

2-Aryl-1,3-Benzoxaphospholes as Unwilling Participants for Catalytic Suzuki–Miyaura CC Coupling Reactions

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ABSTRACT: Under conditions typically effective to achieve a catalytic aryl–aryl bond during palladium Suzuki–Miyaura (SM) coupling reactions of $\text{ArB}(\text{OH})_2$ and ArBr , reactions of *p*-tolylboronic acid and 2-(BrC_6H_4)-1,3-benzoxaphosphole (BrC_6H_4 -BOP, **1**) failed to provide the anticipated product of CC bond coupling, 2-($p\text{-CH}_3\text{C}_6\text{H}_4\text{-C}_6\text{H}_4$)-1,3-benzoxaphosphole. An analysis of reaction mixtures by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic methods showed the presence of numerous broad resonances, suggesting the formation of labile metal complexes with **1**. This possibility was confirmed by determinations of the solid-state structures of $[(^t\text{Bu}_3\text{P})(\text{Ph-BOP})\text{M}]_2$ ($\text{M} = \text{Pt}$, **5**; $\text{M} = \text{Pd}$, **6**) from the reaction of Ph-BOP and $[\text{M}(^t\text{Bu}_3\text{P})_2]$ ($\text{M} = \text{Pt}$, **5**; $\text{M} = \text{Pd}$, **6**). The structures of **5** and **6** are isomorphous and reveal unusual bridging μ_2 -P-BOP bonding modes. Computational studies have explored the structures and relative energies and indicate that dimeric complexes of this form can dissociate easily. Surprisingly, even when $\text{P}=\text{C}$ double bonds of Ar-BOPs are sheltered by coordination to tungsten pentacarbonyl, the Ar-BOP units resist yielding products of CC coupling under similar SM conditions but instead yield unusual products whereby CsOH adds across the $\text{P}=\text{C}$ bonds in $[(\text{CO})_5\text{W}\{2\text{-Ar-BOP}\}]$. Computational studies are consistent with ready addition of hydroxide to the tungsten-protected $\text{P}=\text{C}$ bond.



INTRODUCTION

The palladium-catalyzed Suzuki–Miyaura CC coupling reaction between aryl halides and aryl boronic acids has risen to become a premier catalytic method for forging new carbon–carbon bonds in the synthesis of many important fine chemicals and pharmaceuticals.^{1–9} The coupling reaction has also enjoyed success for the synthesis of a number of π -conjugated polymers and materials.^{10–13} The great functional group tolerance of the catalysts is a highlight of this process.

π -Conjugated polymers and materials are highly studied materials for their potential in various optoelectronic applications. Our work has focused on the development of π -conjugated materials involving $p\pi\text{--}p\pi$ $\text{P}=\text{C}$ bonds.^{14–20} Compounds related by the formal replacement of $\text{C}=\text{C}$ bonds with $\text{P}=\text{C}$ bonds often display similarities in structures and reactivities. These parallels have led to these organophosphorus analogues of unsaturated hydrocarbons to be nicknamed “carbon copies”.^{21–23} Extended π -conjugated materials having $p\pi\text{--}p\pi$ $\text{P}=\text{C}$ units might thus serve as interesting candidates as materials for possible OLED or OPV applications. Notably, the π -ionization energies of the known $\text{P}=\text{C}$ -bonded compounds compare favorably with those of their $\text{C}=\text{C}$ -bonded counterparts, indicating that the occupied π -orbitals have similar energies.²⁴

Despite often being referred to as carbon copies, key differences distinguish pairs of compounds related by exchange of $\text{E}=\text{C}$ bonds ($\text{E} = \text{P}, \text{C}$). For example, materials possessing $\text{P}=\text{C}$ bonds have smaller HOMO–LUMO gaps due to the presence of the weaker π bonds and resulting lower-lying π^* orbitals.^{25–27} We and others have sought to take advantage of reduced HOMO–LUMO gaps to bring forth new strategies to modulate the electronic properties of extended π -conjugated materials.^{15,28–33}

Another way carbon copies differ from their phosphorus-free analogues is that until recently most carbon copies did not display significant luminescence properties. We have, however, demonstrated that 2-aryl-1,3-benzoxaphospholes (Ar-BOPs) and 2,6-diarylbenzobisoxaphospholes ($\text{Ar}_2\text{-BBOPs}$) are an unusually fluorescent class of materials having $p\pi\text{--}p\pi$ $\text{P}=\text{C}$ bonds (Chart 1) and thus act as “photocopies” of analogous phosphorus-free luminescent materials. Other examples of photocopies have since been reported.^{16,17,34–41}

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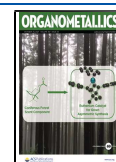
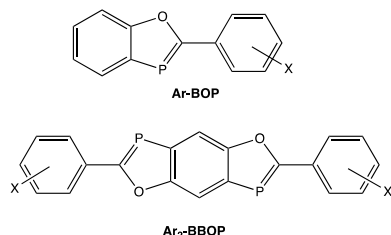


Chart 1. Halogen-Functionalized 2-Aryl-1,3-benzoxaphospholes (Ar-BOPs) and 2,6-Diarylbisoxaphospholes (Ar₂-BBOPs) as Potential Candidates for CC Coupling Reactions



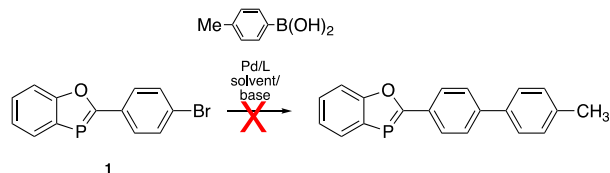
Our recent attention has turned to finding methods to further extending the π -conjugation of benzoxaphospholes and related materials. Fortunately, the synthesis of Ar-BOPs and Ar₂-BBOPs allows ready positioning of halogens onto the peripheral aromatic rings by using appropriately substituted benzoyl chlorides during the synthesis. The resulting functionalized materials should thus be viable candidates for various palladium-catalyzed CC and EC bond-forming reactions.

Palladium-catalyzed Suzuki–Miyaura (SM) reactions involving aryl halides (ArX) and aryl boronic acids (ArB(OH)₂) are an extremely well established class of carbon–carbon coupling reactions⁴² and are suitable for initial studies using functionalized halide-substituted BOPs and BBOPs. Catalytic SM reactions are also known to be fairly functional group tolerant. While one might assume organophosphorus (phosphine) compounds are good Lewis bases and might poison catalysts, there have been a number of reports of using SM coupling reactions on bromo-substituted triarylphosphines and triarylsines to create new biphenyl linkages.^{43–45} Given that the lone pair on phosphorus in the parent BOPs is the HOMO-3, and HOMO-5 in Ar-BOP (*vide infra*) with a corresponding ionization energy much higher than in triarylphosphines, BOPs are likely to be weaker Lewis bases than triarylphosphines.^{46,47}

RESULTS AND DISCUSSION

Screening efforts on the applicability of catalytic SM reactions for BOPs began by examining the reaction of 2-(*p*-BrC₆H₄)-benzoxaphosphole (1) with *p*-tolylboronic acid under typical SM CC coupling protocols (Scheme 1) (Supporting

Scheme 1. Attempted Cross-Coupling Reactions of 1 under Standard Suzuki–Miyaura Conditions

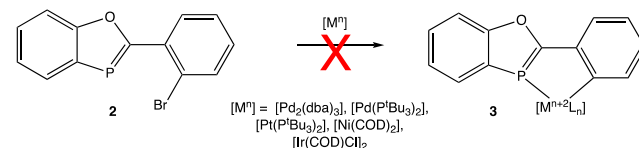


Information). These reactions were characterized by notable color changes that depended on the specific reaction conditions (solvent, base, Pd source). Examination of the reaction mixtures by ³¹P{¹H} NMR spectroscopy revealed in all cases uninterpretable complex spectra having varying numbers of low-intensity signals that were also not located in the region for the anticipated products of the form 2-(*p*-CH₃C₆H₄-C₆H₄)-benzoxaphosphole (ca. δ 75–90 ppm). Attempts to utilize 2-(*p*-IC₆H₄)-benzoxaphosphole, which

might undergo a more facile oxidative addition of the more reactive C–I bond, also did not provide NMR evidence for 2-(*p*-CH₃C₆H₄-C₆H₄)-benzoxaphosphole being produced (Supporting Information).

A key step in the Suzuki–Miyaura CC coupling process involves oxidative addition of the aryl halide to the palladium(0) center. One way to capture and/or to promote the product of this step is to use a precursor that might afford a cyclometalated species such as 3 (Scheme 2).^{48–58}

Scheme 2. Attempted Reactions of the *o*-Bromine Substituted BOP 2



2-(*o*-BrC₆H₄)-benzoxaphosphole (2) was thus prepared using methods reported previously, and the spectroscopic properties were consistent with those of previously reported analogues (Supporting Information). Likewise, the solid-state structure, as ascertained by single-crystal X-ray diffraction methods (Figure 1), is largely in accord with previously published

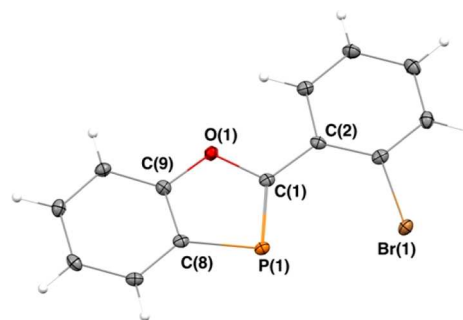


Figure 1. Structural diagram for compound 2. Selected bond lengths (Å) and bond angles (deg): P(1)–C(1), 1.728(3); P(1)–C(8), 1.785(3); O(1)–C(1), 1.386(3); O(1)–C(9), 1.368(3); C(1)–P(1)–C(8), 88.2(1); C(9)–O(1)–C(1), 111.4(2).

structures of BOPs.^{59,60} Interestingly, despite the presence of the large bromine atom, the bromo-aryl ring is able to retain coplanarity with the benzoxaphosphole ring. The phosphorus–bromine contact distance of 3.176 Å is comparable to related intramolecular distances between phosphorus and bromine in *peri*-substituted 8-diorganophosphorus-1-bromonaphthalenes and 6-diorganophosphorus-5-bromonaphthalenes.^{61,62} The calculations predict a planar structure (real minimum) with a slightly longer (3.222 Å) phosphorus–bromine distance. A Bader analysis gave a bond critical point with a small (0.015) electron density, indicating a weak pnictogen interaction.

Reactions of 2 with the commercially available low-valent metal complexes [Pd₂(dba)₃], [Ir(COD)Cl]₂, [Ni(COD)₂], [Pt(P^{*t*}Bu₃)₂], and [Pd(P^{*t*}Bu₃)₂] in various solvents (THF, CDCl₃, toluene, and hexanes) were explored to seek conditions under which a single cyclometalated product of the type 3 could be produced. These reactions (room temperature, overnight), like the earlier reactions, produced solutions that on analysis by ³¹P NMR spectroscopy suggested the formation of multiple unidentifiable and labile mixtures of products and unreacted 2.

The reactions of nonhalogenated BOPs with low-valent Pd and Pt complexes were then investigated to determine if BOPs were interacting or binding in an unproductive fashion with putative intermediates under the conditions of the SM reactions. Pd(0) species are invoked as intermediates during SM catalysis, and thus reactions of Pd(0) and Pt(0) sources with 2-Ar-BOPs lacking halogen substituents were examined. Interestingly, these reactions also produce vivid color changes and complicated $^3\text{P}\{^1\text{H}\}$ NMR spectra. For example, the reaction of 2-Ph-BOP (**4**)¹⁸ with $[\text{Pt}(\text{P}^t\text{Bu}_3)_2]$ in THF, toluene, or hexanes rapidly produces violet solutions. A $^3\text{P}\{^1\text{H}\}$ NMR analysis of such reactions shows that the major signals can be attributed to unreacted **4** and P^tBu_3 , while a number of other unidentified minor resonances are also present.

If the reaction of 2-Ph-BOP (**4**) with $[\text{Pt}(\text{P}^t\text{Bu}_3)_2]$ is conducted in hexanes and the reaction mixture is allowed to sit overnight, tan crystals can be isolated in a modest (17%) yield. The results of a single-crystal X-ray diffraction study are presented in Figure 2. Complex **5** is a dinuclear complex with

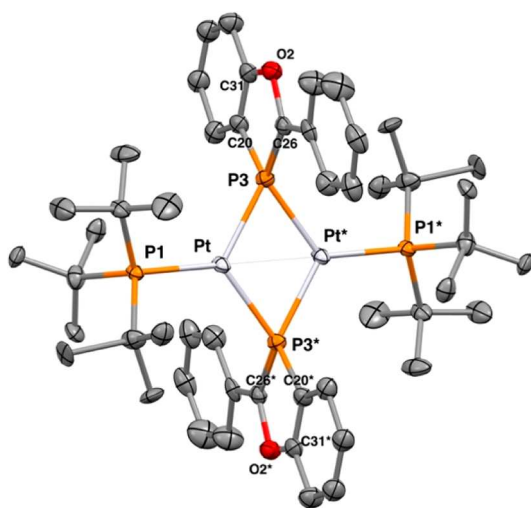


Figure 2. Structural diagram for compound **5**. Hydrogens have been omitted for clarity, and thermal ellipsoids are shown at 50% probability.

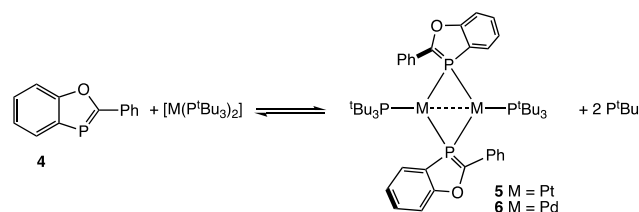
the phosphorus atom of each benzoxaphosphole ligand bridging two $[\text{Pt}(\text{P}^t\text{Bu}_3)]$ fragments. A crystallographic center of symmetry enforces a planar Pt_2P_2 core and relates the two BOP units. Each BOP is disordered over two orientations perpendicular to the Pt_2P_2 core, with Pt–P distances of 2.341(3) and 2.313(2) Å. The corresponding P=C bond distances of 1.72(1) Å are slightly shorter than those found for compound **2**, indicating that the bonding is rather $\mu_2\text{-}2e$ than $\mu_2\text{-}4e$. These values can also be compared to those for $[\text{W}(\text{CO})_5]$ adducts of 2-(*p*-XC₆H₄)-BOP (X = H, Cl, Br, Me, OMe) that have recently been structurally characterized.⁶³ These complexes displayed P=C bonds in a narrow range from 1.706(3) to 1.710(6) Å.

The Pt–Pt* distance of 2.6464(4) Å across the Pt_2P_2 core suggests possible bonding interactions between the two platinum atoms, despite the formal closed shell $d^{10}\text{--}d^{10}$ configurations. Similar MM' short contacts have been reported in several Cp^*M (M = Al or Ga) bridged platinum and palladium complexes.^{64–75} In these materials NBO and AIM methods indicated only weak $d^{10}\text{--}d^{10}$ interactions. Addition-

ally, for **5** our DFT calculations (at the geometry from the crystal structure) show that the bond critical point obtained between the two Pt centers displayed a rather significant (0.066) electron density.

Tan crystals of the analogous palladium complex $[(^t\text{Bu}_3\text{P})(\text{Ph-BOP})\text{Pd}]_2$ (**6**) were obtained (19%) from a violet hexanes solution of **4** with $[\text{Pd}(\text{P}^t\text{Bu}_3)_2]$ allowed to sit overnight (Scheme 3). The results of a crystal structure analysis

Scheme 3. Synthesis of Complexes **5** and **6** from Compound **4**



(Supporting Information) showed the crystals of **6** to be isomorphous with **5**, and a comparison of key structural features is provided in Table 1.

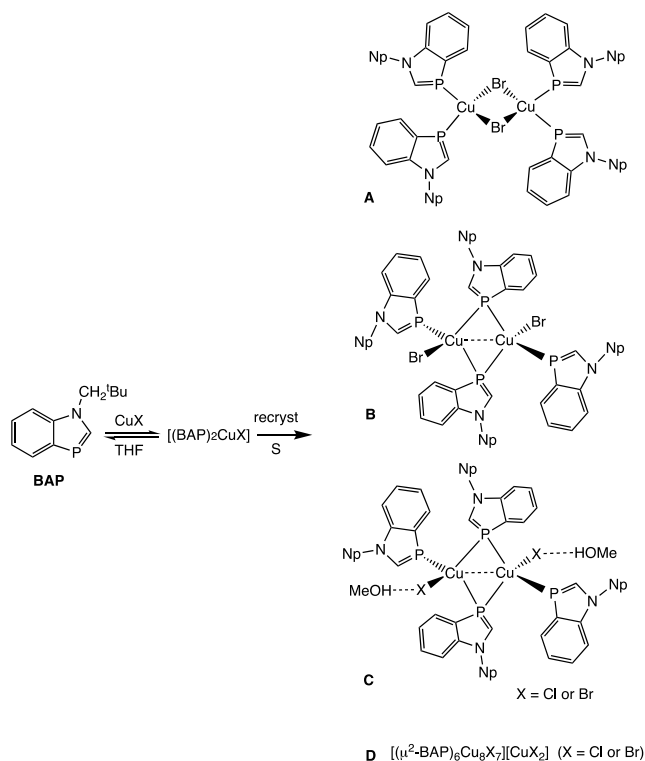
Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **5** and **6**

distances and angles	5	6
M···M'	2.6464(4)	2.6284(3)
M–P(1)	2.288(1)	2.3175(6)
M–P(3)	2.341(3)	2.335(1)
P(3)–C(20)	1.72(1)	1.712(9)
P(3)–C(26)	1.81(1)	1.816(8)
P(1)–M–M	179.73(3)	179.36(2)
P(1)–M–P(3)	124.76(7)	124.04(4)
P(3)–M···M'	55.46(6)	55.62(3)
C(20)–P(3)–C(26)	88.0(7)	87.5(4)
C(31)–O(2)–C(20)	110(1)	110.3(6)

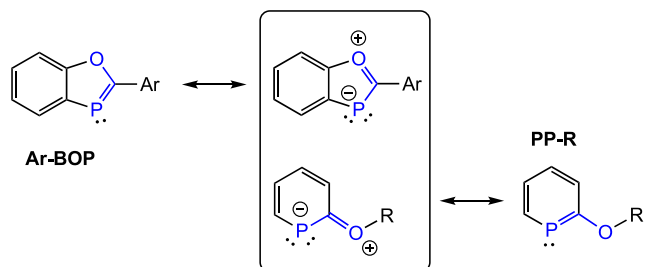
Attempts to record meaningful NMR data for **5** and **6** were unsuccessful. Upon dissolution, samples of **5** and **6** showed multiple ^3P NMR resonances of low intensity as well as resonances for free **3**, suggesting redistribution to a mixture of species in solution, in agreement with the observed low yields of crystalline products. Analogous results were reported for the coordination of *N*-neopentyl-1,3-benzazaphosphole (BAP) to copper halides (Scheme 4). By a subtle variation of the reaction conditions and crystallization solvents single-crystal structures **A–D** were obtained. For example, simply changing the solvents of recrystallization from CH_2Cl_2 /hexane to THF/hexane led to structure **B** rather than structure **A** and a computational study revealed that the stabilities of the reported species and their monomeric building blocks (BAPCuBr) are comparable.^{76–79}

The $\mu_2\text{-P}$ -binding mode for BOPs might be attributed to their electron-rich character, which is similar to that of BAPs,⁷⁷ with resonance structures that place increased electron density onto the phosphorus atoms (Scheme 4). Such complexing ability was also reported for 2-phosphaphenol (PP-R; Scheme 5) derivatives; however, in these compounds the P=C–O bonding motif is only partially incorporated in the cyclic delocalization^{80–82} and likewise for phosphaaniline.⁸³ Although the zwitterionic resonance structures (Scheme 4)

Scheme 4. Literature-Reported Reactions of *N*-Neopentyl-1,3-benzazaphosphole (BAP) with Copper Halides to Give A–D



Scheme 5. Resonance Forms for Ar-BOP and PP-R



indicate a shortening of the C–O bond, the cyclic delocalization (indicated by the -11.9 and -9.7 ppm NICS(1) values for the six- and five-membered rings, respectively) results in a bond length equalization for BOP. Accordingly, the 1.386 Å C–O distance in **2** is somewhat longer than the 1.34 – 1.36 Å distance in 2-phosphaphenol complexes.⁸⁰

In order to probe the structures of **5** and **6** more deeply and also to understand their stability, we have computationally examined how a BOP interacts with model $[\text{Ni}(\text{PMe}_3)]$, $[\text{Pt}(\text{PMe}_3)]$, and $[\text{CuCl}]$ groups (the last metal center was chosen for purposes of comparison to previous computational work on BAP complexes). The key occupied orbitals of the parent BOP are shown in Figure 3.

The high degree of π -delocalization throughout the condensed rings (as for BAP) was already shown by previous photoelectron spectroscopic investigations⁷⁷ and the NICS values (see above) and is also clearly evidenced by the shape of the HOMO and LUMO (Figure 3). As a consequence, the HOMO becomes destabilized and the LUMO is stabilized. The significant phosphorus contribution (P=C character) to

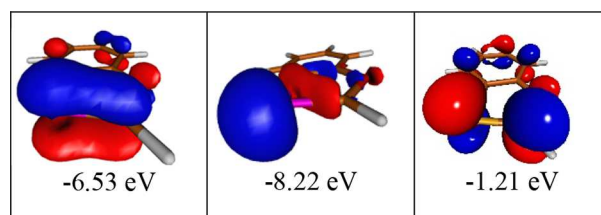


Figure 3. HOMO (left), HOMO-3 (middle), and LUMO (right) for the parent BOP.

the HOMO is in accordance with the zwitterionic resonance structure (Scheme 5). Interestingly, phosphorus has a rather large contribution to the (P=C π^* type) LUMO. Thus, phosphorus in BOP should be the most reactive center. The significant P=C (π^*) character of the LUMO also contributes to the stabilization of this unoccupied orbital,^{25–27} which is indeed of low energy (-1.21 eV), indicating that BOPs are susceptible to nucleophilic addition at this bond. The in-plane lone pair (HOMO-3) is significantly lower in energy, in accordance with the previous photoelectron spectroscopic results.⁷⁷ On consideration of the energies of HOMO and HOMO-3 and their different degree of localization at P, both π and in-plane coordination is feasible, and our computations predict somewhat higher stability for the former (Table 2).

Table 2. M06/cc-pvdz (M06/cc-pvdz-pp) Model Complex Formation Energies (kcal/mol)

	$[\text{Ni}(\text{PMe}_3)]$	$[\text{Pt}(\text{PMe}_3)]$	$[\text{CuCl}]$
	-36.6	-38.7	-9.7
	-44.0	-40.5	-15.4
	-36.9	-38.7	-7.6
	-47.4	-44.3	-13.5

The Ni and Pt π -complexes are only slightly more stable for BOP than for BAP. Since both complexation modes are energetically feasible, it is reasonable to expect that the electron-deficient 1:1 complexes dimerize in a μ_2 -P-binding mode. The Gibbs free energy of the $(\text{PMe}_3)_2\text{Pt} + \text{BOP} = (\text{PMe}_3)\text{PtBOP} + \text{PMe}_3$ exchange reaction is 1.2 kcal/mol, indicating a facile ligand exchange (for the calculations PMe_3 was used instead of P^tBu_3 for economic reasons).

We have also calculated the Gibbs free energies of dimerization for the $(\text{PMe}_3)\text{M} \leftarrow \text{L}$ (M = Ni, Pt; L = BOP, BAP) complexes, which are in alignment with the exper-

imentally realized structures. For comparison, the dimerization Gibbs free energies of LCuCl ($\text{L} = \text{BOP}$, BAP) are also given. The dimerization Gibbs free energy for $(\text{PMe}_3)\text{MBOP}$ (M : Ni, Pt) is slightly exergonic (Table 3), indicating that the dimeric

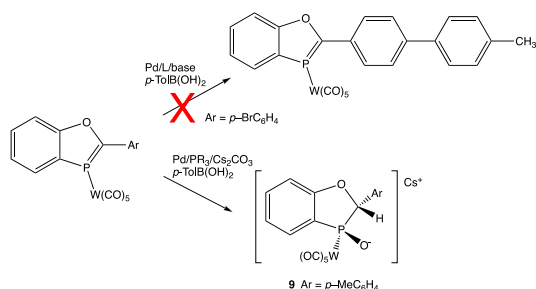
Table 3. Energetics (ΔG) for Dimerization of Model $[\text{LML}']$ Complexes (kcal/mol)

L	$[\text{LNi}(\text{PMe}_3)_2]$	$[\text{LPt}(\text{PMe}_3)_2]$	$[\text{L}_2\text{CuCl}]_2$
	6.6	7.0	-18.0
	6.1	-0.2	-10.6

structure might dissociate, in agreement with the experimental observations. As these calculations are for the model systems, similar calculations for the complete structure of $[(\text{tBu}_3\text{P})(\text{Ph-BOP})\text{Pt}]_2$ (**5**) were undertaken. In this case, the dimerization energy of the $[(\text{tBu}_3\text{P})(\text{Ph-BOP})\text{Pt}]$ unit was 9.1 kcal/mol more favorable. The optimized structure of the four-membered Pt_2P_2 ring, however, was somewhat distorted in comparison to the X-ray structural results, with the two BOP rings being tilted with respect to the PP vector. This result may reflect a rather flat potential energy surface for this binuclear complex.

As was mentioned above, we had access to reference BOP complexes where the phosphorus atom is coordinated to the $[\text{W}(\text{CO})_5]$ entity. Since $[\text{W}(\text{CO})_5]$ is a well-known protecting group for phosphorus with low coordination numbers, we have investigated the possibility of using the previously reported $[(\text{CO})_5\text{W}\{2-(p\text{-BrC}_6\text{H}_4)\text{-BOP}\}]$ (**7**)⁶³ as a candidate for the palladium-catalyzed Suzuki–Miyaura coupling reaction with p -tolylboronic acid (Scheme 6, upper path).

Scheme 6. Attempted Suzuki–Miyaura Cross-Coupling Reaction of **8 with p -Tolylboronic Acid (Top) and Formation of **9** (Bottom)**



Screening reactions were first conducted using Cs_2CO_3 as the inorganic base and catalyst mixtures of $\text{Pd}(\text{OAc})_2$ and either 3 equiv of PPh_3 or XPhos at a 1% loading. The reactions were conducted at 100 °C for 18 h in either dioxane or toluene. In each case the major or sole product observed displayed a resonance at δ 98 ppm ($J_{\text{PW}} = 262$ Hz) in the ^{31}P NMR spectra for reaction aliquots. When p -tolylboronic acid is replaced with p -anisylboronic acid, methylboronic acid, or isopropylboronic acid, similar results are obtained. The ^{31}P

chemical shift of δ 98 ppm is not consistent with formation of a product such as $[(\text{CO})_5\text{W}\{2-(p\text{-R-C}_6\text{H}_4)\text{-BOP}\}]$, as related complexes display resonances in the region δ 52–66 ppm (**7**: δ 66.4).⁶³ Further examination of the reaction showed that the presence or absence of the bromine atom on the BOP unit coordinated to tungsten yielded similar results. For example, the reaction of $[(\text{CO})_5\text{W}\{2-(p\text{-MeC}_6\text{H}_4)\text{-BOP}\}]$ (**8**: δ 58.2)⁶³ and p -tolylboronic acid under the same conditions yields a product (**9**) with a nearly identical chemical shift. In fact, the presence of palladium and phosphine was *not* required to affect the formation of these new species. Compound **9** was more conveniently prepared by the reaction of **8** with a mixture of Cs_2CO_3 and p -tolylboronic acid in CH_2Cl_2 at room temperature (11%, 48 h).

Single crystals of **9** were grown by vapor diffusion of hexanes into a CH_2Cl_2 solution of **9**, and the results of a single-crystal X-ray diffraction study are shown in Figures 4 and 5.

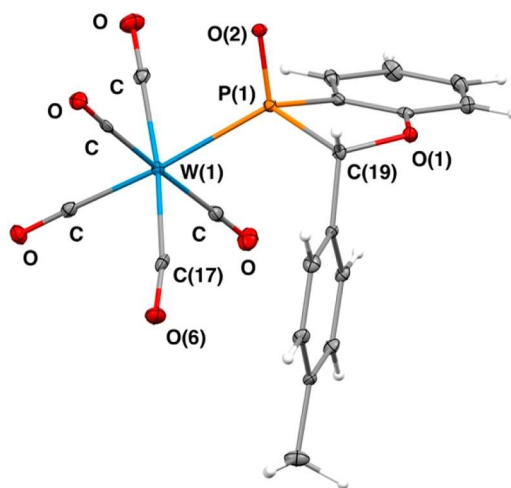


Figure 4. Structural diagram of the anionic portion of **9**. Selected bond distances (Å) and angles (deg): W(1)–P(1), 2.529(1); P(1)–O(2), 1.537(3); P(1)–C(19), 1.902(4); C(19)–O(1), 1.472(4); W(1)–P(1)–O(2), 115.6(1); W(1)–P(1)–C(19), 107.7(2).

Interestingly, the formal addition of OH has occurred across the $\text{P}=\text{C}$ bond (Scheme 6, bottom). The bulkiest $[\text{W}(\text{CO})_5]$

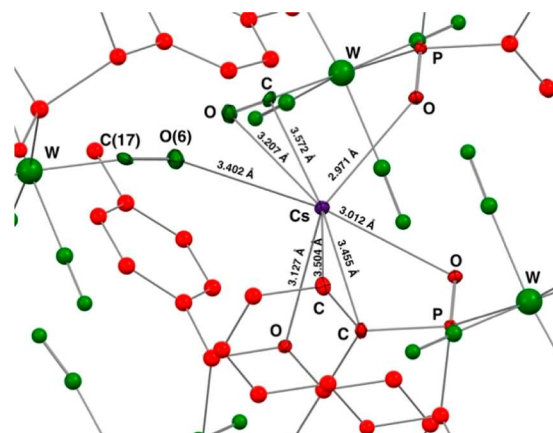


Figure 5. Structural diagram representing part of the 3-D coordination surrounding the Cs ions (purple) in **9**. The $[\text{W}(\text{CO})_5]$ units are shown in green and the organophosphorus anions in red. Primary contacts to Cs are provided in the figure.

and Ar substituents are found to be *trans* to one another. The P–O bond distance of 1.537(3) Å is in a range similar to that for the P–O coordinated bonds in cesium 18-crown-6 dihydrogenphosphate salts (1.510–1.550 Å). The W(1)–C(17)–O(6) bond angle of 171.0(3)° is notably distorted from linearity in comparison to the five other tungsten carbonyl units (177.8(4)–178.9(4)°). This distortion is likely due to the close Cs···O(6) interaction (3.402(3) Å, Figure 5).

The formation of **9** is not surprising, given the initial attack of OH[−] (formed in the presence of the strong Cs₂CO₃ base from the boronic acid and/or fortuitous water) at the phosphorus center. Such an attack is understandable, considering that the aforementioned low-lying BOP LUMO (the effect of W(CO)₅ complexation is small on this orbital) makes a large contribution at the highly oxophilic phosphorus atom (see Figure 3). Accordingly, we could optimize the resulting anionic structure, which can be transformed to **9**, via a subsequent 1,3-H shift. This process is exergonic by 16.9 kcal/mol and has a 12.1 kcal/mol Gibbs free energy activation barrier via a four-membered-ring transition structure. Although this low barrier facilitates the direct H shift, a deprotonation/reprotonation mechanism cannot be excluded.

The individual anionic tungsten units in **9** are bridged by cesium ions to form a complex three-dimensional network in the crystal. The shortest interactions of the cesium cation involve Cs–O contacts of 2.971 and 3.012 Å to the formally negatively charged phosphoryl oxygens of two different anionic tungsten units. Weaker associations with the oxygen atoms of two carbonyl groups and the ether oxygens are also present. Interestingly, the cesium coordination sphere displays short Cs···C(phenyl) contacts of 3.455 and 3.504 Å. Such contacts are common in cesium coordination chemistry. For example, Cs···C(phenyl) contacts of 3.411 and 3.405 Å are observed in the structure of [(18-C-6)Cs{P(H)Mes*}]·0.5(toluene) (Mes* = 2,4,6-*t*Bu₃C₆H₂).^{84,85} For the solvent- and crown-free material [Cs{P(H)Mes*}], a Cs···C(phenyl) contact as short as 3.219 Å is observed.

Since the transformation involved net addition of CsOH, the reaction of CsOH with **8** was examined. Indeed, in CH₂Cl₂ the reaction proceeds to provide **9** in 95% yield. An analysis of the resulting ³¹P spectrum indicates that the major product peak resonates at δ 98 ppm (*J*_{PW} = 266 Hz), which matches that of the reaction carried out under previously discussed Suzuki–Miyaura conditions, with minor unidentified side products occurring at δ 35 and 78 ppm, respectively.

In an effort to better understand how these interactions affect free BOPs, reactions involving CsOH with a series of free BOP compounds were also examined. The experimental outcome for each case suggests oxidation of the P=C bond; a mixture of oxidized products was observed in the ³¹P spectra in the regions ranging from δ 0 to 25 ppm. As a representative case, the reaction of *p*-tolylBOP with CsOH demonstrates three dominant species in the resulting product that resonate at δ 27, 10, and 1 ppm, respectively. The compound mixture also revealed the presence of P–H coupling around δ 1 ppm (515 Hz) in the coupled ³¹P spectra, which is consistent with the presence of oxidized P(V) species. The crude mixture proved difficult to purify, and attempts to isolate and crystallize the products from these experiments were unsuccessful.

CONCLUSIONS

In summary, our results establish that BOPs are poor substrates for the catalytic Suzuki–Miyaura coupling reaction

under typical conditions. While the degree of delocalization in BOP is high, as shown by the NICS values and by the shape of the π -orbitals, the contribution of phosphorus is significant in particular in the HOMO, but also in the LUMO. Accordingly, μ_2 -P-complex formation with the Pd(0) catalyst complicates the reaction. Protection of the phosphorus lone pairs in BOPs by coordination with [W(CO)₅] also failed to effect carbon–carbon bond formation but instead led to addition of CsOH across the P=C bond, since the low-lying LUMO orbital (which is unaffected by the [W(CO)₅] coordination) facilitates the attack of the OH[−] group formed from the reactant boric acid derivative under the highly basic conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.1c00462>.

General information for syntheses and reactions, characterization data, NMR spectra, and computational details (PDF)

Cartesian coordinates for the calculated structures (TXT)

Accession Codes

CCDC 2077211–2077214 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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