pd(1) 118.2(2), S(2)-Pd(2)-C(2) 169.7(10), P(22)-Pd(2)-P(21) 167.09(3), C(51)-C(2)-C(41) 121.8(3), C(41)-C(2)-Pd(2) 118.4(2), C(51)-C(2)-Pd(2) 119.5(2).

Although transition metal complexes bearing bi-radical ligands are known,[41-43] **4** represents the first crystallographically characterized such a species generated from the oxidation of a carbene precursor. Recent results also show that cyclic (alkyl)(amino)carbene form diradicaloids with unusual electronic properties and a remarkable reactivity when coordinated to zinc, manganese, and silicon, or separated by conjugated organic spacers.[44-47] This result prompted us to investigate the oxidation of **1** with another two-electron oxidant, specifically 9,10-anthracenedione. Treatment of **1** with 9,10-anthracenedione in benzene at room temperature led to an immediate color change from dark brown to blue-green, from which a dark green crystalline solid, $[\{PC^{\bullet}(sp^2)P\}^{tBu}\ PdO(C_{14}H_{10})OPd\{PC^{\bullet}(sp^2)P\}^{tBu}]$ (**5**), could be isolated in 77% yield after recrystallization from *n*-pentane at -35 ^{o}C. Compound **5** is also paramagnetic as evidenced from its silent ^{1}H and $^{31}P\{^1H\}$ NMR spectra; its solid-state molecular structure was determined by X-ray diffraction studies (Figure 4). Similar to **4**, **5** is also a bi-radical carbene with the two palladium centers linked via an anthracene-9,10-diolate bridge; however, unlike **4**, **5** contains an inversion center. The trigonal planar carbene carbon (Σ_{angles} at C_{carbene} are 359.9°) exhibited the shortest Pd-C_{carbene} distance (2.004(2)Å) among the known radical carbene series of $[\{PC^{\bullet}(sp^2)P\}^{tBu}PdX]$ (2.022(3), 2.019(2) and 2.024(2) Å for X = I, $NH^{p}Tol$, and NPh_2, respectively). The elongated O1-C(54) distance of 1.322(3) Å clearly indicated the reduction of 9,10-anthracenedione to the corresponding diolate. The square plane of palladium is nearly perpendicular to the plane of the anthracene ring with a dihedral angle of 82.12° to avoid an interaction with the phosphines *iso*-propyl groups.

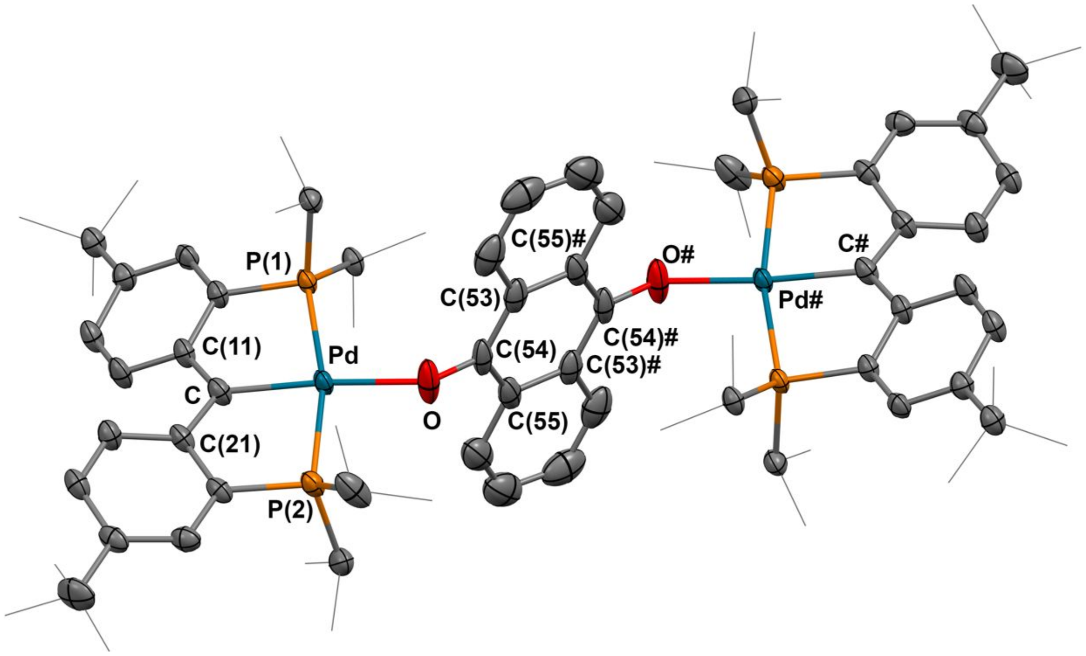


Figure 4. Thermal ellipsoid (50% probability level) representation of **5**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Pd-C 2.004(2), Pd-P(1) 2.310(6), Pd-P(2) 2.272(6), Pd-O 2.059(17), O-C(54) 1.322(3), C-Pd-O 171.43(8), P(1)-Pd-P(2) 166.79(2), C(11)-C-C(21) 121.8(2), C(21)-C-Pd 119.22, C(11)-C-Pd 118.99(16).

To further confirm the bi-radical nature of **4** and **5**, their EPR spectra were recorded. Compound **4** produced a signal with a g factor of 2.0210 and a hyperfine pattern corresponding to three pairs of equivalent protons and a ^{105}Pd nucleus, while **5** produced an unresolved signal with a g factor of 2.0100 and a peak-to-peak width of ΔH_{pp} = 0.8 mT. The spectrum of **4** shows hyperfine coupling parameters characteristic of an isolated Pd-carbene radical fragment (six phenyl ring protons and a single ^{105}Pd nucleus), pointing to a lack of interaction between the two carbene radical centers in **4**. On the other hand, the noisy, unresolved EPR signal of **5** may result from a greater spin-spin exchange interaction between the two radical fragments, likely due to an extended conjugation through the anthraquinone bridge. For both compounds, the effective magnetic moment measured in solution (μ_{eff} = 3.51 μ_B for **4** and μ_{eff} = 3.12 μ_B for **5**) is consistent with the presence of two unpaired electrons.

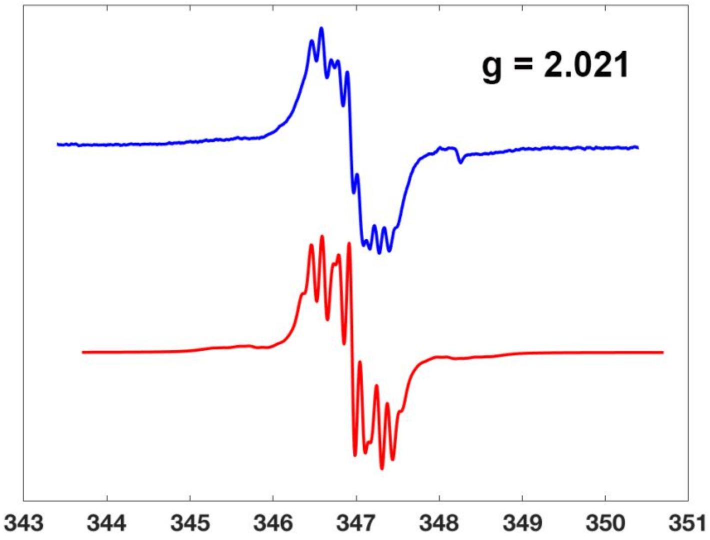


Figure 5. EPR spectrum of **4** (298 K, 1 mM solution in CH_2Cl_2, X-band). The blue line represents the experimental data and the red line the simulated spectrum.

Conclusions

In summary, we extended the family of palladium radical carbene complexes from neutral, mono-radical species to cations and bi-radicals, and thus greatly demonstrated the versatility of the radical feature within our PCP palladium carbene framework. In the current radical carbene series, various functional groups, including halides (Cl, Br, and I), amides (NH^{p}Tol and NPh_2), benzyl, sulfide (**4**), as well as anthracene-diolate (**5**) could be installed on palladium via a one-electron oxidation of the carbene complex **1**, highlighting a broad scope of this synthetic strategy. The structural and spectroscopic features of these compounds provide valuable models in the field of transition metal radical carbene chemistry. Because of their redox, non-innocent behavior, the combination with late transition metals that are redox active should lead to versatile transformations involving metal-ligand cooperation mechanisms.

Experimental

All experiments were 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. Compound **1**[48] and 1,8-naphthylene disulfide were prepared according to literature procedures.[49] Magnetic moments were determined by the Evans method[50] 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 a microwave power of 2 mW, modulation frequency of 100 kHz, and amplitude of 0.01 mT. Elemental analyses were performed on a CE-440 Elemental analyzer or by Midwest Microlab.

Synthesis of 2: $[Cp_2Fe][BAr^F_4]$ (53 mg, 0.050 mmol) in 1 mL of diethyl ether was slowly added to **1** (35 mg, 0.050 mmol) in 1 mL of diethyl ether at -35 °C. The resulting green solution was stirred at room temperature for 20 min and then filtered through Celite. The resulting solution was layered with 7 mL of *n*-pentane and then stored at -35 °C to afford **2** as pale-green needles. Yield: 47 mg (60%). Anal. Calcd for $C_{68}H_{73}BF_{24}P_3Pd$: C, 52.48; H, 4.73. Found: C, 52.38; H, 5.12. Evans: $\mu_{eff} = 2.03\ \mu_B$. EPR (X-band, 9.814 GHz): g = 2.0200, ^{31}P splitting = 1.2 mT. Crystal data for $C_{68}H_{73}BF_{24}PPd$; M_r = 1556.38; Triclinic; space group P-1; a = 13.6492(7) Å; b = 17.8440(9) Å; c = 18.4747(9) Å; α = 66.0282(14)°; β = 76.7560(15)°; γ = 88.0975(15)°; V = 3993.1(3) Å^3; Z = 2; T = 120(2) K; λ = 0.71073 Å; μ = 0.384 mm^{-1}; d_{calc} =

1.294g.cm^{-3}; 97651 reflections collected; 14055 unique (R_{int} = 0.0347); giving R_1 = 0.0500, wR_2 = 0.1349 for 11839 data with [I>2σ(I)] and R_1 = 0.0616, wR_2 = 0.1416 for all 14055 data. Residual electron density (e^-.Å^{-3}) max/min: 1.910/-0.828.

Synthesis of 3: Compound **1** (105 mg, 0.151 mmol) in 2 mL of THF was slowly added to a slurry of $[Cp_2Fe][PF_6]$ (50 mg, 0.151 mmol) in 2 mL of THF at -35 °C. The reaction mixture was stirred at room temperature for 3 h, during which time a green solution was formed gradually. The green solution was filtered through Celite and then layered with 7 mL of *n*-pentane. Storing it at -35 °C led to **3** as a green solid. Yield: 119 mg (94%). Anal. Calcd for $C_{36}H_{61}F_6P_4Pd$: C, 51.59; H, 7.34. Found: C, 51.38; H, 7.12. $\mu_{eff} = 1.85\ \mu_B$.

Synthesis of 4: 1,8-naphthylene disulfide (6.9 mg, 0.036 mmol) in 1 mL of benzene was added to **1** (50 mg, 0.072 mmol) in 1 mL of benzene at room temperature. The resulting dark brown solution was then stirred for 2 h. The volatiles were removed under a reduced pressure and the residue was extracted with 6 mL of diethyl ether, and filtered through Celite. After reducing the volume of the solution to about 0.5 mL, the solution was stored at -35 °C to give **4** as a brown crystalline solid. Yield: 33 mg (64%). Anal. Calcd for $C_{76}H_{110}P_4Pd_2S_2$: C, 64.08; H, 7.78. Found: C, 64.72; H, 7.99. $\mu_{eff} = 3.51\ \mu_B$. EPR (X-band, 9.814 GHz): g = 2.0210. Crystal data for $C_{76}H_{110}P_4Pd_2S_2$; M_r = 1424.43; Monoclinic; space group $P2_1/c$; a = 14.6121(3) Å; b = 36.4414(8) Å; c = 15.6562(3) Å; α = 90°; β = 90.1128(12)°; γ = 90°; V = 8336.7(3) Å^3; Z = 4; T = 120(2) K; λ = 1.54178 Å; μ = 4.931 mm^{-1}; d_{calc} = 1.135g.cm^{-3}; 184805 reflections collected; 14180 unique (R_{int} = 0.0617); giving R_1 = 0.0401, wR_2 = 0.0966 for 12246 data with [I>2σ(I)] and R_1 = 0.0479, wR_2 = 0.1009 for all 14180 data. Residual electron density (e^-.Å^{-3}) max/min: 1.146/-1.083

Synthesis of 5: A slurry of 9,10-anthracenedione (6 mg, 0.029 mmol) in 2 mL of benzene was added to **1** (40 mg, 0.058 mmol) in 1 mL of benzene at room temperature. The reaction mixture was stirred for 2 h, during which time a blue-green solution was formed. The volatiles were removed under a reduced pressure and the residue was extracted with 5 mL of *n*-pentane, and filtered through Celite. After reducing the volume of the solution to about 1 mL, the solution was stored at -35 °C to give **5** as a dark-green crystalline solid. Yield: 32 mg (77%). Anal. Calcd for $C_{80}H_{112}O_2P_4Pd_2$: C, 66.61; H, 7.83. Found: C, 66.20; H, 7.75. $\mu_{eff} = 3.12\ \mu_B$. EPR (X-band, 9.814 GHz): g = 2.0100. Crystal data for $C_{85}H_{123}O_2P_4Pd_2$; $M_r = 1513.51$; Triclinic; space group P-1; *a* = 11.8407(12) Å; *b* = 13.4567(13) Å; *c* = 13.9043(13) Å; α = 100.199(3)°; β = 109.735(2)°; γ = 98.037(3)°; V = 2004.2(3) Å^3; Z = 1; T = 120(2) K; λ = 0.71073 Å; μ = 0.573 mm^{-1}; d_{calc} = 1.254g.cm^{-3}; 48850 reflections collected; 7042 unique (R_{int} = 0.0384); giving $R_1 = 0.0287$, $wR_2 = 0.0698$ for 6199 data with [$I>2\sigma(I)$] and $R_1 = 0.0361$, $wR_2 = 0.0724$ for all 7042 data. Residual electron density (e$^-$.Å^{-3}) max/min: 0.554/-0.330

Electronic Supplementary Information (ESI) available: Characterization data for all new compounds, single crystal X-ray structure analysis of **2, 4**, and **5**. CCDC 1894466-1894468. See DOI: 10.1039/x0xx00000x

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TOC Synopsis: A series of mono and bi-radical carbenes

TOC Graphic: