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Experimental and Theoretical Study on Palladium-Catalyzed C−P Bond Formation via Direct Coupling of Triarylbismuths with P(O)−H Compounds

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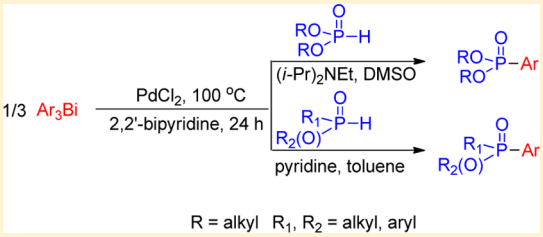
Supporting Information

ABSTRACT: A novel and highly efficient Pd-catalyzed cross-coupling of triarylbismuths with a variety of P(O)−H compounds has been developed that proceeds smoothly without exclusion of moisture or air and provides a general and powerful tool for the preparation of various valuable arylphosphonates, arylphosphinates, and arylphosphine oxides, with high atom-economy, operational simplicity of the procedure, and good to high yield. The coupling reaction is the first example of transition-metal-catalyzed C−P bond construction using triarylbismuth compounds as substrates. DFT calculations reveal that C−P bond formation is the rate-determing step.



INTRODUCTION

Organophosphorus compounds are an extremely important class of chemicals, which are widely used in biological, catalytic, pharmaceutical, and material sciences with desired properties.[1,2] In particular, arylphosphorus compounds such as arylphosphonates, arylphosphinates, and arylphosphine oxides have attracted considerable attention due to their prime application as ligands[3] in transition-metal-catalyzed reactions, as retardant materials,[4] and as valuable synthetic intermediates.[5] In the 1980s, Hirao and co-workers described the first examples of aryl and vinyl halide couplings with dialkyl phosphites under catalysis of Pd(0).[6] Following this, remarkable progress in the development of C_{sp2}−P bond formation by cross-coupling has been reported in the past decade, including the methods of nickel-,[7] copper-,[8] manganese-,[9] and palladium-catalyzed[10] direct activation of the P−H bond. However, most of these methods suffer from relatively strict reaction conditions or poor substrate scope, and there is still a strong need for preparation of arylphosphorus compounds from readily available starting materials.

The last two decades have witnessed rapid development of bismuth chemistry.[11] Organobismuth compounds are nontoxic and easily available building blocks among the heavy non-radioactive main group elements.[12] Undoubtedly, these attractive features of bismuth compounds occupy a special place in medicinal chemistry[13] and organic synthesis and catalysis.[14] For instance, trivalent organobismuth compounds, especially for triarylbismuth which could be easily obtainable according to the reported methods,[12a] were used efficiently in Pd-catalyzed C- and N-arylation reactions.[15] Notably, in some cases the transfer of all of the aryl groups from triarylbismuth was observed in these arylation reactions,[15a−g] in line with the Principles of Green Chemistry.[16] Recently, a number of experimental studies of transition-metal-catalyzed cross-coupling of organobismuth favored palladium catalysts,[15] such as $Pd(PPh_3)_4$ and $Pd(OAc)_2$. Since the C−Bi bond is weak,[17] it may easily add to Pd(0) species. To support our hypothesis, we first performed gas-phase density functional theory (DFT) calculations at the B3LYP/6-31+G(d)+LanL2DZ level (Table 1). The transition states (**TS**) appeared to be only 2.4 and 4.4 kcal/mol (free energy) relative to the corresponding model substrates **A**, respectively,[18] indicating that oxidative addition of organobismuth compounds to Pd(0) catalyst is a very facile step. Inspired by these results, our ongoing interests[7a,b,8a,19] in transition-metal-catalyzed C−P bond-forming reactions have led us to investigate a novel, atom-economical, operationally simple Pd-catalyzed cross-coupling reaction of triarylbismuths with P(O)−H compounds (Scheme 1). To the best of our knowledge, this method is the first example of transition-metal-catalyzed cross-coupling of triarylbismuths with P(O)−H compounds leading to arylphosphonates, arylphosphinates, and arylphosphine oxides.

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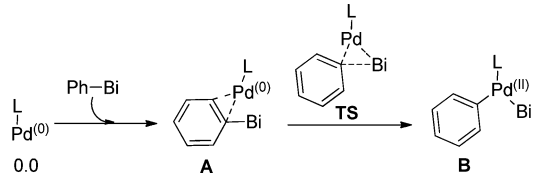
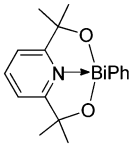
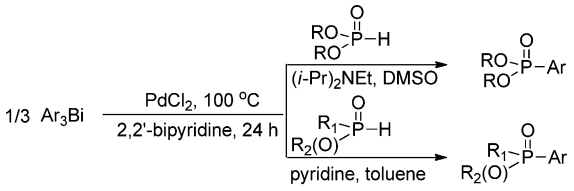
Table 1. Oxidative Addition of Various Organobismuth Compounds to Pd(0)PPh_3 (Free Energy Units: kcal/mol, L= PPh_3)



	A	TS	B	Barrier
Ph_2BiPh	-15.0	-12.6	-19.0	2.4
	-18.9	-14.5	-22.4	4.4

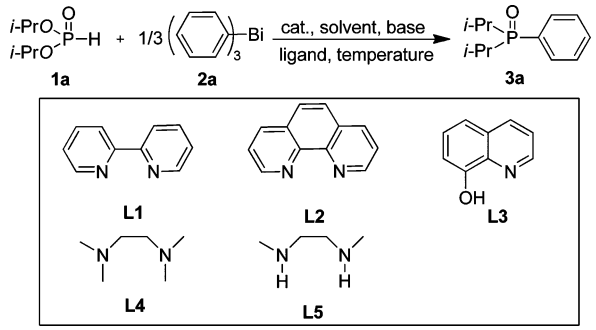
Scheme 1. Pd-Catalyzed Preparation of Arylphosphonates, Arylphosphinates, and Arylphosphine Oxides



RESULTS AND DISCUSSION

Based on our calculations, we selected the Pd-catalyzed cross-coupling reaction of diisopropyl phosphonate **1a** with triphenylbismuth **2a** as the standard reaction to optimize the catalysis conditions, as shown in Table 2. Taking into account atom efficiency,[20] we directly used 1/3 equiv of triphenylbismuth to start our study. Initially, when **1a** (0.2 mmol, 1 equiv, 33 mg) was added to a mixture of **2a** (0.067 mmol, 1/3 equiv, 29 mg), $Pd(PPh_3)_4$ (0.006 mmol, 7 mg), 2,2′-bipyridine (0.012 mmol, 2 mg), and pyridine (0.3 mmol, 0.024 mL) in toluene at 100 °C for 24 h under an air atmosphere, the desired P-arylation product **3a** was obtained in 29% yield determined by the ^{31}P NMR signal-integration method (Table 2, entry 1). Encouraged by this result, we further examined the effect of catalyst, solvent, ligand, temperature, and base on the reaction yield. Under similar reaction conditions, various transition-metal complexes including Pd, Ni, and Cu salts were examined, with the finding that palladium salts, especially $PdCl_2$, were the most effective catalyst to produce the desired product **3a** (Table 2, entries 1−3). In contrast, other metal salts such as $Ni(OAc)_2$, $NiCl_2$, CuI, and CuO did not or only sluggishly catalyze this reaction (Table 2, entries 4−7). The type of ligand was vital to the present catalytic reaction. 2,2′-Bipyridine (bpy) **L1** was found to be the best choice (Table 2, entries 3 and 8−11). Gratifyingly, further exploration suggested that a good 86% yield of **3a** was afforded when DMSO was employed as a solvent (Table 2, entry 12). Other solvents including DMF, CH_3CN, and 1,4-dioxane were less effective (Table 2, entries 13−15). We next turned our attention to further improve the yield of **3a** by investigating the effect of bases. Among the various bases screened, $(i\text{-Pr})_2NEt$ turned out to be the best

Table 2. Optimization of the Reaction Conditions[a]



entry	catalyst	ligand	solvent	base	yield[b] (%)
1	$Pd(PPh_3)_4$	**L1**	toluene	pyridine	29
2	$Pd(OAc)_2$	**L1**	toluene	pyridine	0
3	$PdCl_2$	**L1**	toluene	pyridine	37
4	$Ni(OAc)_2$	**L1**	toluene	pyridine	0
5	$NiCl_2$	**L1**	toluene	pyridine	0
6	CuI	**L1**	toluene	pyridine	25
7	CuO	**L1**	toluene	pyridine	0
8	$PdCl_2$	**L2**	toluene	pyridine	0
9	$PdCl_2$	**L3**	toluene	pyridine	0
10	$PdCl_2$	**L4**	toluene	pyridine	23
11	$PdCl_2$	**L5**	toluene	pyridine	0
12	$PdCl_2$	**L1**	DMSO	pyridine	86
13	$PdCl_2$	**L1**	DMF	pyridine	46
14	$PdCl_2$	**L1**	CH_3CN	pyridine	7
15	$PdCl_2$	**L1**	1,4-dioxane	pyridine	43
16	$PdCl_2$	**L1**	DMSO	Et_3N	83
17	$PdCl_2$	**L1**	DMSO	K_2CO_3	72
18	**$PdCl_2$**	**L1**	**DMSO**	**$(i\text{-Pr})_2NEt$**	**95 (80)**
19	$PdCl_2$	**L1**	DMSO	$(i\text{-Pr})_2NEt$	28[c]
20	$PdCl_2$	**L1**	DMSO	$(i\text{-Pr})_2NEt$	80[d]
21	$PdCl_2$	**L1**	DMSO	$(i\text{-Pr})_2NEt$	81 (71)[e]
22	**$PdCl_2$**	**L1**	**toluene**	**pyridine**	**98 (81)[e]**

[a]Reaction conditions: diisopropyl phosphonate (0.2 mmol), triphenylbismuth (0.067 mmol), catalyst (0.006 mmol), ligand (0.012 mmol), base (0.3 mmol), solvent (0.8 mL) at 100 °C for 24 h, under air. [b]Determined by ^{31}P NMR. Yields are based on **1a**. Yields in parentheses are isolated yields. [c]At 80 °C. [d]Under argon. [e]Using diphenylphosphine oxide (0.2 mmol).

base and promoted the coupling to provide **3a** in 95% yield (Table 2, entry 18), along with a trace of homocoupling product biphenyl.[15e] Other bases and corresponding yields of **3a** were as follows: pyridine, 86%; Et_3N, 83%; and K_2CO_3, 72% (Table 2, entries 12, 16, and 17). The choice of temperature also highly affected this reaction. The coupling did not occur at room temperature; however, the yield of product **3a** increased slowly when the temperature was raised to 80 °C (Table 2, entry 19), and the catalytic reaction proceeded quite well, affording the corresponding product **3a** in an excellent yield of 95% when the temperature was raised to 100 °C (Table 2, entry 18). In contrast to the yield of 95% under air, the coupling of diisopropyl phosphonate **1a** with triphenylbismuth **2a** gave a lower 80% NMR yield under an argon atmosphere, indicating that oxygen might be involved in the reaction process.

Under the optimized conditions shown in footnote a, Table 3, we next explored the cross-coupling of various H-phosphonate diesters with **2a** to understand the scope of the reaction. As shown in Table 3, in regard to the reactant, in

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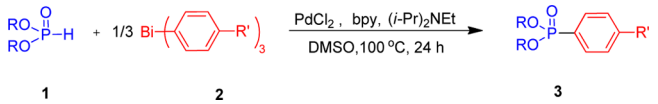
Table 3. Pd-Catalyzed Cross-Coupling of Triarylbismuth with Dialkyl H-Phosphite[a]



entry	1	2	3	yield (%)
1	*i*-PrO, *i*-PrO P(O)–H **1a**	Bi(C6H5)3 **2a**	*i*-PrO, *i*-PrO P(O)C6H5	**3a**	80
2	EtO, EtO P(O)–H **1b**	**2a**	EtO, EtO P(O)C6H5	**3b**	70
3	*n*-BuO, *n*-BuO P(O)–H **1c**	**2a**	*n*-BuO, *n*-BuO P(O)C6H5	**3c**	67
4	$H_3C(H_2C)_{11}O$, $H_3C(H_2C)_{11}O$ P(O)–H **1d**	**2a**	$H_3C(H_2C)_{11}O$, $H_3C(H_2C)_{11}O$ P(O)C6H5	**3d**	72
5	BnO, BnO P(O)–H **1e**	**2a**	BnO, BnO P(O)C6H5	**3e**	73
6	**1a**	Bi(C6H4F)3 **2b**	*i*-PrO, *i*-PrO P(O)C6H4F	**3f**	81
7	**1a**	Bi(C6H4C6H5)3 **2c**	*i*-PrO, *i*-PrO P(O)C6H4C6H5	**3g**	74

[a]Reaction conditions: P(O)–H (0.4 mmol), triarylbismuth (0.13 mmol), $PdCl_2$ (0.012 mmol), bpy (0.024 mmol), $(i\text{-Pr})_2NEt$ (0.6 mmol), DMSO (1 mL), 100 °C for 24 h, under air.

addition to diisopropyl (**1a**), diethyl (**1b**), dibutyl (**1c**), didodecyl (**1d**), and dibenzyl phosphonate (**1e**) all could be efficiently coupled with **2a** to afford the corresponding aryl phosphonates in good yields, demonstrating that this Pd-catalyzed coupling is a general and practically useful method for the synthesis of aryl phosphonates. It is particularly noteworthy that each phenyl group from triphenylbismuth can be involved in this transformation. For example, diethyl phosphonate and didodecyl phosphonate coupled with 1/3 equiv triphenylbismuth, giving the desired products in 70% and 72% yields, respectively (Table 3, entries 2 and 4). However, some reported carbon–heteroatom bond-forming reactions could not completely transfer the three aryl groups of triarylbismuth into the desired products.[15h] Tris(4-fluorophenyl)bismuth **2b** and tri([1,1′-biphenyl]-4-yl)bismuth **2c** as substrates were suitable for this protocol, and the corresponding products were obtained in 81% and 74% yields, respectively (Table 3, entries 6 and 7).

To gain more insight into the substrate scope of the reaction, various phosphine oxides and H-phosphinate as cross-coupling partners were investigated (Table 4). Initially, under the above optimized reaction conditions (footnote a, Table 3), the cross-coupling of diphenylphosphine oxide with triphenylbismuth using $(i\text{-Pr})_2NEt$ as a base in DMSO was performed and afforded only an 81% NMR yield (Table 2, entry 21). Gratifyingly, the cross-coupling of diphenylphosphine oxide with triphenylbismuth using pyridine as a base in toluene proceeded quite well, and the expected product **3g** was obtained in a quantitative yield (Table 2, entry 22). Thus, using pyridine as a base and toluene as a solvent as the standard conditions (footnote a, Table 4), we first surveyed the cross-coupling of various substituted triarylbismuths with diphenylphosphine oxide **1f** to understand the scope of the organobismuth source. As demonstrated in Table 4, a variety of arylphosphine oxides could be conveniently and efficiently afforded by this novel Pd-catalyzed cross-coupling of triarylbismuth with diphenylphosphine oxide (Table 4, entries 1–6). In general, various functional groups were well tolerated, and the desired coupling products were obtained in moderate to good yields. Noting that triarylbismuth with the electron-rich substituents (Table 4, entries 2 and 3) such as *o*-Me and *p*-OMe gave lower yields than those with electron-deficient substituents such as *p*-F, *p*-Cl and *p*-CF_3 (Table 4, entries 4–6). Both tri(naphthalen-1-yl)bismuth **2h** and tri([1,1′-biphenyl]-4-yl)bismuth **2c** were also found to be suitable reaction partners with high yields (Table 4, entries 7 and 8), clearly indicating that steric hindrance was not evident in this reaction. In regard to aromatic secondary phosphine oxides, in addition to **1f**,**g** with an electron-donating MeO group on the benzene ring also could be used as the substrate, generating the corresponding products in good yields (Table 4, entries 9 and 10). It is noteworthy that H-phosphinate **1h** (Table 4, entries 11 and 12) and secondary phosphine oxides **1i** (Table 4, entries 13 and 14) also reacted well with triarylbismuth, affording the corresponding alkyl diarylphosphinates and alkyl diarylphosphine oxides in moderate to good yields. Moreover, heterocycle-substituted

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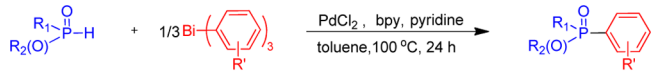
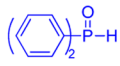
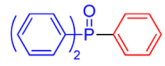
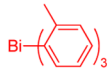
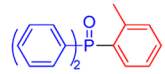
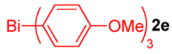
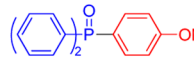
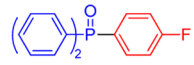
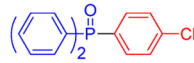
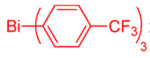
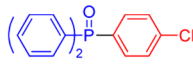
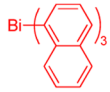
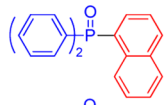
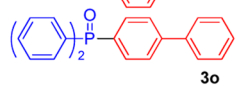
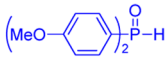
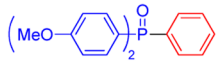
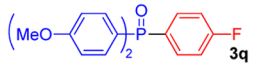
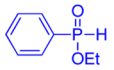
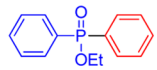
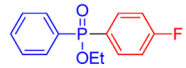
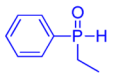
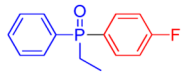
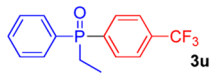
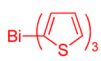
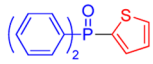
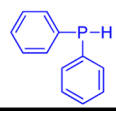
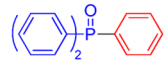
Table 4. Pd-Catalyzed Cross-Coupling of Triarylbismuths with P(O)−H Compounds[a]



1 2 3

entry	1	2	3	yield (%)
1	 1f	2a	 3h	81
2	1f	 2d	 3i	67
3	1f	 2e	 3j	60
4	1f	2b	 3k	81
5	1f	 2f	 3l	83
6	1f	 2g	 3m	88
7	1f	 2h	 3n	87
8	1f	2c	 3o	85
9	 1g	2a	 3p	79
10	1g	2b	 3q	84
11	 1h	2a	 3r	83
12	1h	2b	 3s	80
13	 1i	2b	 3t	68
14	1i	2g	 3u	63
15	1f	 2i	 3v	63
16	 1j	2a	 3h	86

[a]Reaction conditions: P(O)−H (0.4 mmol), triarylbismuth (0.13 mmol), $PdCl_2$ (0.012 mmol), bpy (0.024 mmol), pyridine (0.6 mmol), toluene (1 mL), 100 °C for 24 h, under air.

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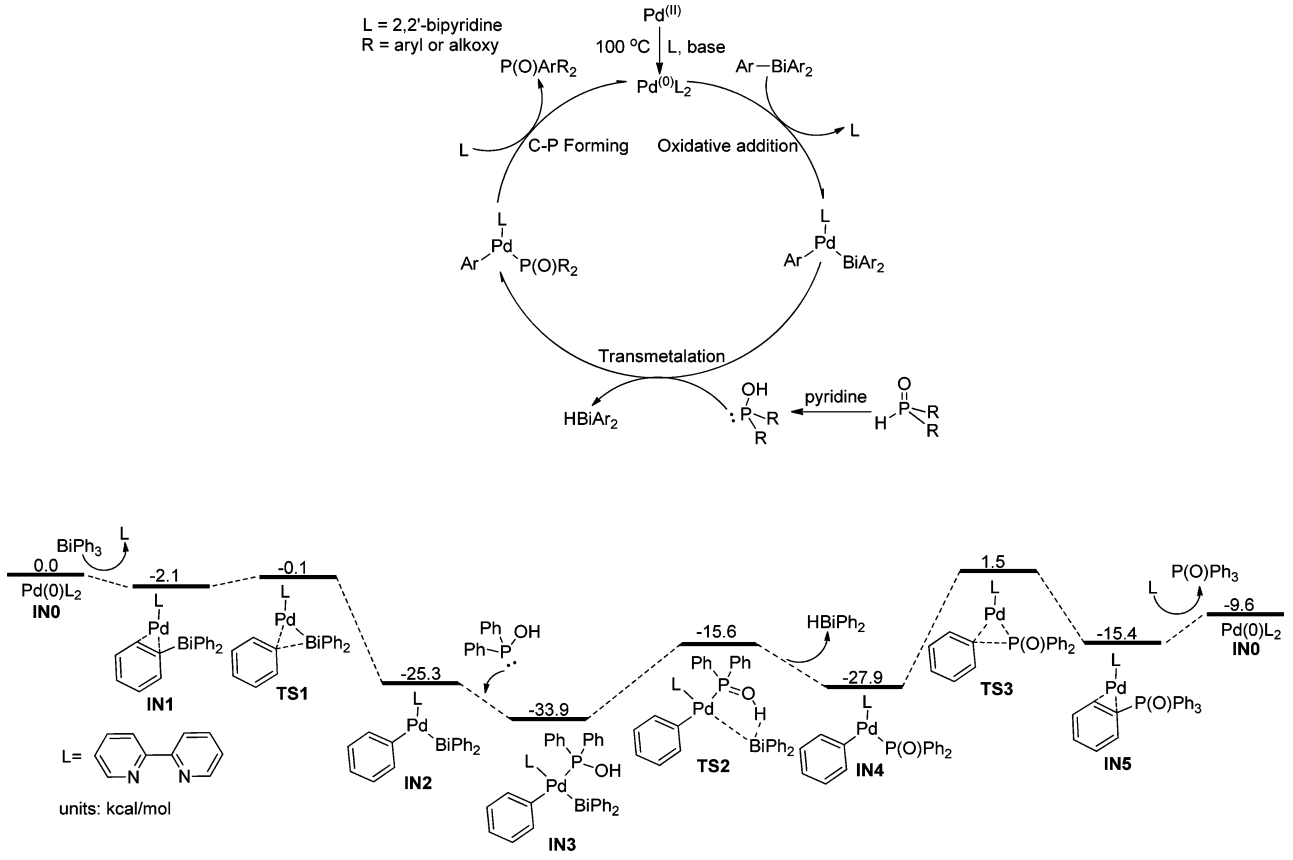

Figure 1. Mechanistic studies.

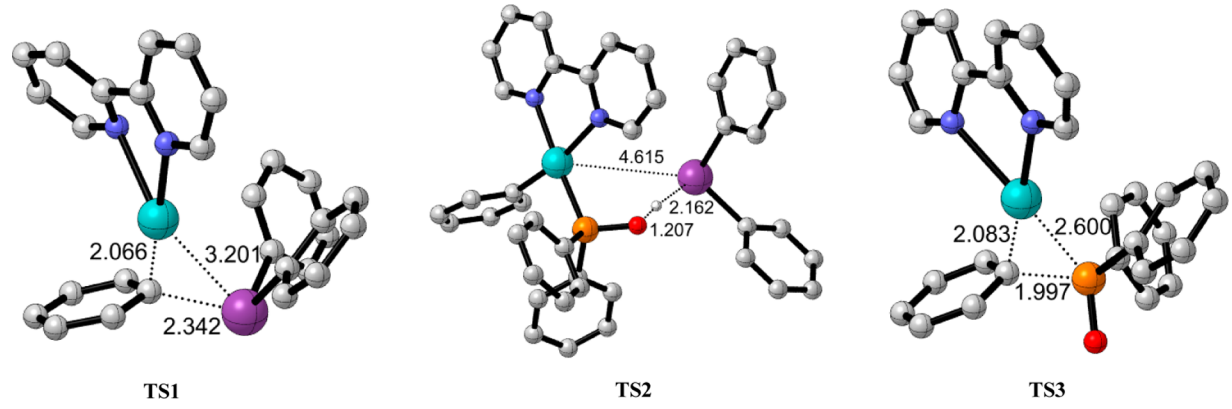

Figure 2. Structure of located transition states.[28]

triarylbismuth could also be used as the substrate to give **3v** in a 63% yield (Table 4, entry 15). Interestingly, diphenylphosphine could also be used in this coupling reaction to afford the desired product **3h** in high yield (Table 4, entry 16, 86%), without observing the generation of triphenylphosphine, and the reaction process might involve the cross-coupling of diphenylphosphine with **2a** and oxidation of triphenylphosphine to triphenylphosphine oxide by air under the catalysis of Pd(0).[21] Notably, this Pd-catalyzed coupling reaction proceeded smoothly without exclusion of moisture or air.

Transition-metal-catalyzed C−P bond-forming reactions involving a variety of substrates have been studied computationally by some groups.[22] The commonly acceptable mechanism involves three basic steps: oxidative addition, transmetalation, and reductive elimination. Based on the previous palladium-catalyzed cross-coupling reaction mechanisms,[23] we report a possible mechanism of the Pd-catalyzed cross-coupling of triarylbismuths with P(O)−H compounds and the first theoretical study of the catalytic cycles using (DFT) (Figure 1). The model substrates triphenylbismuth, diphenylphosphine oxide, and catalyst Pd(0)(bpy)$_2$ (**IN0**) were chosen. Relative free energies in solution are employed to analyze the reaction mechanism. Initially, the catalyst precursor $PdCl_2$ was reduced in the presence of base at elevated temperature, resulting in the generation of the active catalytic species Pd(0).[15e] The approach of $BiPh_3$ toward **IN0** leads to the formation of an η^2 complex **IN1** by removal of one bpy ligand. From **IN1** a three-centered transition state **TS1** (Figure 2, left) is located for the oxidative addition. Not surprisingly, the activation barrier from **IN0** to **TS1** is only 2.0 kcal/mol,

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indicating that oxidative addition is not energy-demanding. The product of oxidative addition is a tetracoordinated Pd(II) intermediate **IN2** (−25.3 kcal/mol relative to **IN0**). The transmetalation step takes place when diphenylphosphine oxide via the form of the hydroxydiphenylphosphine[24,25] coordinates to **IN2**, giving a four-coordinated Pd(II) intermediate **IN3** with a negative energy of −8.6 kcal/mol, where the bpy uses only one nitrogen atom to coordinate to the Pd(II) center. Subsequently, a very late transition state **TS2** (Figure 2, middle) is identified with an activation barrier of +18.3 kcal/mol, concomitant with the hydrogen migrating from O to Bi centers and the cleavage of Pd−Bi bond. After the removal of neutral Ph_2BiH species,[26] a square planar Pd(II) intermediate **IN4** is formed exergonically. Noting that Ph_2BiH might disproportionate to Ph_3Bi and BiH_3[26] which could involve in next catalytic cycle and be oxidized by air to provide Bi−O compounds, respectively.[26] Next, the reductive elimination of **IN4** proceeds through a three-centered transition state **TS3** (Figure 2, right).[23] In **TS3**, the bond lengths of C−P, Pd−C, and Pd−P are 1.997, 2.083, and 2.600 Å, respectively. The free energy of **TS3** is +29.4 kcal/mol higher than that of **IN4**, illustrating that the reductive elimination is a rate-limiting step for the overall catalytic cycle, in line with the experimental observation that this Pd(II)-catalyzed reaction was carried out at 100 °C.[23,27] Finally, the C−P bond formation and ligand exchange give the desired product and complete the catalytic cycle by regenerating **IN0** as a catalytically active species.

CONCLUSION

In summary, we first developed the cross-coupling reaction of readily available P(O)−H compounds with various triarylbismuths leading to versatile arylphosphorus compounds including arylphosphonates, arylphosphinates, and arylphosphine oxides. This coupling has many notable features, such as: (i) triarylbismuths act as nontoxic, nonradioactive and atom-efficient coupling reagents; (ii) 1 equiv of triarylbismuths gives 3 equiv of coupling products; (iii) the reaction is tolerant of moisture and air; (iv) various valuable products can be conveniently obtained using the simply operating procedure; (v) DFT calculations provide key insight into the mechanism of Pd-catalyzed C−Bi bond cleavage to C−P functionalization and open a new avenue to the design of efficient catalysts. Further mechanistic details and synthetic applications in the construction of bioactive molecule, valuable ligands, and advanced materials are currently underway.

COMPUTATIONAL METHODS

The calculations were performed with the Gaussian 03 programs.[29] The gas-phase geometries of all compounds were optimized without any constraint by the density functional theory (DFT) method B3LYP.[30] The 6-31+G(d)[31] basis set was used for C, H, N, and O. Pd, Bi, and P atoms were described by the effective core potentials of Hay and Wadt with a valence double-ζ basis set (LANL2DZ).[32] Polarization functions were added for Pd (ξ_f =1.472), Bi (ξ_d = 0.202) and P (ξ_d = 0.387) to the standard LanL2DZ basis set.[33] Frequency analysis was performed after optimization to verify the minima and transition states. Transition states were examined by vibrational analysis and then submitted to intrinsic reaction coordinate (IRC)[34] calculations to determine two corresponding minima. The results from these IRC calculations are provided in the Supporting Information. For compounds that had multiple conformations, efforts were made to find the lowest energy conformation by comparing the structures optimized from different starting geometries. To calculate the single-point electronic energies in solution, the B3LYP method with a mixed basis set employing 6-311++G(2d,p)[35] for C, H, N, O, P, and SDD[36] for Ni and Bi were used. The default self-consistent reaction field (SCRF) polarizable continuum model (PCM) was used with toluene as solvent (dielectric constant ε = 2.3741), while Bondi radii[37] were chosen as the atomic radii to define the molecular cavity. The gas-phase geometry was used for all of the solution phase calculations. The dispersion correction calculations using the corresponding B3LYP-D functional were performed with the DFT-D3 program of Grimme.[38] The Gibbs energy corrections from frequency calculations and dispersion corrections were added to the single-point energies to obtain the Gibbs energies in solution. All the solution-phase free energies reported in the paper correspond to the reference state of 1 mol/L, 298 K.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of 3a−f. For **3a−f**: P(O)−H (0.4 mmol, 1 equiv) was added to a mixture of $PdCl_2$ (0.012 mmol, 0.03 equiv, 2 mg), 2,2′-bipyridine (bpy) (0.024 mmol, 0.06 equiv, 4 mg), *N*,*N*-diisopropylethylamine (0.6 mmol, 1.5 equiv, 0.10 mL), and Ar_3Bi (0.13 mmol, 0.33 equiv) in commercial dimethyl sulfoxide (1 mL) in a Schlenk tube and stirred at 100 °C for 24 h in an air atmosphere. The resulting mixture was cooled and then concentrated under vacuum, and the crude product was purified by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent.

General Procedure for the Synthesis of 3g−u. For **3g−u**: P(O)−H (0.4 mmol, 1 equiv) was added to a mixture of $PdCl_2$ (0.012 mmol, 0.03 equiv, 2 mg), 2,2′-bipyridine (bpy) (0.024 mmol, 0.06 equiv, 4 mg), pyridine (0.6 mmol, 1.5 equiv, 0.048 mL), and Ar_3Bi (0.13 mmol, 0.33 equiv) in toluene (1 mL) in a Schlenk tube and stirred at 100 °C for 24 h in an air atmosphere. The resulting mixture was cooled and then concentrated under vacuum, and the crude product was purified by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent.

Diisopropyl phenylphosphonate (**3a**, CAS No.: 7237-16-3): light yellow oil; 77 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.78 (m, 2H), 7.54−7.50 (m, 1H), 7.46−7.41 (m, 2H), 4.73−4.64 (m, 2H), 1.36 (d, J = 6.2 Hz, 6H), 1.22 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0 (d, J = 2.2 Hz), 131.7 (d, J = 9.5 Hz), 130.0 (d, J = 189.2 Hz), 128.2 (d, J = 14.7 Hz), 70.6 (d, J = 5.9 Hz), 24.0 (d, J = 4.4 Hz), 23.8 (d, J = 5.1 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 16.3; ESI-MS $[M + Na]^+$ m/z for $C_{12}H_{19}O_3PNa^+$ 264.6.

Diethyl phenylphosphonate (**3b**, CAS No.: 1754-49-0): colorless oil; 60 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.78 (m, 2H), 7.57−7.52 (m, 1H), 7.48−7.43 (m, 2H), 4.18−4.04 (m, 4H), 1.32 (t, J = 7.14 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3 (d, J = 3.6 Hz), 131.7 (d, J = 10.3 Hz), 128.4 (d, J = 14.7 Hz), 128.3 (d, J = 188.5 Hz), 62.0 (d, J = 5.1 Hz), 16.3 (d, J = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.9; ESI-MS $[M + Na]^+$ m/z for $C_{10}H_{15}O_3PNa^+$ 237.2.

Dibutyl phenylphosphonate (**3c**, CAS No.: 1024-34-6): light yellow oil; 72 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.77 (m, 2H), 7.57−7.52 (m, 1H), 7.48−7.43 (m, 2H), 4.11−3.96 (m, 4H), 1.68−1.61 (quint, J = 7.1 Hz, 4H), 1.43−1.34 (sext, J = 7.4 Hz, 4H), 0.90 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2 (d, J = 2.88 Hz), 131.7 (d, J = 9.7 Hz), 128.4 (d, J = 15.0 Hz), 128.3 (d, J = 188.3 Hz), 65.7 (d, J = 5.7 Hz), 32.4 (d, J = 6.4 Hz), 18.7, 13.5. ;^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.0; ESI-MS $[M + Na]^+$ m/z for $C_{14}H_{23}O_3PNa^+$ 293.1.

Didodecyl phenylphosphonate (**3d**, CAS No.: 82594-76-1): light yellow oil; 142 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.78 (m, 2H), 7.57−7.53 (m, 1H), 7.49−7.45 (m, 2H), 4.11−3.96 (m, 4H), 1.67 (m, 4H), 1.36−1.25 (m, 36H), 0.89 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1 (d, J = 3.7 Hz), 136.0, 133.6 (d, J = 17.8 Hz), 133.3, 132.2, 131.9 (d, J = 2.2 Hz), 131.3 (d, J = 10.0 Hz), 129.0 (d, J = 14.7 Hz), 128.6 (d, J = 12.2 Hz), 120.1 (d, J = 103.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 24.2; ESI-MS $[M + Na]^+$ m/z for $C_{30}H_{55}O_3PNa^+$ 517.4.

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Dibenzyl phenylphosphonate (**3e**, CAS No.: 19236-61-4): light yellow oil; 98 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.82 (m, 2H), 7.58−7.54 (m, 1H), 7.49−7.44 (m, 2H), 7.38−7.31 (m, 10H), 5.16−5.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1 (d, J = 6.8 Hz), 132.5, 131.8 (d, J = 10.1 Hz), 128.5, 128.3 (d, J = 15.2 Hz), 128.2, 127.8 (d, J = 189.7 Hz), 126.9, 67.5 (d, J = 5.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.6; ESI-MS $[M + Na]^+$ m/z for $C_{20}H_{19}O_3PNa^+$ 361.1.

Diisopropyl (4-fluorophenyl)phosphonate (**3f**, new compound): yellow oil; 84 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.77 (m, 2H), 7.15−7.09 (m, 2H), 4.71−4.63 (m, 2H), 1.36 (d, J = 6.2 Hz, 6 H), 1.21 (d, J = 6.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (dd, J = 252.9 Hz, 3.8 Hz), 134.2 (dd, J = 11.4 Hz, 8.8 Hz), 126.1 (dd, J = 193.4 Hz, 3.3 Hz), 115.5 (dd, J = 21.4 Hz, 16.3 Hz), 70.8 (d, J = 5.6 Hz), 24.0 (d, J = 4.1 Hz), 23.7 (d, J = 4.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 15.5; HR-ESI-MS $[M + H]^+$ m/z calcd for $C_{12}H_{18}O_3FPH^+$ 261.1056, found 261.1055. Anal. Calcd for $C_{12}H_{18}O_3FP$: C, 55.38; H, 6.97. Found: C, 55.60; H, 7.01.

Diisopropyl biphenyl-4-ylphosphonate (**3g**, new compound): colorless oil; 94 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.87 (m, 2H), 7.70−7.61 (m, 2H), 7.62−7.61 (m, 2H), 7.48−7.45 (m, 2H), 7.41−7.37 (m, 1H), 4.77−4.69 (m, 2H), 1.40 (d, J = 6.1 Hz, 6H), 1.27 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8 (d, J = 3.1 Hz), 140.0, 132.2 (d, J = 10.2 Hz), 128.8, 128.6 (d, J = 190.2 Hz), 128.0, 127.2, 126.9 (d, J = 15.2 Hz), 70.7 (d, J = 5.6 Hz), 24.0 (d, J = 3.8 Hz), 23.8 (d, J = 4.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 16.1; HR-ESI-MS $[M + H]^+$ m/z calcd for $C_{18}H_{23}O_3PH^+$ 319.1463, found 319.1465. Anal. Calcd for $C_{18}H_{23}O_3P$: C, 67.91; H, 7.28. Found: C, 68.04; H, 7.25.

Triphenylphosphine oxide (**3h**, CAS No.: 791-28-6): white solid; 90 mg; 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.66 (m, 6H), 7.57−7.53 (m, 3H), 7.49−7.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (d, J = 104.1 Hz), 132.1 (d, J = 9.9 Hz), 131.9 (d, J = 2.7 Hz), 128.5 (d, J = 12.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.1; ESI-MS $[M + Na]^+$ m/z for $C_{18}H_{15}OPNa^+$ 301.1.

(*o*-Tolyl)diphenylphosphine oxide (**3i**, CAS No.: 6840-26-2): light yellow solid; 78 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.64 (m, 4H), 7.58−7.54 (m, 2H), 7.50−7.41 (m, 5H), 7.31−7.28 (m, 1H), 7.16−7.01 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3 (d, J = 8.1 Hz), 133.4 (d, J = 12.5 Hz), 132.7 (d, J = 103.4 Hz), 132.1 (d, J = 2.1 Hz), 131.9 (d, J = 10.3 Hz), 131.7 (d, J = 2.9 Hz), 130.7 (d, J = 103.4 Hz), 128.5 (d, J = 11.7 Hz), 125.1 (d, J = 12.5 Hz), 21.6 (d, J = 4.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 32.0; ESI-MS $[M + Na]^+$ m/z for $C_{19}H_{17}OPNa^+$: 315.2.

(*p*-Methoxyphenyl)diphenylphosphine oxide (**3j**, CAS No.: 795-44-8): yellow oil; 74 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.62 (m, 4H), 7.60−7.55(m, 2H), 7.53−7.49 (m, 2H), 7.45−7.41 (m, 4H), 6.97−6.94 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 2.8 Hz), 133.8 (d, J = 11.2 Hz), 132.8 (d, J = 104.5 Hz), 131.9 (d, J = 10.0 Hz), 131.7 (d, J = 2.7 Hz), 128.3 (d, J = 12.2 Hz), 123.4 (d, J = 100.4 Hz). 114.0 (d, J = 13.2 Hz), 113.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.1; ESI-MS $[M + Na]^+$ m/z for $C_{19}H_{17}O_2PNa^+$ 331.1.

(*p*-Fluorophenyl)diphenylphosphine oxide (**3k**, CAS No.: 18437-73-5): white solid; 96 mg; 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.65 (m, 6H), 7.59−7.55 (m, 2H), 7.51−7.46 (m, 4H), 7.19−7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (d, J = 256.7 Hz), 134.6 (d, J = 20.5 Hz), 134.5 (d, J = 2.9 Hz), 132.4 (d, J = 104.9 Hz), 132.0 (d, J = 9.8 Hz), 128.6 (d, J = 106.5 Hz), 128.5 (d, J = 12.5 Hz), 115.9 (dd, J = 21.4 Hz, 13.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.4; ESI-MS $[M + Na]^+$ m/z for $C_{18}H_{14}OFPNa^+$ 319.0.

(*p*-Chlorophenyl)diphenylphosphine oxide (**3l**, CAS No.: 34303-18-9): white solid; 103 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.63 (m, 5H), 7.61−7.54 (m, 4H), 7.49−7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5 (d, J = 3.2 Hz), 133.4 (d, J = 10.7 Hz), 132.1 (d, J = 2.7 Hz), 132.0 (d, J = 104.9 Hz), 131.9 (d, J = 9.7 Hz), 131.1 (d, J = 104.7 Hz), 128.8 (d, J = 12.6 Hz), 128.5 (d, J = 12.1 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 28.5; ESI-MS $[M + Na]^+$ m/z for $C_{18}H_{14}OClPNa^+$ 335.0.

(4-(Trifluoromethyl)phenyl)diphenylphosphine oxide (**3m**, CAS No.: 374674-98-3): light yellow oil; 122 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.80 (m, 2H), 7.73−7.64 (m, 4H), 7.59−7.55 (m, 2H), 7.51−7.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2 (d, J = 101.1 Hz), 133.6 (d, J = 35.4 Hz), 132.5 (d, J = 10.3 Hz), 132.3 (d, J = 2.9 Hz), 131.9 (d, J = 9.9 Hz), 131.6 (d, J = 104.9 Hz), 128.6 (d, J = 12.3 Hz), 125.3−125.1 (m), 123.5 (d, J = 272.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 27.9; ESI-MS $[M + H]^+$ m/z for $C_{19}H_{14}OF_3PH^+$ 347.1.

1-Naphthyldiphenylphosphine oxide (**3n**, CAS No.: 3095-33-8): white solid; 114 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.71−7.67 (m, 4H), 7.52−7.47 (m, 2H), 7.45−7.40 (m, 6H), 7.39−7.35 (m, 1H), 7.34−7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 133.6 (d, J = 11.9 Hz), 133.5, 133.4, 133.3 (d, J = 9.9 Hz), 131.8, 128.6, 128.4 (d, J = 12.3 Hz), 127.4 (d, J = 5.7 Hz), 126.7, 124.0, 123.9 (d, J = 14.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 32.4; ESI-MS $[M + Na]^+$ m/z for $C_{22}H_{17}OPNa^+$ 351.1.

(4-Biphenylyl)diphenylphosphine oxide (**3o**, CAS No.: 1942-83-2): white solid; 120 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.67 (m, 8H), 7.61−7.58 (m, 2H), 7.57−7.52 (m, 2H), 7.49−7.42 (m, 6H), 7.39−7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (d, J = 2.9 Hz), 139.7, 133.0, 132.4 (d, J = 10.2 Hz), 132.0, 131.9, 131.8 (d, J = 2.9 Hz), 131.0 (d, J = 104.9 Hz), 128.8, 128.4 (d, J = 12.5 Hz), 127.5 (d, J = 107.1 Hz), 127.1; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 28.9; ESI-MS $[M + Na]^+$ m/z for $C_{24}H_{19}OPNa^+$ 377.1.

Bis(4-methoxyphenyl)phenylphosphine oxide (**3p**, CAS No.: 799-55-3): light yellow oil; 107 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.59 (m, 2H), 7.56−7.51 (m, 4H), 7.47−7.43 (m, 1H), 7.42−7.35 (m, 2H), 6.97−6.85 (dd, J = 8.8 Hz, 2.0 Hz 4H), 3.76 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J = 2.7 Hz), 133.6 (d, J = 11.2 Hz), 132.1 (d, J = 106.3 Hz), 131.7 (d, J = 10.0 Hz), 131.4 (d, J = 2.2 Hz), 128.1 (d, J = 12.1 Hz), 123.7 (d, J = 110.7 Hz), 113.8 (d, J = 13.2 Hz), 55.1; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 28.8; ESI-MS $[M + Na]^+$ m/z for $C_{20}H_{19}O_3PNa^+$ 361.1.

(4-fluorophenyl)bis(4-methoxyphenyl)phosphine oxide (**3q**, CAS No.: 302595-04-6): light yellow oil; 119 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.62 (m, 2H), 7.59−7.53 (m, 4H), 7.16−7.11 (m, 2H), 6.98−6.95 (m, 4H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9 (d, J = 253.0 Hz), 162.5 (d, J = 2.8 Hz), 134.5 (d, J = 2.4 Hz), 134.4 (d, J = 20.0 Hz), 133.8 (d, J = 11.2 Hz), 123.8 (d, J = 111.7 Hz), 115.7 (dd, J = 21.3 Hz, 13.2 Hz), 114.1 (d, J = 13.3 Hz), 55.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 28.2; ESI-MS $[M + Na]^+$ m/z for $C_{20}H_{18}O_3FPNa^+$ 379.1.

Ethyl diphenylphosphinate (**3r**, CAS No.: 1733-55-7): light yellow oil; 82 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.76 (m, 4H), 7.48−7.44 (m, 2H), 7.42−7.37 (m, 4H), 4.11−4.03 (m, 2H), 1.32 (t, J = 7.1 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.9 (d, J = 2.4 Hz), 131.5 (d, J = 137.0 Hz), 131.4 (d, J = 10.2 Hz), 128.3 (d, J = 13.1 Hz), 60.9 (d, J = 5.9 Hz), 16.3 (d, J = 6.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 31.4; ESI-MS $[M + H]^+$ m/z for $C_{14}H_{15}O_2PH^+$ 247.1.

(4-Fluorophenyl)ethyl phenyl phosphinate (**3s**, new compound): light yellow oil; 84 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.78 (m, 4H), 7.56−7.52 (m, 1H), 7.49−7.45 (m, 2H), 7.18−7.12 (m, 2H), 4.16−4.09 (m, 2H), 1.39 (t, J = 7.0 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2 (d, J = 250.2 Hz), 134.2 (d, J = 2.9 Hz), 134.1 (d, J = 20.6 Hz), 132.2 (d, J = 2.6 Hz), 131.6 (d, J = 10.2 Hz), 131.5 (d, J = 138.4 Hz), 128.6 (d, J = 13.2 Hz), 115.9 (dd, J = 21.4 Hz, 14.3 Hz), 61.2 (d, J = 5.8 Hz), 16.4 (d, J = 6.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 30.5; HR-ESI-MS $[M + Na]^+$ m/z calcd for $C_{14}H_{14}O_2FPNa^+$ 287.06077, found 287.06078. Anal. Calcd for $C_{14}H_{14}O_2FP$: C, 63.64; H, 5.34. Found: C, 63.70; H, 5.35.

(4-Fuorophenyl)ethyl phenylphosphine oxide (**3t**, new compound): colorless oil; 67 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.71 (m, 4H), 7.57−7.47 (m, 3H), 7.20−7.15 (m, 2H), 2.33−2.24 (m, 2H), 1.27−1.17 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9 (d, J = 249.5 Hz), 133.4, 133.3 (d, J = 19.1 Hz), 132.1, 131.9 (d, J = 3.0 Hz), 130.8 (d, J = 9.1 Hz), 128.7 (d, J = 11.7 Hz), 116.0 (dd, J = 21.4 Hz, 12.5 Hz), 22.8 (d, J = 73.7 Hz), 5.5 (d, J = 5.1 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 33.7; HR-ESI-MS $[M + Na]^+$ m/z calcd for

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$C_{14}H_{14}OFPNa^+$ 271.06585, found 271.06532. Anal. Calcd for $C_{14}H_{14}O_2FP$: C, 67.74; H, 5.68. Found: C, 69.94; H, 5.65.

(4-(Trifluoromethyl)phenyl)ethylphenylphosphine oxide (**3u**, new compound): colorless oil; 75 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.87 (m, 2H), 7.78−7.73 (m, 4H), 7.59−7.49 (m, 3H), 2.38−2.29 (m, 2H), 1.27−1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9 (d, J = 37.3 Hz), 137.5 (d, J = 93.8 Hz), 133.5 (d, J = 32.7 Hz, 2.8 Hz), 132.1 (d, J = 2.5 Hz), 131.9 (d, J = 99.0 Hz), 131.3 (d, J = 9.5 Hz), 130.8 (d, J = 9.4 Hz), 128.9 (d, J = 11.6 Hz), 125.5−125.3 (m), 22.5 (d, J = 73.3 Hz), 5.4 (d, J = 5.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 27.9; HR-ESI-MS $[M + Na]^+$ m/z calcd for $C_{15}H_{14}OF_3PNa^+$ 321.06266, found 321.06283. Anal. Calcd for $C_{15}H_{14}OF_3P$: C, 60.41; H, 4.73. Found: C, 60.53; H, 4.75.

2-Thienyldiphenylphosphine oxide (**3v**, CAS No.: 56966-27-9); colorless oil; 72 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.73 (m, 4H), 7.72−7.71 (m, 1H), 7.58−7.53 (m, 1H), 7.49−7.45 (m, 6H), 4.32−4.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9 (d, J = 10.0 Hz), 133.9 (d, J = 5.0 Hz), 133.8 (d, J = 112.2 Hz), 132.8 (d, J = 110.0 Hz), 132.1 (d, J = 2.6 Hz), 131.7 (d, J = 10.3 Hz), 128.4 (d, J = 12.7 Hz), 128.2 (d, J = 13.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 21.8; ESI-MS $[M + H]^+$ m/z for $C_{16}H_{13}OSPH^+$ 285.0.

Triphenylphosphine oxide (3h, CAS No.: 791-28-6): white solid; 96 mg; 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.65 (m, 6H), 7.56−7.51 (m, 3H), 7.48−7.43 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0, 132.0 (d, J = 10.0 Hz), 131.8 (d, J = 2.5 Hz), 128.4 (d, J = 12.1 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.1; ESI-MS $[M + Na]^+$ m/z for $C_{18}H_{15}OPNa^+$ 301.1.

■ ASSOCIATED CONTENT

Supporting Information

The Cartesian coordinates and 3D structures for the optimized structures. ^{1}H, ^{31}P, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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