P Ligands

Synthesis and Application of 2,6-Bis(trifluoromethyl)-4-pyridyl Phosphanes: The Most Electron-Poor Aryl Phosphanes with Moderate Bulkiness**

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In transition-metal catalysis, PPh₃ and more electron-rich tertiary phosphanes are popular ligands for controlling catalytic activity and selectivity. In contrast, efficient catalysts using highly electron-poor phosphanes,[1] such as $P(C_6F_5)_3$, have rarely been reported. However, in recent years this phosphane has been used as an effective ligand, particularly in gold[2] or iridium[3] catalysts. Furthermore, a prominent ligand-acceleration effect (LAE) by a highly electron-poor phosphane has been shown in some cases. Recently, we demonstrated that the Rh/MeO-F_{12}-biphep[4] catalyst showed a remarkably high turnover frequency (TOF = 53 000 h^{-1}) and turnover number (TON = 320 000) with 98% *ee* in asymmetric 1,4-addition.[5] These high values are inherently due to the electronic effect of highly electron-poor MeO-F_{12}-biphep. Although introduction of perfluoroaromatics into the diphosphane produced a more electron-poor ligand, MeO-F_{28}-biphep bearing 4-CF$_3$C$_6$F$_4$ groups showed only a low LAE.[5b] The low effect is attributed to the insufficient complexation of MeO-F_{28}-biphep with Rh for steric reasons. The *ortho*-fluorine atoms in the PAr moiety significantly increase the cone angle[6] and further destabilize the metal–phosphorus bond, which is inherently weakened by the electron-deficient P atom.[7] This destabilization often had resulted in severe catalyst instability to give lower catalytic activity when aryl phosphanes bearing perfluoroaromatics such as $P(C_6F_5)_3$ were used.[8] These critical problems reduce the utility value of a highly electron-poor phosphane ligand, although it is potentially useful by virtue of its electronic properties.[2,3,9] To overcome this drawback, we designed and developed a novel type of phosphane ligand that has both low σ-donating ability, like $P(C_6F_5)_3$, and moderate bulkiness, like PPh₃, to facilitate practical complexation with a metal catalyst.

As an appropriate candidate for the aryl group of the phosphane, we chose the 2,6-bis(trifluoromethyl)-4-pyridyl (BFPy) group (Figure 1). The Taft's σ* value[10] of the BFPy group[11] is larger than those of the C₆F₅ or 4-CF₃C₆F₄ groups, thus indicating that the BFPy group is the most powerful
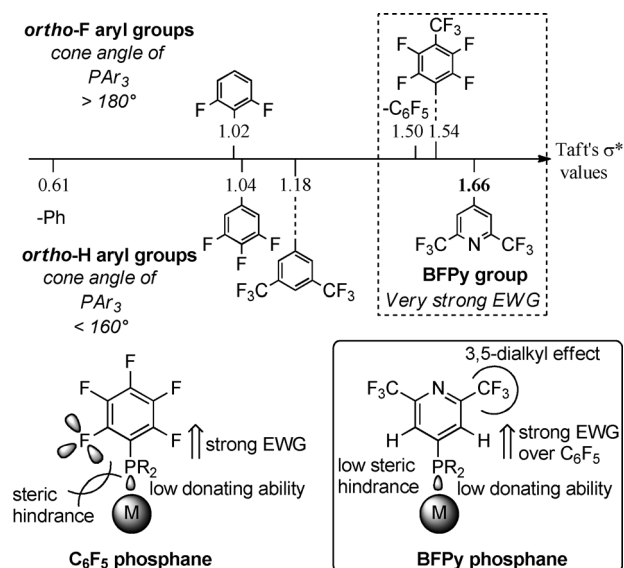

Figure 1. Concept of BFPy phosphane.

electron-withdrawing group (EWG) among aromatic groups. The structure of the BFPy group, which has no *ortho*-fluorine atoms, is analogous to that of the 3,5-(CF₃)₂C₆H₃ group. The ligand P{3,5-(CF₃)₂C₆H₃}₃ shows a cone angle similar to that of PPh₃ (160° vs. 155° as determined by Howell et al.),[12] thus suggesting that the steric bulkiness of P(BFPy)₃ is similar to that of PPh₃ and smaller than that of $P(C_6F_5)_3$, the cone angle of which is considerably larger than that of PPh₃ (184° vs. 145° as determined by Tolman).[13] Although BFPy phosphane will show lower σ-donating ability than C₆F₅ or 4-CF₃C₆F₄ phosphanes, its moderate bulkiness will facilitate its complexation with the metal catalyst (Figure 1). Furthermore, the *meta*-CF₃ groups in BFPy phosphane assure the 3,5-dialkyl effect.[14] Because these BFPy phosphorous compounds have not been known so far, we attempted to synthesize BFPy phosphanes.

The phosphane ligands triaryl phosphane **1a**, dppe analogue **2a**, and MeO-biphep analogue (±)- or enantiomerically pure **3a** could be synthesized from the corresponding $R_{1-x}PCl_{x+2}$ (x = 0 or 1) with an excess amount of BFPyMgBr·LiCl,[15] which was prepared from 4-bromo-2,6-bis(trifluoromethyl)pyridine[16] with magnesium and LiCl in the presence of diisobutylaluminum hydride (DIBAL-H) (Scheme 1). The use of a usual Grignard reagent, BFPyMgBr, gave the products in low yield.

The electronic properties of **1a**, **2a**, and **3a** were estimated using metal carbonyl complexes (Table 1). The complexes

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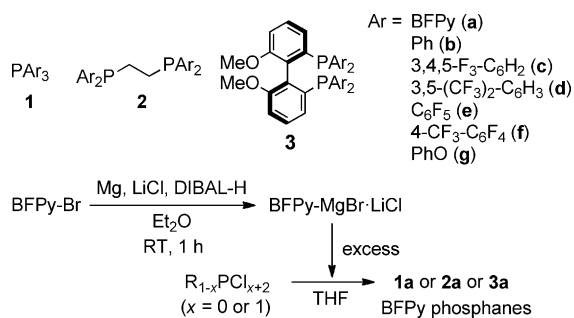
Scheme 1. Synthesis of BFPy phosphanes.

Table 1: Electronic properties of BFPy phosphane ligands.

Ar in phosphane	4[a,b]		5[a]	6[c]
	ν^{CO} [cm^{-1}]	δ [ppm] (J_{Rh-P} [Hz])	ν^{CO} [cm^{-1}]	ν^{CO} [cm^{-1}]
BFPy (a)	2017	31.9 (138.6)	2047	(7a)
PhO (g)	2016	113.9 (213.6)		
4-CF$_3$-C$_6$F$_4$ (f)	2016	−22.5 (157.0)	2045	(7f)
C$_6$F$_5$ (e)	2008	−23.4 (152.6)	2041	
3,5-(CF$_3$)$_2$-C$_6$H$_3$ (d)	2000	32.7 (133.5)	2037	2044
3,4,5-F$_3$-C$_6$H$_2$ (c)	1997	34.0 (134.8)	2031	2036
Ph (b)	1978	29.5 (125.9)	2021	2014

[a] IR spectra in CH$_2$Cl$_2$. [b] ^{31}P NMR spectra in CDCl$_3$. [c] IR spectra in CHCl$_3$.

trans-[RhCl(CO)(**1a**)$_2$] (**4a**) and [Mo(CO)$_4$(**2a**)] (**5a**) were easily synthesized according to the typical method.[17,18] The chemical shift of **4a** in the ^{31}P NMR spectrum was within the range of those of **4b**–**4d**, which have *ortho*-H aryl phosphanes. The J_{Rh-P} value of **4a** was higher than those of the complexes **4b–d**, indicating that P atoms of **1a** have a high electron-withdrawing character.[19] The ν^{CO} values of both **4a** and **5a** were highest among each analogue, indicating that **1a** and **2a** have the lowest σ-donating ability and the highest π-acceptor ability among each type of aryl phosphane ligand, including C$_6$F$_5$ and 4-CF$_3$C$_6$F$_4$ phosphanes (**1e**, **1f**, **2e** and **2f**). Note that the π-acceptor ability of **1a** was comparable with that of triphenyl phosphite (P(OPh)$_3$, **1g**). In the synthesis of *cis*-[RhCl(CO)(**3a**)] (**6a**),[20] *cis*-[{RhCl(**3a**)}$_2$] (**7a**) was obtained instead of **6a**. This decarbonylation indicates that **3a** is a more electron-poor ligand than MeO-F$_{12}$-biphep **3c**[5b] or **3d**[21] in a similar case when MeO-F$_{28}$-biphep (**3f**) was used to obtain **7f**.[5b]

The stability of the BFPy phosphane ligand towards metal complex formation was confirmed using [PtCl$_2$(**2**)] complex **8**.

The chelate effect of highly fluorinated dfppe (**2e** bearing C$_6$F$_5$) stabilizes the metal–phosphorus bond, although **2e** has a large cone angle.[1] However, ligand **2e** in complex **8e** was replaced with **2a** to give **8a** quantitatively in (CD$_3$)$_2$CO in 24 h at room temperature (Scheme 2). In contrast, complex
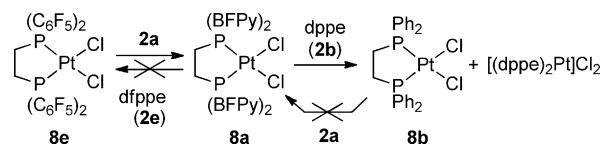
Scheme 2. Stabilization of BFPy phosphane **2a** toward Pt complex.

8a was stable in the presence of **2e**. When the more basic dppe (**2b**) ligand was added to the solution of **8a**, ligand exchange occurred to give a mixture of **8b** and [(dppe)$_2$Pt]Cl$_2$,[22] and **8b** did not react with **2a**. The stabilities of ligand **2** towards platinum complex **8** decreased in the order of **2b** > **2a** > **2e**, which is inconsistent with the σ-donating ability of the ligand (**2a** vs. **2e**, see Table 1 **5a** vs. **5e**). These results show that less hindered and highly electron-poor **2a** constructs a stronger bond with Pt than the sterically hindered dfppe (**2e**).

The LAE of BFPy phosphanes was demonstrated by using several metal-catalyzed reactions. First, we performed Pd/**1a**-catalyzed Stille coupling. The Stille coupling of iodobenzene prefers less σ-donating ligands. Farina and Krishnan reported that triphenyl arsine (AsPh$_3$) considerably accelerated the Stille coupling.[23] However, highly electron-poor P(C$_6$F$_5$)$_3$ did not accelerate the reaction because of catalyst decomposition.[23] We performed the Stille coupling of iodobenzene with tributyl(vinyl)stannane using **1a** (Table 2). The reaction in the presence of 1 mol% [Pd$_2$(dba)$_3$] (dba = dibenzylideneacetone) with 4 mol% **1a** (**1a**/Pd = 2) in THF at 65°C for 12 h gave styrene (**9**) in 94% yield (Table 2, entry 2), which exceeded the yields obtained with other ligands including AsPh$_3$ and P(OPh)$_3$ (Table 2, entries 3 and 4). In this reaction, the rate-determining step is known to be the transmetalation of the vinyl group to Pd.[23,24] The ligand effect in this step was evaluated by DFT calculation of the reaction of [L(Ph)PdI] (L = **1a**, **1b** and AsPh$_3$) with (vinyl)SnMe$_3$ (Figure 2).[24,25] Although we found the T-shaped intermediate *trans*-

Table 2: LAE of **1a** on Stille coupling.

Entry	Pd/Ligand	Ligand	Yield of 9 [%][a]
1	1:0	none	7
2	1:2	**1a**	94
3	1:2	AsPh$_3$	72
4	1:2	P(OPh)$_3$ (**1g**)	84
5	1:2	PPh$_3$ (**1b**)	65
6	1:2	P(C$_6$F$_5$)$_3$ (**1e**)	6
7	1:3	**1a**	92
8	1:3	AsPh$_3$	73
9	1:3	P(OPh)$_3$ (**1g**)	62
10	1:3	PPh$_3$ (**1b**)	6
11	1:3	P(C$_6$F$_5$)$_3$ (**1e**)	6

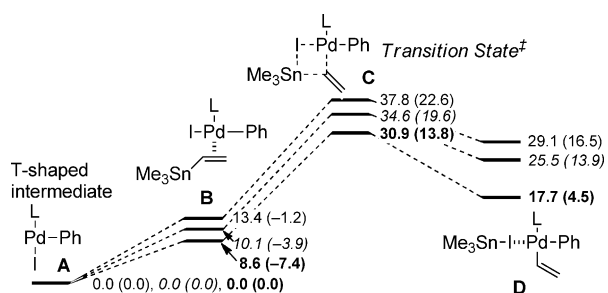[a] Yields were determined by ^{1}H NMR spectroscopy.

Figure 2. Energy profile for the transmetalation of the Stille coupling. The relative free energies and potential energies (in parentheses) obtained from the DFT calculations are given in kcal mol⁻¹. Plain typeface L = **1b**, *italic* L = AsPh₃, **bold** L = **1a**.

[L(I)PdPh] (**A**), the isomer with *cis* arrangement of L and I was not obtained in all cases. The overall relative energy profile (**A–D**) of the **1a** system is smaller than those of the other systems. In particular, the activation barrier of the **1a** system (30.9 kcal mol⁻¹) is significantly lower than that of the corresponding AsPh₃ or **1b** systems (34.6 and 37.8 kcal mol⁻¹, respectively), thus indicating that highly electron-poor **1a** electronically accelerates the transmetalation step. However, similar electron-poor ligand **1e** showed no LAE in the Stille coupling (Table 2, entries 6 and 11 vs. 1). ³¹P NMR spectroscopy revealed that a large amount of **1e** was not complexed with Pd in the reaction mixture.[23] In the **1a** system, no inhibitory effect of excess ligand was observed (Table 2, entry 2 vs. 7) although the effect was apparent in the **1b** system (Table 2, entry 5 vs. 10).[23] The results show that the lower σ-donating ability of **1a** enables it to control the electronic properties of the catalyst while avoiding catalyst inactivation caused by coordination of additional ligands.[26]

The BFPy phosphane ligand accelerated the rhodium-catalyzed 1,2-addition of aryl boronic acid to an unactivated ketone. Although many examples of similar reactions using aldehyde have been reported, this type of 1,2-addition to a ketone had been limited, except for a few examples,[27] to activated ketones,[28] intramolecular reactions,[28] and the side reaction of 1,4-addition to an enone.[29] Furthermore, the exceptional successful cases[27] required high reaction temperatures (80–120 °C), a long reaction times (10–24 h), an equivalent amount of additive, and aryl boron derivatives instead of aryl boronic acid. The reaction of acetophenone (**10a**) with three equivalents phenylboronic acid (**11a**) in the presence of 1.5 mol% [{RhOH(cod)}₂] and 3 mol% (±)-**3a** in toluene/H₂O gave 94% yield of 1,1-diphenylethanol (**12aa**) when the reaction was carried out at 40 °C for 1 h without any additives (Table 3, entry 6). It is obvious that the large LAE of (±)-**3a** can be attributed to its electronic effect. [{RhOH-(cod)}₂] (1.5 mol%) showed no catalytic activity (Table 3, entry 1) and further addition of (±)-binap or (±)-**3f** resulted in no acceleration (Table 3, entries 2 or 5). The Rh catalyst with electron-poor phosphanes (±)-**3c** and **3d** gave the product in poor to moderate yields (Table 3, entries 3 and 4). The Rh/(±)-**3a** catalyst provided an excellent yield of the product in the reactions with other ketones and aryl boronic acids when allowed to react for 1 h at a temperature between 20 and 40 °C (Table 3, entries 7–14). The reaction mechanism

**Table 3:** Rhodium-catalyzed 1,2-addition of aryl boronic acid to ketone.
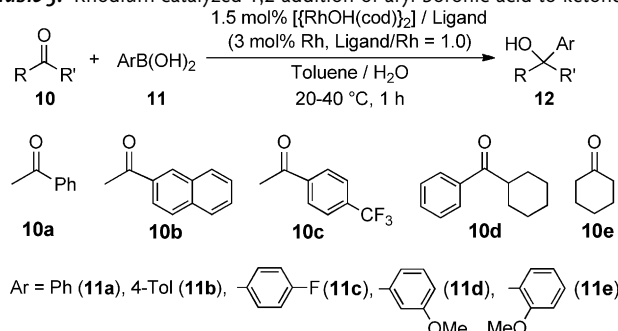
Entry	10	11	Ligand	T [°C]	Yield [%][a]
1	**10a**	**11a**[b]	none	40	0 (**12aa**)
2	**10a**	**11a**[b]	(±)-binap[d]	40	0 (**12aa**)
3	**10a**	**11a**[b]	(±)-**3c**	40	35 (**12aa**)
4	**10a**	**11a**[b]	(±)-**3d**	40	72 (**12aa**)
5	**10a**	**11a**[b]	(±)-**3f**	40	2 (**12aa**)
6	**10a**	**11a**[b]	(±)-**3a**	40	94 (**12aa**)
7	**10b**	**11a**[b]	(±)-**3a**	40	91 (**12ba**)
8	**10c**	**11a**[c]	(±)-**3a**	20	99 (**12ca**)
9	**10d**	**11a**[b]	(±)-**3a**	30	81 (**12da**)
10	**10e**	**11a**[c]	(±)-**3a**	20	98 (**12ea**)
11	**10e**	**11b**[c]	(±)-**3a**	20	95 (**12eb**)
12	**10e**	**11c**[c]	(±)-**3a**	20	96 (**12ec**)
13	**10e**	**11d**[c]	(±)-**3a**	20	94 (**12ed**)
14	**10e**	**11e**[b]	(±)-**3a**	20	93 (**12ee**)

[a] Yield of isolated product. [b] 3 equiv was used. [c] 2 equiv was used. [d] binap = 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl.

is presumed to be similar to that of Rh- or Pd-catalyzed 1,2-addition to an aldehyde[27a] involving the transmetalation of **11** to Rh, insertion of **10** into the Rh−Ar bond and then hydrolysis to give **12**. Because an excess amount of **11** was required, the rate-determining step is assumed to be the insertion step,[30] and highly electron-poor **3a** is expected to substantially accelerate the insertion.[5] As a result, an efficient Rh-catalyzed 1,2-addition of aryl boronic acids to unactivated ketones near room temperature was achieved using highly electron-poor ligand (±)-**3a** without any additives. We are currently making efforts to develop the asymmetric variants.[31]

Highly enantioselective catalysis using (R)-**3a** was achieved in the asymmetric arylation of aryl imine (Table 4).[32,33] The reaction of N-tosylimine **13** with one equivalent **11a** in the presence of 0.025 mol% [{RhCl(C₂H₄)₂}₂] (0.05 mol% Rh) and 0.05 mol% (R)-**3a** in toluene/H₂O with 20 mol% KOH at 20 °C for 1 h gave N-tosylamine (S)-**14** in 98% yield and with 98% ee (Table 4, entry 1). When 0.008 mol% Rh/ (R)-**3a** was used, the TOF was 6900 h⁻¹ (Table 4, entry 2). This value is notable because similar known catalytic reactions using activated imine required 1.5–3 mol% catalyst loading, a longer reaction time (3–12 h, typically TOF < 10 h⁻¹ [34]), and higher reaction temperature.[32,33] The catalysis using (R)-binap or (R)-**3f** gave no product under these conditions (Table 4, entries 4 and 7). Although the use of the electron-poor phosphanes (R)-**3c** or (R)-**3d** showed acceptable TOF values (Table 4, entries 5 and 6), the values were much lower than that obtained with (R)-**3a**. Ultimately, the

Communications

Table 4: Rhodium-catalyzed asymmetric arylation of *N*-tosylimine.
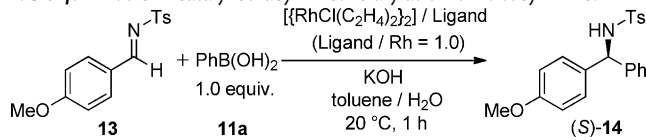
Entry	Ligand	Rh [mol%]	Yield [%][a]	ee [%][b]	TOF [h^{-1}]
1	(*R*)-**3a**	0.05	98	98	1960
2	(*R*)-**3a**	0.008	55	96	6900
3[c]	(*R*)-**3a**	0.008	87	95	10900
4	(*R*)-**3f**	0.05	0	–	0
5	(*R*)-**3d**	0.05	31	98	620
6	(*R*)-**3c**	0.05	25	97	500
7	(*R*)-binap	0.05	0	–	0

[a] Yield of isolated product. [b] Determined by HPLC on a chiral stationary phase. [c] 2 equiv **11a** was used at 40°C.

TOF value using 0.008 mol% Rh/(*R*)-**3a** reached 10 900 h^{-1} at 40°C (Table 4, entry 3). The prominent activity of the Rh/(*R*)-**3a** catalyst is considered to come from the large acceleration of the insertion step by the strong electronic effect of (*R*)-**3a**,[5b] and the scope and the detailed mechanism of this catalytic reaction will be explored in near future.

In summary, BFPy phosphanes were developed as a novel type of aryl phosphane ligand, in which the low σ-donating ability and low steric demands enabled them to control the electronic properties of the metal catalyst, providing a large LAE in the Stille coupling, the Rh-catalyzed 1,2-addition of aryl boronic acid to unactivated ketone, and the asymmetric arylation of *N*-tosylimine. Particularly in the last two cases, the BFPy phosphane achieved the record of the highest catalytic activity. BFPy phosphanes will be effective ligands for many metal-catalyzed reactions, in particular those involving transmetalation, insertion, or reductive elimination[18] processes.

Experimental Section

Synthesis of 1a: A dried flask was flushed with argon and charged with magnesium turnings (365 mg, 15 mmol), LiCl (318 mg, 7.5 mmol), and Et$_2$O (20 mL). A solution of DIBAL in hexane (1.0 M, 100 μL, 0.10 mmol) was added and stirred for 5 min. Then 4-bromo-2,6-bis(trifluoromethyl)pyridine (1.77 g, 6.0 mmol) was added and the reaction mixture was stirred for 1 h. After addition of trichlorophosphane (131 μL, 1.5 mmol), the solution was stirred for 1 h and then saturated NH$_4$Cl(aq) was added. After extraction with EtOAc, the organic layer was dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The resulting solid was purified by silica gel column chromatography (hexane/EtOAc = 6:1) to give **1a** (0.79 g, 78% yield) as a white solid. M.p. > 220°C (decomp.). ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 8.48$ ppm (d, $J = 6.6$ Hz). ^{13}C NMR (100 MHz, [D$_6$]acetone): $\delta = 121.9$ (q, $^1J_{F\text{-}C} = 274.3$ Hz), 129.6 (d, $^2J_{P\text{-}C} = 17.8$ Hz), 149.2 (dq, $^2J_{F\text{-}C} = 35.8$ Hz, $^3J_{P\text{-}C} = 5.9$ Hz), 150.0 ppm (d, $^1J_{P\text{-}C} = 22.5$ Hz). ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta = -64.6$ (s). ^{31}P NMR (121 MHz, [D$_6$]acetone): $\delta = 0.53$ ppm (s). Elemental anal. calcd (%) for C$_{21}$H$_6$F$_{18}$N$_3$P: C 37.46, H 0.90, N 6.24; found: C 37.39, H 1.26, N 6.37.

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