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**A Cation-Captured Palladium(0) Anion:
Synthesis, Structure, and Bonding of $[\text{PdBr}(\text{PPh}_3)_2]^-$ Ligated
by an *N*-Heterocyclic Phosphenium Cation**

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Abstract

Unsaturated N-heterocyclic phosphonium cations (μ NHP) stabilize the $[\text{Pd}^0(\text{PR}_3)_2\text{X}]^-$ anion proposed over the past decade to be the crucial but elusive intermediate in palladium-catalyzed cross-coupling reactions ($\text{X} = \text{halide}$). Insertion of metal into the P–Br bond of the precursor mesityl-substituted bromophosphine gives the structurally characterized Pd(0)-phosphenium complex (μ NHPMes)Pd(PPh₃)₂Br, which features a long Pd–Br bond (2.7240(9) Å) and the shortest known Pd–P bond (2.1166(17) Å). The reaction is proposed to proceed by an associative pathway involving a Pd-bromophosphine complex that undergoes P-to-Pd bromide transfer.

Introduction

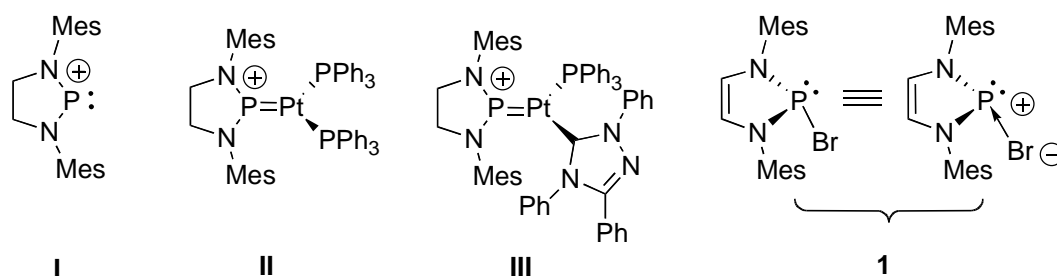
Palladium(0)-phosphine complexes play a pivotal role in a wide variety of catalytic C–C bond-forming reactions that since the 1970s have become part of the standard lexicon of organic synthesis. The scope, utility, and sophistication of Heck, Suzuki, Sonogashira, Stille and Negishi couplings, among others, have championed the use of palladium as the workhorse for demanding connections, and have spurred the development of a vast array of tailor-made phosphine ligands.¹

The traditional wisdom that oxidative addition of R–X to linear Pd(0)-bis(phosphine) complexes generates the requisite organo-palladium(II) intermediates during these catalytic cycles has been challenged over the last decade by Amatore and Jutand, who have argued convincingly, based on kinetic, spectroscopic, electrochemical and computational evidence, that the active species in these additions is the tricoordinate, Pd(0) anion, $[\text{Pd}(\text{PR}_3)_2\text{X}]^-$ ($\text{X} = \text{halide, acetate, etc.}$).^{2–4} In accord with chemical intuition

and on the basis of DFT calculations, these researchers have proposed that the stability of $[\text{Pd}(\text{PR}_3)_2\text{X}]^-$ should increase with increasing electron-withdrawing character of the phosphine ligands and with increasing electron donating character of the X^- anion.⁴ However, such putative anionic intermediates have never submitted to isolation and structural characterization.

Our recent investigations have shown that *N*-heterocyclic phosphonium (NHP) cations are powerful π -acids that aggressively sequester electron rich Group 10 metal(0) centres.⁵ For example, $[\text{NHP}^{\text{Mes}}]\text{OTf}$ (**I**, Chart 1) reacts quantitatively with $\text{M}(\text{PPh}_3)_4$ ($\text{M} = \text{Pd}, \text{Pt}$) to give the $\text{M}(0)$ adducts $[(\text{NHP}^{\text{Mes}})\text{M}(\text{PPh}_3)_2]\text{OTf}$ (**II**), which are properly regarded as a phospho-Fischer carbenes; the Pt species contains the shortest known Pt–P bond (2.107(3) Å).⁵ In addition, Baker and coworkers have demonstrated that $[(\text{NHP}^{\text{Mes}})\text{Pt}(\text{NHC})(\text{PPh}_3)]\text{OTf}$ (**III**) may be formed by reaction of $\text{Pt}(\text{PPh}_3)_3$ with an $\text{NHC} \rightarrow \text{NHP}$ adduct (NHC = an Enders-type *N*-heterocyclic carbene).⁶ These two findings, coupled with the view of bromophosphine **1** as the bromide adduct of an *unsaturated* NHP cation ($\text{Br} \rightarrow u\text{NHP}^{\text{Mes}}$), and together with the DFT calculations by Amatore and Jutand,³ set the stage for the first isolation and structural characterization of a $\text{Pd}(0)$ -halide fragment, in this case trapped by an NHP cation (**4**, Scheme 1).

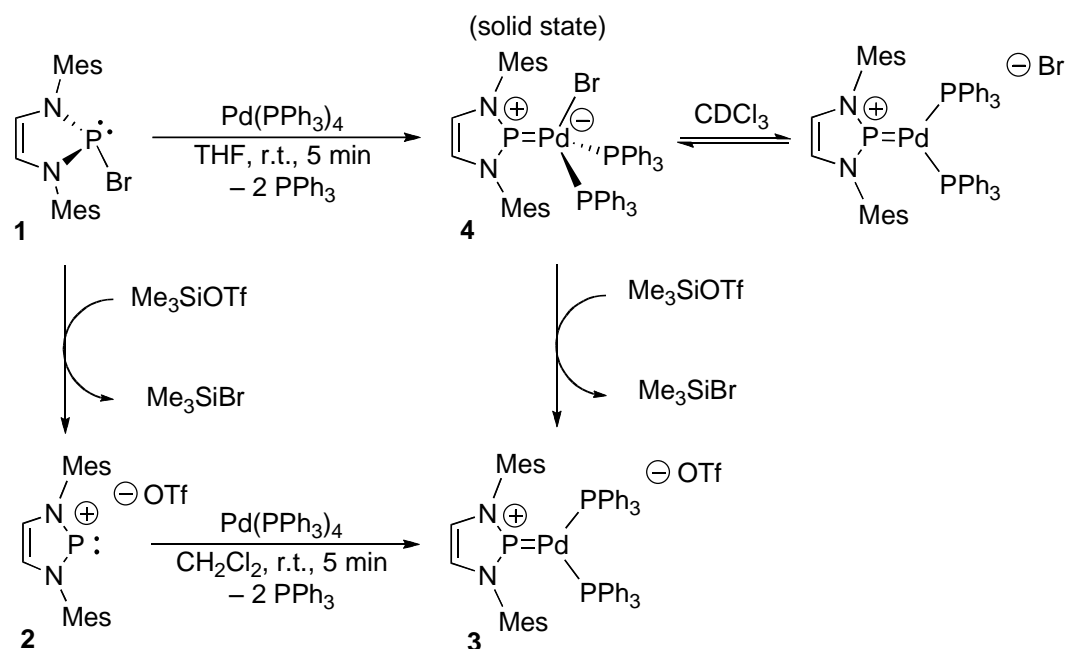
Chart 1. Compounds relevant to this work.^a



^a All anions are trifluoromethanesulfonate (TfO[−], not shown). Mes = 2,4,6-trimethylphenyl.

Results and Discussion

Bromophosphine **1**⁷ was made using the redox method of Macdonald and coworkers by the reaction of PBr₃ with *N,N'*-dimesityl-1,4-diazabutadiene in the presence of cyclohexene as a scrub for the Br₂ byproduct.⁸ Its ³¹P{¹H} NMR spectrum was characterized by a singlet at δ_P 175.1. The molecular structure of **1** is shown in Figure 1. This compound featured a relatively long P–Br bond of *ca.* 2.62 Å, which was shorter than the sum of the van der Waals radii of P and Br (3.65 Å), but significantly longer than the bonds in PBr₃ (2.22 Å). The P–Br distance in **1** was also longer than the corresponding bonds found in the three crystallographically independent molecules observed by Macdonald and coworkers in the unit cell of (^{Mes}BIAN)P–Br, which spanned 2.432(3)–2.506(3) Å (^{Mes}BIAN = 1,2-bis(2,4,6-trimethylphenylimino)acenaphthene). Gudat's group has structurally characterized chloro analogues having unusually long P–Cl bonds (2.32–2.69 Å)⁹ that were attributed to a combination of π(C₂N₂)–σ*(P–Cl) hyperconjugation and P–Cl bond polarization by intermolecular influences.^{9,10} It is likely that similar effects were at play in **1**. The C–C and intraanular C–N distances in **1** were in the expected range for double and single bonds, respectively. Compared to the free diimine, the C–C bond was shortened in **1** (1.341(5) *vs.* 1.463(3) Å) while the C–N bonds were lengthened (1.398(4) *vs.* 1.273(2) Å),¹¹ which indicated formal two-electron reduction of the diazabutadiene fragment as expected for this synthetic approach:



Scheme 1. Synthesis of Pd(0)-*u*NHP complexes, including the cation captured Pd(0)-bromide, (*u*NHP^{Mes})PdBr(PPh₃)₂ (**4**).

Reaction of **1** with Me_3SiOTf cleanly gave the known phosphonium triflate [*u*NHP^{Mes}]⁺OTf[−] (**2**) which has been made by Gudat using a different approach.¹² Concomitant with halide abstraction was the expected dramatic downfield shift in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (δ_{P} 204.7; $\Delta\delta_{\text{P}}$ 29.6), which indicated only weak contact between the cation and anion in solution. In addition, the “backbone” *CH* protons gave rise to a peak in the ^1H NMR spectrum of **2** (δ 8.30) that was significantly downfield of the corresponding peak in the spectrum of **1** (δ 6.67), which was consistent with the 6π aromatic nature of the phosphonium ion. The [*u*NHP^{Mes}]⁺ cation has also been isolated by Cowley in both I_3^- and BPh_4^- salts.¹³ Our spectroscopic data agreed with those previously reported.⁹

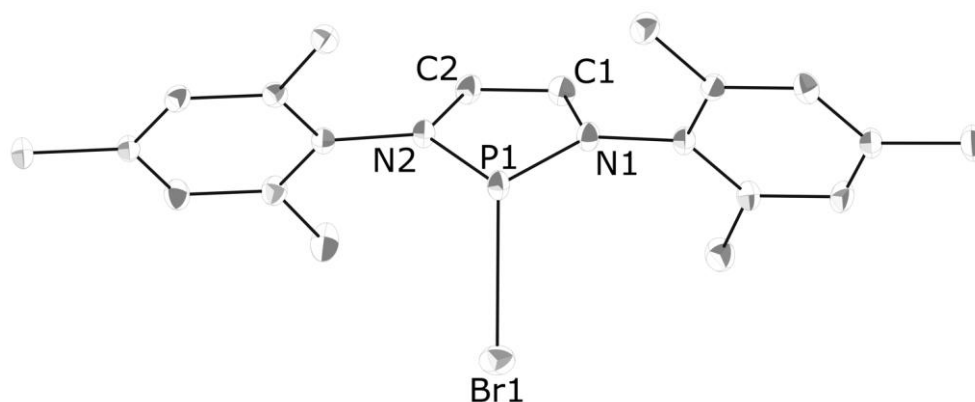


Figure 1. ORTEP representation of the molecular structure of **1** (30 % ellipsoids). Selected bond distances (Å) and angles (°), with estimated standard deviations in parentheses: P1–Br1, 2.6181(10); P1–N1, 1.674(3); P1–N2, 1.673(3); N1–C1, 1.398(4); N2–C2, 1.398(4); C1–C2, 1.341(5); N1–P1–N2, 89.58(13); N1–P1–Br1, 104.13(10); N2–P1–Br1, 102.31(10); N1–C1–C2, 111.1(3); N2–C2–C1, 111.5(3).

The salt **2** reacted quantitatively with $\text{Pd}(\text{PPh}_3)_4$ in CH_2Cl_2 solution at room temperature (rt) to give the three-coordinate Pd(0) complex $[(\mu\text{NHP}^{\text{Mes}})\text{Pd}(\text{PPh}_3)_2]\text{OTf}$ (**3**) within 5 min (Scheme 1). Its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum featured a downfield triplet and upfield doublet ($^2J_{\text{PP}} = 138$ Hz) in a 1:2 integral ratio consistent with a coordinated NHP ($\delta_{\text{P}} 213.0$) coupled to two equivalent phosphine ligands ($\delta_{\text{P}} 23.0$). This pattern of spectral features was similar to that which we reported recently for the saturated analogue, $[(\text{NHP}^{\text{Mes}})\text{Pd}(\text{PPh}_3)_2]\text{OTf}$; however, in the latter case, the coordinated phosphonium cation gave rise to a peak that was much further downfield ($\delta_{\text{P}} 260$). The solid state structure of **3** is shown in Figure 2. To the best of our knowledge, this compound is the first structurally characterized Pd complex of an NHP cation. The Pd–NHP bond (2.1229(11) Å) was shorter than any other Pd–P contact reported to date in the literature

(but slightly longer than that in **4**), consistent with double bond character and very strong π -backbonding. This description of bonding was supported by computational analyses, which indicated that π -backbonding formed 65% of the total orbital interaction energy within the Pd–P bond (see Supporting Information). The near trigonal planar nature of both the NHP P- and Pd-atoms indicated that this cation was accurately described as a Pd(0)-phosphenium rather than a Pd(II)-phosphide, as we have reported for the metal complexes **II** (Chart 1).⁵

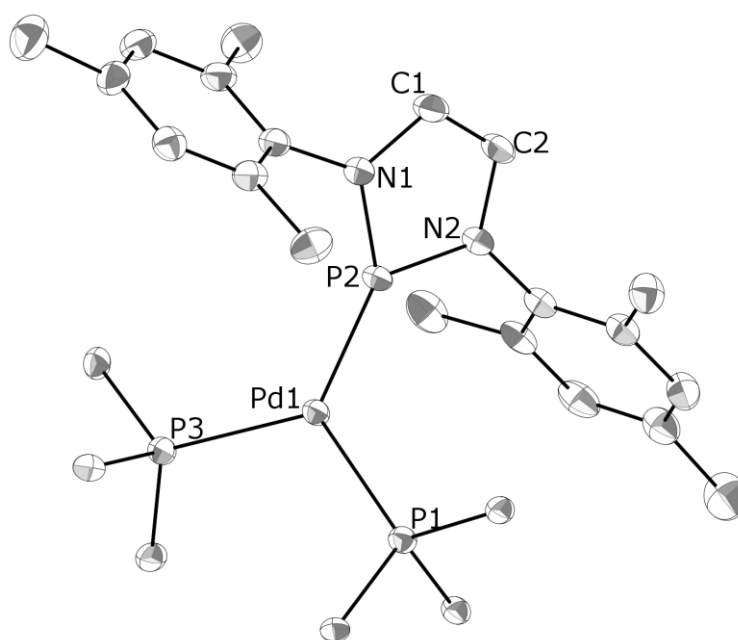


Figure 2. ORTEP representation of the molecular structure of **3** (30 % ellipsoids) with all but the ipso C-atoms of the phenyl rings on the phosphine ligands, TfO[−] anion and solvent (THF) removed for clarity. Selected bond distances (Å) and angles (°), with estimated standard deviations in parentheses and calculated values in square brackets: Pd1–P1, 2.3606(9) [2.414]; Pd1–P2, 2.1229(11) [2.191]; Pd1–P3, 2.3677(10) [2.414]; P2–N1, 1.674(3) [1.733]; P2–N2, 1.663(3) [1.733]; C1–C2, 1.344(5) [1.363]; C1–N1, 1.396(4)

[1.383]; C2–N2, 1.385(4) [1.383]; N1–P2–N2 89.29(14) [87.8]; N1–P2–Pd1 138.37(11) [136.1]; N2–P2–Pd1 131.92(10) [136.1]; P1–Pd1–P2, 120.11(4) [120.6]; P1–Pd1–P3, 114.03(4) [118.8]; P2–Pd1–P3, 125.85(3) [120.6].

Reaction of bromophosphine **1** with Pd(PPh₃)₄ in THF at rt gave (*u*NHP^{Mes})Pd(PPh₃)₂Br (**4**) as a red solid that deposited from solution within minutes (Scheme 1). A putative square planar geometry for **4** – arising from oxidative addition of P–Br to Pd(0) – was possible in principle given the precedent afforded by the structural characterization of *trans*-[PdCl(NHC)(PPh₃)₂]⁺,¹⁴ which should be very similar to **4** in terms of steric crowding of the ligands about the metal, but this was not observed. Instead, the geometry of the metal centre was a distorted tetrahedron (Σ angles = 651.8°, ranging from *ca.* 94.1° – 117.9°; Σ angles for a perfect tetrahedron = 657°) while that of the NHP P-atom was perfectly trigonal planar (Σ angles = 360.0°) (Figure 3). Deviations of the ligand-metal-ligand angles from the ideal 109.5° could be accounted for by considering the sterics of the system: all Br–Pd–P angles were more acute (spanning *ca.* 94.1–111.6°) than all P–Pd–P angles (*ca.* 114.5–117.9°) on account of the bromide ligand being the least bulky of the ligands. As was the case for **3**, these metrical considerations strongly favoured the identification of **4** as a Pd(0)-phosphenium, rather than a Pd(II)-phosphide. The bond angles between the two PPh₃ ligands at Pd were almost identical in **3** and **4** (114.03(4)° and 114.50(7)°, respectively), but the Ph₃P–Pd–NHP angles were smaller in **4** (*ca.* 117.7° vs. *ca.* 123.0° on average) because of the presence of a fourth ligand. The Pd–NHP bond was slightly shorter in **4** than in **3** in agreement with increased Pd→P backbonding (68 % of total orbital interactions) in the more electron rich neutral

complex over the cation. This trend was paralleled by calculated total bonding energies, which indicated greater electrostatic and orbital contribution in **4** over **3** (see Supporting Information for calculated data).

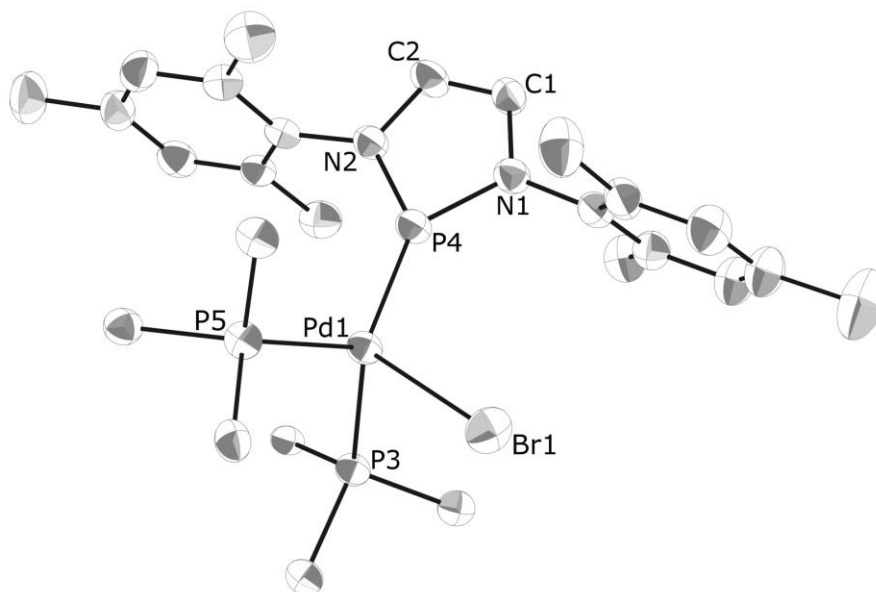


Figure 3. ORTEP representation of the molecular structure of **4** (30 % ellipsoids) with all but the ipso C-atoms of the phenyl rings on the phosphine ligands and solvent (THF) removed for clarity. Selected bond distances (Å) and angles (°), with estimated standard deviations in parentheses and calculated values in square brackets: Pd1–P4, 2.1166(17) [2.177]; Pd1–P3, 2.4033(19) [2.410]; Pd1–P5, 2.4178(19) [2.439]; Pd1–Br, 2.7240(9) [2.704]; P4–N1, 1.678(5) [1.761]; P4–N2, 1.671(5) [1.761]; N1–C1, 1.393(7) [1.382]; N2–C2, 1.309(8) [1.382]; P3–Pd1–P4, 117.88(6) [117.3]; P3–Pd1–P5, 114.50(7) [112.6]; P3–Pd1–Br, 95.82(5) [96.1]; P4–Pd1–P5, 117.50(7) [112.6]; P4–Pd1–Br, 111.61(5) [108.0]; P5–Pd1–Br, 94.08(5) [100.2], N1–P4–N2, 88.0(2) [85.7].

The Pd–Br bond in **4** was very long (2.7240(9) Å), indicative of a weak interaction. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this compound in CDCl_3 solution at r.t. showed two broad resonances (δ_{p} 23.4 and 213.9) whose chemical shifts were similar to those in the solution spectrum of **3**. This broad spectrum, which resolved to an upfield doublet and downfield triplet when the temperature was lowered to 253 K, was probably the result of reversible binding of the bromide ion to palladium in solution. Isolation of **3** as a salt and **4** as a molecular solid further confirmed predictions by Amatore and Jutand that the proposed $[\text{Pd}(\text{PR}_3)_2\text{X}]^-$ anion should be stabilized not only by electron-withdrawing phosphines (in our case, by the π -acidic phosphonium cation), but also by strongly electron-donating X^- anions (Br^- being a substantially better donor than TfO^-). Treatment of **4** with Me_3SiOTf cleanly gave **3** for which there was no structural or spectroscopic evidence for triflate coordination.

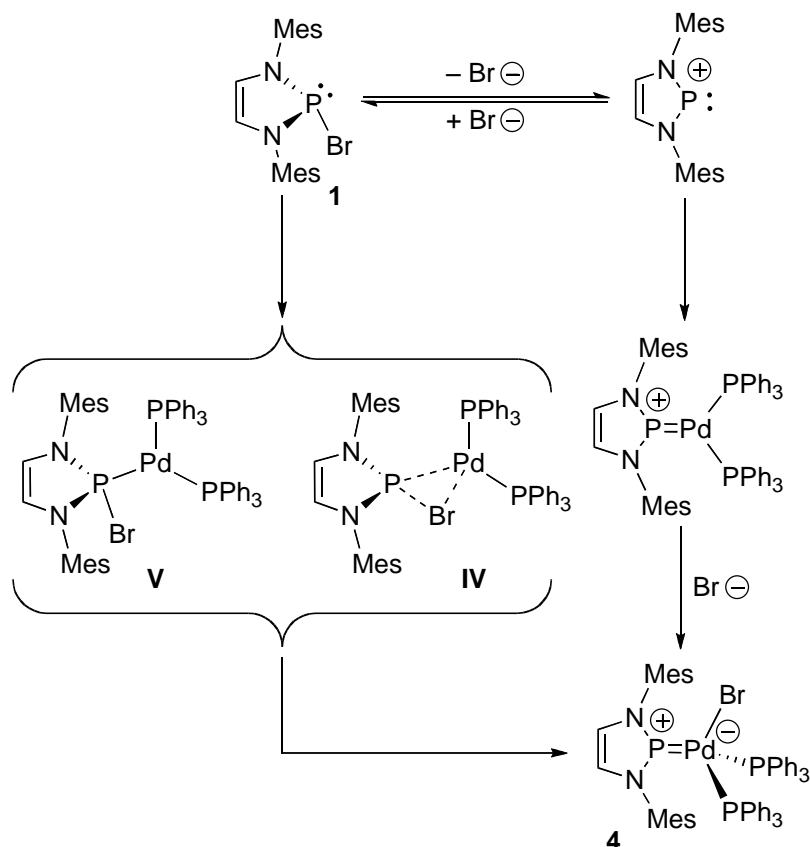
Addition of E–X (E = B, C, P; X = halogen) to M(0) precursors to give carbene and carbene analogues may proceed formally by one of two routes: homolysis with oxidative addition of the metal, and heterolysis without. The first case has been reported for E = C by Fürstner who showed that chloroimidazolium salts reacted with $\text{Pd}(\text{PPh}_3)_4$ in refluxing CH_2Cl_2 to give (structurally characterized) *trans*- $[\text{PdCl}(\text{NHC})(\text{PPh}_3)_2]\text{Cl}$.¹⁴ These compounds had square planar coordination geometries clearly indicative of Pd(II); chloropyridiniums have been shown by Herrmann to react similarly to give Pd(II)-pyridinylidenes.¹⁵ For E = B, analogous oxidative addition of bromoboranes to Pd(0) precursors gave square planar Pd(II)-boryl complexes.¹⁶ And for E = P, Dyer reported production of 42-electron tripalladium clusters featuring bridging phosphide ligands by reaction of acyclic bis(dialkylamino)chlorophosphines with $\text{Pd}_2(\text{dba})_3$.¹⁷ We are not aware

of reports of P–X heterolysis without oxidative addition mediated by Pd(0) that predate the present disclosure, but the first example of this general transformation was by Gudat who showed that an unsaturated, cyclic diaminochlorophosphine similar to **1** added to M(0)(CO)₄(bipy) (M = Mo, W) to give M(0)-phosphenium complexes.¹⁸ Likewise in this work, the addition of P–Br to Pd(0) did not bring about a change in oxidation state of the metal on account of the stability of the phosphorus-centred cation; the reaction may be thought of as a formal heterolysis of the P–Br bond and ligation of the resultant P⁺ and Br[−] fragments by Pd(0). This concept reinforced the validity of viewing **1** as a Br→P Lewis acid-base adduct.

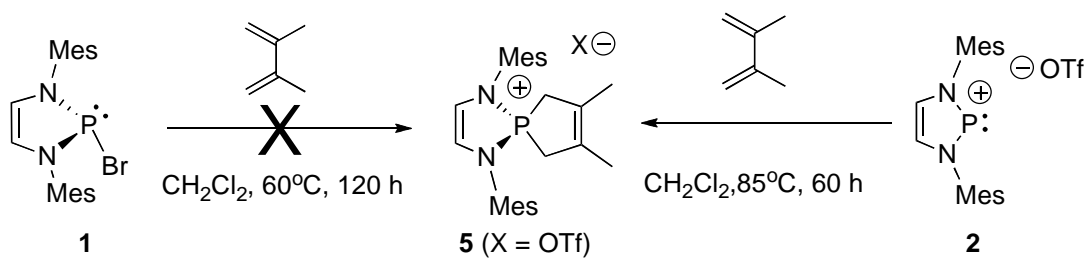
We envisioned that **4** might be formed by either associative or dissociative mechanisms (Scheme 2). If the bromophosphine **1** were in equilibrium with its salt in solution, the first step might involve reaction between Pd(PPh₃)₂ (or a similar, low-coordinate Pd(0)-phosphine) and the “naked” NHP cation [*u*NHP^{Mes}]⁺ to give [(*u*NHP^{Mes})Pd(PPh₃)₂]⁺, *i.e.*, the cation of **3**, which could then be ligated by bromide to give the insoluble neutral compound **4**. Alternatively, reaction between the intact bromophosphine and Pd(PPh₃)₂, with concomitant or subsequent transfer of bromide to the metal would also generate **4**. We note that Burck and Gudat have shown by calculation that chloride transfer between chlorophosphines and phosphenium cations probably goes via halide-bridged species, which when applied to our case would favor a concerted P-to-Pd bromide transfer.¹⁰

In order to distinguish between these possibilities, we treated **1** and **2** with excess 2,3-dimethyl-1,3-butadiene in parallel reactions under identical conditions. This test relied on our earlier observation of the cycloaddition reaction between saturated NHP cations and dienes to give spirocyclic diazaphospheniums.¹⁹ Although the reaction was

much more sluggish than that of its saturated analogue, the phosphonium triflate **2** underwent the expected cycloaddition with prolonged heating (Scheme 3). The bromophosphine **1** by comparison was completely unreactive. This difference strongly implied that despite its long P–Br bond, **1** did not dissociate bromide in solution and that the formation of **4** probably proceeded initially by an associative reaction between bromophosphine and a low coordinate Pd(0)-phosphine species. The driving force for the bromide transfer may be the strong, stabilizing backbonding interaction between the Pd(0) anion and the cationic NHP ligand. We note that reactions between saturated NHP cations and Wilkinson's catalyst gave not only the phosphonium complexes $[(\text{NHP}^{\text{Ar}})\text{RhCl}(\text{PPh}_3)_2]^+$, but also the chlorophosphine $\text{Cl-NHP}^{\text{Ar}}$ and $[\text{Rh}(\text{PPh}_3)_3]^+$ by transfer of chloride from the metal to phosphorus,²⁰ which is precisely opposite to what we have observed.



Scheme 2. Proposed associative and dissociative mechanisms for the formation of **4** by reaction of **1** with $\text{Pd(PPh}_3)_2$.



Scheme 3. Attempted cycloaddition reactions between **1** and **2** and 2,3-dimethyl-1,3-butadiene.

We have also investigated the reversibility of the formation of **4** by incubating the isolated complex with $\text{Br} \rightarrow \mu\text{NHP}^{\text{Dipp}}$ (Dipp = 2,6-diisopropylphenyl) at rt for several hours. None of the statistically expected complex $(\mu\text{NHP}^{\text{Dipp}})\text{Pd}(\text{PPh}_3)_2\text{Br}$ was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, which showed that insertion reaction was essentially irreversible at rt.

Conclusions

We believe that the successful isolation and structural characterization of **4** provides indirect experimental evidence for the feasibility of the proposed anion $[\text{Pd}(\text{PR}_3)_2\text{X}]^-$ by giving credence to its calculated stability trends. The high Lewis acidity of the unsaturated NHP cation and the basicity of the Br^- anion have allowed us to isolate this elusive species as Lewis acid-base adduct. To the best of our knowledge, **4** represents the only structurally characterized Pd(0) halide. Investigations into its onward chemistry including catalytic applications, are ongoing.

Experimental Section

$\mu\text{NHP}^{\text{Mes}}\text{Br}$ (1). This compound was made by a slight modification to the procedure developed by Macdonald and coworkers.⁸ Tribromophosphine (0.58 mL, 6.1 mmol) was added dropwise over 10 min to a solution of dimesityldiimine (1.80 g, 6.10 mmol) and cyclohexene (1.85 mL, 18.3 mmol) in CH_2Cl_2 (20 mL) at r.t. The brown solution was stirred at r.t. for 48 h. The solvent was removed *in vacuo* to give a dark green solid, which was washed with Et_2O (5 mL) and dried. Yield: 2.60 g (99 %). ^1H NMR (CDCl_3): δ 2.32 (s, 6H, *p*- CH_3), 2.43 (s, 12H, *o*- CH_3), 6.67 (s, 2H, *CH*), 6.99 (s, 4H, Ar). $^{31}\text{P}\{^1\text{H}\}$ NMR

(CDCl₃): δ 175.1 (s). ¹³C{¹H} NMR (CDCl₃): δ 19.2, 20.9, 123.3, 130.0, 133.2, 135.5, 138.6. HRMS C₂₀H₂₄BrN₂P calcd (found) 402.0860 (402.0858).

[*u*NHP^{Mes}]OTf (2). The halide abstraction agent Me₃SiOTf (0.71 mL, 3.9 mmol) was added dropwise to a solution of **1** (1.33 g, 3.60 mmol) in CH₂Cl₂ (15 mL). The mixture was stirred at r.t. for 2 h. The solvent was removed *in vacuo* to give a yellow solid, which was washed with Et₂O (5 mL) and dried. Yield: 1.47 g (86 %). Characterization data were identical to those previously reported by Gudat and coworkers.⁹

[(*u*NHP^{Mes})Pd(PPh₃)₂]OTf (3). In a small vial, Pd(PPh₃)₄ (0.67 g, 0.58 mmol) and **2** (0.24 g, 0.58 mmol) were dissolved in CH₂Cl₂ (5 mL) to give a dark orange solution. After 5 min, the solvent was removed *in vacuo* to give an orange residue, which was washed with Et₂O (2 × 10 mL) to remove free PPh₃, then dried *in vacuo* to give an orange solid. Yield: 0.62 g (78 %). ¹H NMR (CDCl₃, 263 K): δ 1.78 (s, 12H, *o*-CH₃), 2.36 (s, 6H, *p*-CH₃), 6.80 (pt, 12H, Ar), 6.88 (s, 2H, Ar), 7.1 (t, 18H, Ar, ³J_{HH} = 7.2 Hz), 7.13 (t, 6H, Ar, ³J_{HH} = 7.2 Hz), 7.69 (br d, 2H, CH). ¹³C{¹H} NMR (CDCl₃, 253 K): δ 17.5, 21.3, 128.7 (br), 129.7, 132.0, 133.4 (br), 134.8, 139.9. ³¹P{¹H} NMR (CDCl₃): δ 23.1 (d, ²J_{PP} = 138 Hz), 213.9 (t, ²J_{PP} = 138 Hz). ¹⁹F NMR (CDCl₃): δ -78.6 (s). ESI-MS: C₅₆H₅₄N₂P₃Pd⁺ calcd (found) 953.3 (953.1, M⁺), (691.0, M⁺ - PPh₃). Anal. calcd for C₅₇H₅₄F₃N₂O₃P₃PdS: C, 62.0; H, 4.9; N, 2.5 %. Found: C, 62.5; H, 5.2; N, 2.2 %.

(*u*NHP^{Mes})PdBr(PPh₃)₂ (4). In a small vial, Pd(PPh₃)₄ (0.12 g, 0.11 mmol) and **1** (0.040 g, 0.11 mmol) were dissolved in CH₂Cl₂ (5 mL) to give a dark orange solution. After 5

min, the solvent was removed *in vacuo* to give an orange residue, which was washed with Et₂O (2 × 7 mL) to remove free PPh₃, then dried *in vacuo* to give the title compound as an orange solid. Yield: 0.06 g (60 %). ¹H NMR (CDCl₃): δ 1.78 (s, 12H, o-CH₃), 2.36 (s, 6H, p-CH₃), 6.87 (s, 2H, Ar), 7.06 (br, 1H, Ar, ²J_{HH} = 7.2 Hz), 7.08 (t, 13H, Ar, ²J_{HH} = 7.2 Hz), 7.27 (t, 12H, Ar). ³¹P{¹H} NMR (CDCl₃): δ 23.4 (br), 213.9 (br). ¹³C{¹H} NMR (CDCl₃): δ 17.9, 21.4, 128.0, 128.8, 129.4, 130.0, 130.1, 132.6, 133.6, 134.7, 135.1, 135.4, 139.9; HRMS: C₅₆H₅₄N₂P₃Pd (4-Br) calcd (found) 953.2535 (953.2513). Anal. calcd for C₅₆H₅₄BrN₂P₃Pd: C, 65.0; H, 5.3; N, 2.7 %. Found: C, 65.8; H, 5.2; N, 2.5 %.

1,4-dimesityl-7,8-dimethyl-1,4-diaza-5-phosphoniaspiro[4.4]nona-2,7-diene

trifluoromethane sulfonate salt (5). A large excess of 2,3-dimethyl-1,3-butadiene (1.75 mL, 15.5 mmol) was added to a solution of **2** (0.099 g, 0.21 mmol) in CH₂Cl₂ (1.5 mL). The mixture was heated to 85 °C for 60 h. The progress of the reaction was monitored by ³¹P{¹H} NMR spectroscopy until there was no further change. The solvent was removed *in vacuo* to give a brown wax. Yield: 0.10 g (62 % conversion by NMR; residual **2** could not be removed). ¹H NMR (CDCl₃): δ 1.59 (d, 6H CH₃, ⁴J_{HH} = 1.2 Hz), 2.31 (s, 6H, *p*-CH₃), 2.35 (s, 12H, *o*-CH₃), 3.11 (dd, 4H, PCH₂, ⁴J_{HH} = 1.2 Hz, ²J_{PH} = 9.6 Hz), 6.20 (d, 2H, NCH, ³J_{PH} = 18 Hz), 7.01 (s, 4H, Ar). ³¹P{¹H} NMR (CDCl₃): δ 86.0 (s). ¹³C{¹H} NMR (CDCl₃): δ 16.0 (d, ³J_{CP} = 14.2 Hz), 18.5, 21.1, 34.0 (d, ¹J_{CP} = 62.3 Hz), 119.9 (d, ²J_{CP} = 11.3 Hz), 126.7 (d, ²J_{CP} = 11.5 Hz), 130.4, 130.7, 137.0, 140.4. ¹⁹F{¹H} NMR (CDCl₃): δ -78.76 (s). HRMS C₂₆H₃₄N₂P calcd (found) 405.2460 (405.2440).

Supporting Information Available

General experimental considerations, a tabulated summary of crystallographic data, and full crystallographic data for **1**, **3** and **4** as CIF. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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