Syntheses of a Novel Fluorinated Trisphosphinoborate Ligand and Its Copper and Silver Complexes. Catalytic Activity toward Nitrene Transfer Reactions

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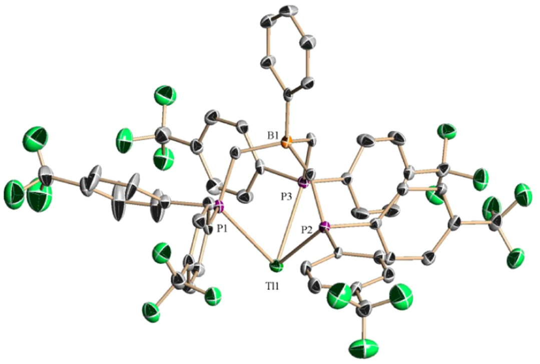
ABSTRACT. A novel fluorinated ligand, the anionic $PhB(CH_2P(p\text{-}CF_3C_6H_4)_2)_3$ ($PhBP_3{}^{p\text{-}CF3Ph}$), has been synthesized and characterized, as well as its corresponding thallium, copper, and silver derivatives. The presence of fluorine atoms in the ligand structure induced the desired effect of enhancing electrophilic character at the metal center, without promoting substantial changes in the ligand skeleton compared with the parent ligand $PhB(CH_2PPh_2)_3^-$ ($PhBP_3$). Olefin aziridination and C−H amidation reactions have been induced with those complexes as catalyst precursors. The copper derivative catalyzed the olefin aziridination of an array of olefins bearing either electron-donating or electron-withdrawing groups. The silver analogue was found to promote the C−H amidation of a series of substrates in moderate to high yields.



INTRODUCTION

Trispyrazolylborate ligands (Tp^x, Figure 1) have contributed with great achievements to organometallic chemistry and homogeneous catalysis.[1] These are formed by three pyrazolyl rings bonded to a tetracoordinated boron atom. Those heterocycles may bear up to three different substituents, providing a great number of Tp^x ligands with variable steric and electronic properties. Usually, these ligands form very stable metal complexes.[2] However, their syntheses are laborious and require high temperatures, and often yields are low to moderate. Because of this, we have recently focused on another family of ligands, the trisphosphinoborate $PhB(CH_2PPh_2)_3^-$.[3,4] We recently described[5] the synthesis and the catalytic properties of the copper complex $[PhB(CH_2PPh_2)_3]Cu(PPh_3)$ (**1**) bearing the tridentate ligand $PhB(CH_2PPh_2)_3^-$ ($PhBP_3$ from now on). This complex was found to be a good catalyst for reactions that did not require a somewhat electron deficient metal center, such as carbene or nitrene transfer reactions to unsaturated substrates, insertion into X−H bonds, or reactions in which a relatively electron-rich metal center is preferred, such as the Atom Transfer Radical Addition (ATRA) or Atom Transfer Radical Polymerization (ATRP) (Scheme 1).[5]

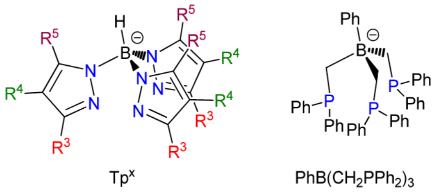
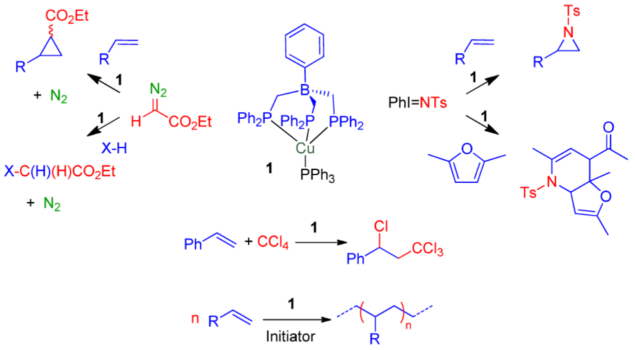


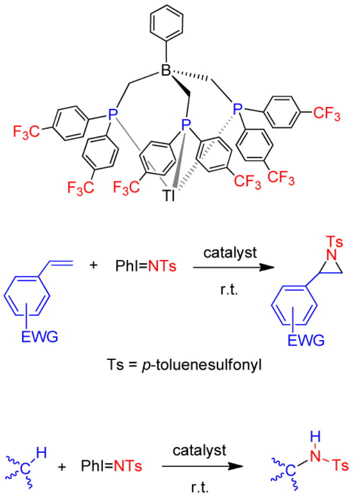
Figure 1. Trispyrazolylborate and trisphosphinoborate ligands.

Unfortunately, complex **1** did not catalyze reactions in which a more electrophilic metal center is desired.[6,7] We wondered whether the attachment of electron-withdrawing groups to the aryl moieties of the ligand could induce such an effect. Since such ligands have not been reported yet, we focused on a synthetic route of the derivative containing a trifluoromethyl group in the *para* position (Scheme 2). To verify if such incorporation originates the desired effect at the metal center, we have chosen metal-catalyzed nitrene transfer reactions as probes (Scheme 2): the electron-poor olefin aziridination for which the use of complex **1** proved to be unsuccessful and the more challenging C−H bond amidation reaction, that could not be observed in the presence of **1** as the catalyst. In this contribution we describe the synthesis and characterization of a novel trisphosphinoborate

Scheme 1. Catalytic Activity Reported for $[(PhBP_3)Cu(PPh_3)]$ (1)



Scheme 2. Targeted New Ligand and Probe Catalytic Reactions in This Work



ligand containing fluorinated, electron-withdrawing groups in the P-substituents and the corresponding copper and silver complexes. The presence of those groups affected the electron density at metals in such a way that catalytic properties not observed with the parent ligand are now described.

RESULTS AND DISCUSSION

Synthesis of $Tl[PhB(CH_2P(p\text{-}CF_3C_6H_4)_2)_3]$. The synthesis of $Tl[PhB(CH_2P(p\text{-}CF_3C_6H_4)_2)_3]$ ($PhBP_3^{p\text{-}CF3Ph}$ from now on) is illustrated in Scheme 3, following a reaction sequence similar to that reported for the parent $Tl[PhB(CH_2PPh_2)_3]$ compound.[3,4] First, dichloromethyl phosphine was reacted with 2 equiv of p-$CF_3C_6H_4MgBr$ in Et_2O, followed by protection of the phosphine with $BH_3{\cdot}THF$. The boronate group plays an important role, since it protects the phosphine from oxidation and increases the acidity of the methyl group, thus favoring the next step. Attempts to carry out deprotonation of unprotected phosphine led to complex mixtures, as previously reported by Peters and coworkers.[8] Consequently, $MeP(p\text{-}CF_3C_6H_4)_2(BH_3)$ was reacted with *sec*-BuLi at −78 °C for 3 h, and then $PhBCl_2$ was added, allowing the mixture to slowly warm to room temperature overnight. After workup, the lithium salt of BH_3-protected trisphosphine was obtained in 80% yield. The ^1H NMR spectrum showed a unique set of resonances for the aryl substituents, consistent with the existence of $PhB(CH_2P(BH_3)(p\text{-}CF_3C_6H_4)_2)_3^-$ anions. The $^{11}B\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra were also in agreement with such a formulation (see Experimental Section).

Deprotection of the phosphine−borane complex was readily accomplished upon heating the ligand with an excess of diethylamine overnight.[9] Examination of an aliquot by $^{31}P\{^1H\}$ NMR showed a clean conversion, as inferred from the observation of a single resonance at −7.2 ppm, at variance with that of 19.5 ppm of the BH_3-protected species (Scheme 3). A transmetalation reaction with $TlNO_3$ was carried out with the previous crude product,[10] affording the $Tl[PhB(CH_2P(p\text{-}CF_3C_6H_4)_2)_3]$ as a white solid in 65% yield. The $^{31}P\{^1H\}$ NMR consisted of a broad signal centered at 1.4 ppm. Although multinuclear NMR data were in accord with the expected product, an X-ray diffraction study, carried out with single crystals grown from slow diffusion of hexane into a dichloromethane solution of the complex at −20 °C, was performed in order to verify the structure. Figure 2 shows the ORTEP view of the molecules of $Tl[PhB(CH_2P(p\text{-}CF_3C_6H_4)_2)_3]$, corroborating the coordination of the novel $PhBP_3^{p\text{-}CF3Ph}$ ligand to the thallium center in a tridentate fashion. When compared with the parent $PhBP_3^-$ ligand, the presence of the CF_3 groups in the ligand did not significantly modify the Tl−P distances (average 2.95 Å for $PhBP_3^{p\text{-}CF3Ph}$ and 2.92 Å for $PhBP_3$) or the P−Tl−P bond angles (73.89° for $PhBP_3^{p\text{-}CF3Ph}$ and 75.02° for $PhBP_3$).

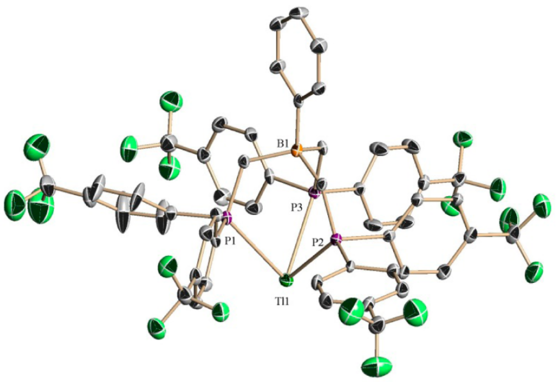
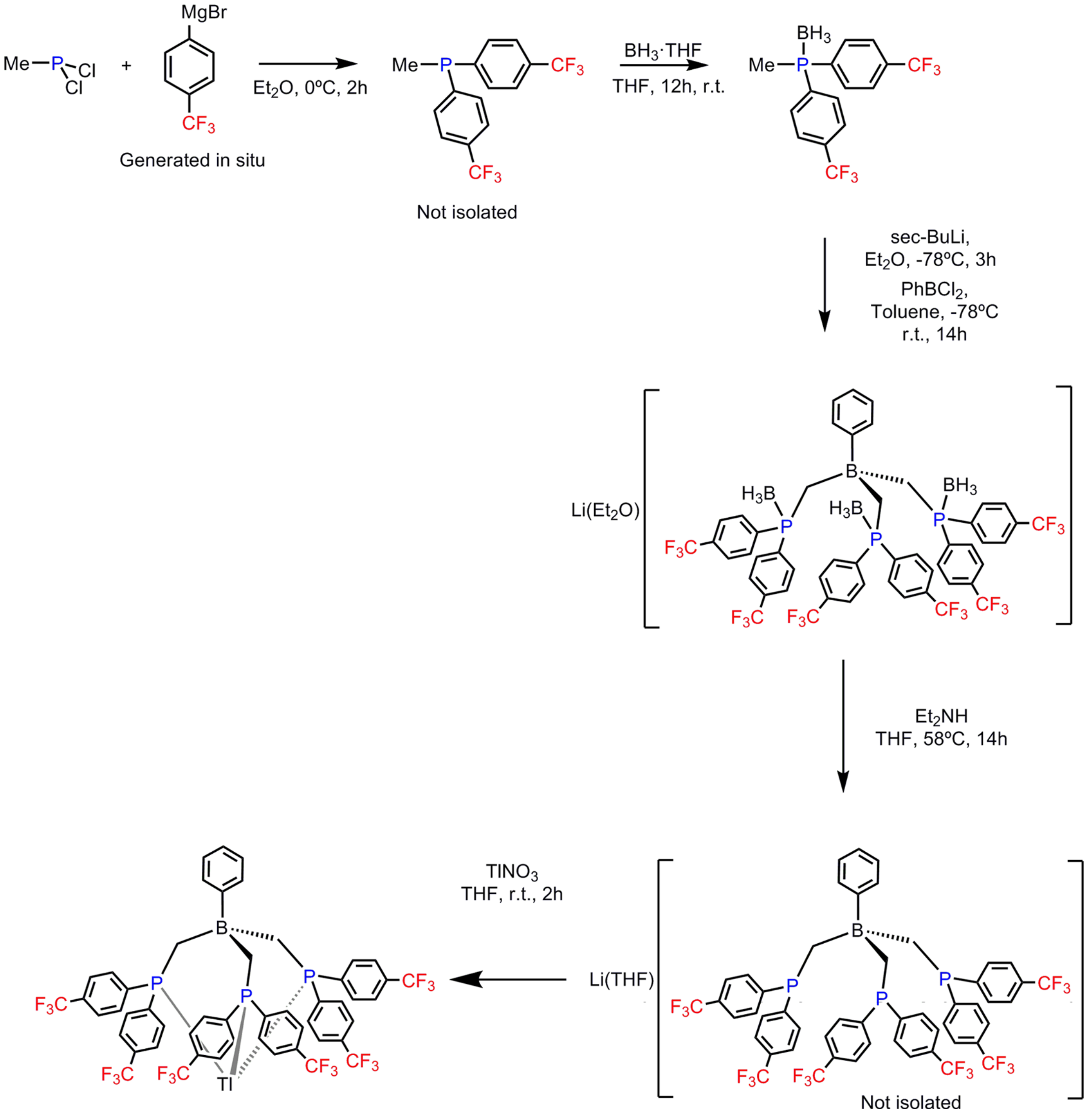


Figure 2. Molecular structure of $Tl[PhBP_3^{p\text{-}CF3Ph}]$. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for $PhBP_3^{p\text{-}CF3Ph}$ ligand: Tl(1)−P(1) = 2.932(2), Tl(1)−P(2) = 2.9626(18), Tl(1)−P(3) = 2.9647(18), P(1)−Tl(1)−P(2) = 73.97(5), P(1)−Tl(1)−P(3) = 74.57(5), P(2)−Tl(1)−P(3) = 73.15(5).

Synthesis of Copper and Silver Complexes Bearing the $PhP(CH_2PAr_2)_3^-$ Ligands (Ar = Ph; p-$CF_3C_6H_4$). The new copper and silver complexes were obtained following a procedure similar to that employed for complex **1**.[5] Therefore, complex $[PhP(CH_2P(p\text{-}CF_3C_6H_4)_2)_3]Cu(PPh_3)$ (**2**) was prepared upon reacting $Tl[PhBP_3^{p\text{-}CF3Ph}]$, copper iodide, and PPh_3 in tetrahydrofuran as the solvent, at room temperature, and isolated in 80% yield (eq 1). The $^{31}P\{^1H\}$ NMR spectrum showed two broad signals centered at 11.1 and −5.7 ppm corresponding to the $P(p\text{-}CF_3Ph)_2$ and PPh_3 ligands, respectively. VT NMR experiments at −80 °C only showed a slight sharpening of the resonance, with no observation of defined lines. The resonances of the P nuclei of the tripodal ligand shifted to lower field compared with that of complex **1** (−5.8 ppm),[5] due to the presence of the fluorine atoms in the ligand framework. Multinuclear NMR data collected were also in agreement with the existence of a C_3 symmetry axis in solution, located along the B−Cu axis (see Experimental Section). The effect of the

Scheme 3. Synthesis of Tl[PhB(CH$_2$P(p-CF$_3$C$_6$H$_4$)$_2$)$_3$]



fluorinated groups on the electronic properties at the metal center was evaluated upon bubbling carbon monoxide through a solution of **2** in THF, and the concomitant generation of the carbonyl derivative [PhB{CH$_2$P(p-CF$_3$C$_6$H$_4$)$_2$}$_3$]Cu(CO). The solution IR spectrum showed one absorption centered at 2068 cm^{-1}, corresponding to ν(CO), assessing a lower electronic density at the metal center in **2** compared with that of **1** (2055 cm^{-1}).[5] In our related investigations with Tp^{x}M (M = Cu, Ag), we have observed that the attachment of ligands containing electron-withdrawing groups induces an increase in the ν(CO) values of the Tp^{x}M(CO) complexes, as well as a parallel augment of the catalytic activity toward carbene or nitrene transfer reactions.[6,7] Thus, the observed increase from **1** to **2** seems to point toward the targeted goal, as discussed below.

$$\mathrm{Tl[PhB(CH_2P(\mathit{p}\text{-}CF_3C_6H_4)_2)_3]} \xrightarrow[\substack{\mathrm{THF} \\ \mathrm{rt,\ 20\ min}}]{\mathrm{CuI, PPh_3}} \underset{(\mathbf{2})}{\mathrm{[PhB(CH_2P(\mathit{p}\text{-}CF_3C_6H_4)_2)_3]Cu(PPh_3)}} \qquad (1)$$

The solid state structure of complex **2** has been elucidated (Figure 3). The copper ion is located in a distorted tetrahedron formed by the four phosphorus atoms. The structure is similar to that described for **1**, although some comments have to be addressed. The P−Cu−P average angle for the tripodal donor atoms is 94.6°, slightly lower than that observed for **1** (95.7°). The PPh$_3$ ligand occupies the fourth coordination site, being displaced from the ideal position along the B−Cu axis (B−Cu−P angle of 174.71°). This effect has also been observed in related complexes of formula Tp^{x}Cu(NCMe).[11] Overall, the presence of CF$_3$ groups in the *para* position of the phenyl groups of the tripodal ligand has little effect on the structural parameters.

$$\underset{\mathrm{M=Tl,\ Li}}{\mathrm{M[PhB(CH_2PAr_2)_3]}} \xrightarrow[\mathrm{THF,\ rt}]{\substack{\mathrm{AgCl\ or\ AgOTf} \\ \mathrm{PPh_3}}} \underset{\substack{\mathrm{Ar=Ph,\ \mathbf{3}} \\ \mathrm{Ar=\mathit{p}\text{-}CF_3C_6H_4,\ \mathbf{4}}}}{\mathrm{[PhB(CH_2PAr_2)_3]Ag(PPh_3)}} \qquad (2)$$

The silver analogues of **1** and **2** were prepared following a related procedure. The corresponding ligand was reacted with the silver source (see the Experimental Section) and 1 equiv of PPh$_3$ in tetrahydrofuran as the solvent (eq 2) to afford the complexes [PhP(CH$_2$PPh$_2$)$_3$]Ag(PPh$_3$) (**3**) and [PhP(CH$_2$P-(p-CF$_3$C$_6$H$_4$)$_2$)$_3$]Ag(PPh$_3$) (**4**), in 70% and 75% yield, respectively. In contrast with the copper analogues (which gave broad signals),

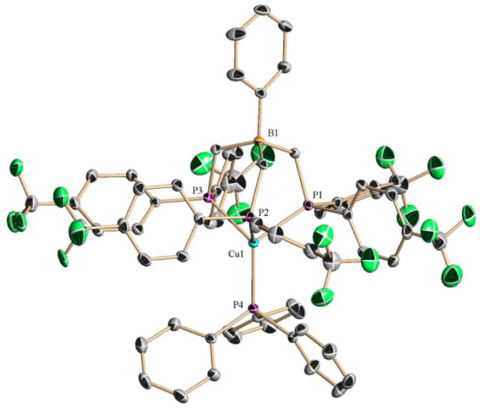


Figure 3. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **2**: Cu(1)−P(1) = 2.3399(10), Cu(1)−P(2) = 2.3640(10), Cu(1)−P(3) = 2.3315(10), Cu(1)−P(4) = 2.2823(10), P(1)−Cu(1)−P(2) = 94.11(4), P(1)−Cu(1)−P(3) = 95.69(3), P(1)−Cu(1)−P(4) = 117.47(4), P(2)−Cu(1)−P(3) = 94.03(4), P(2)−Cu(1)−P(4) = 126.25(4), P(3)−Cu(1)−P(4) = 121.96(4).

the $^{31}P\{^1H\}$NMR spectrum was highly informative. Figure 4 shows that of **3**, which displayed one doublet of pseudoquintets at 16.2 ppm and a doublet of doublets of doublets, centered at −2.7 ppm, with relative integrals of 1:3, therefore corresponding to PPh_3 and the tripodal ligand. The observed pattern of lines is explained as the result of the coupling of the P nuclei to the two NMR active isotopes of silver, ^{107}Ag, and ^{109}Ag. Thus, both pseudoquintets must be considered as four quartets with partial overlap of lines (Figure 4). The higher coupling constants correspond to those induced by the heavier isotope ^{109}Ag ($^1J(P{-}^{109}Ag)$ = 397.4 Hz, $^1J(P{-}^{107}Ag)$ = 338.6 Hz, $^2J(P{-}P)$ = 30 Hz). The high field resonance of the coordinated PPh_2 moiety also shows the splitting due to both metal isotopes ($^1J(P{-}^{109}Ag)$ = 215 Hz, $^1J(P{-}^{107}Ag)$ = 192.3 Hz, $^2J(P{-}P)$ = 30 Hz). Complex **4** showed similar NMR spectra (see Experimental Section).

Single crystals of **3** were obtained, and an X-ray diffraction study was carried out, with the structure of the molecules being shown in Figure 5. Marks and co-workers have described[12] related complexes such as $[PhB\{CH_2P(Ph)_2\}_3]Ag(PEt_3)$. The structure of **3** is similar to that, with a distorted-tetrahedral geometry consisting of four P donors (from the tridentate $PhBP_3$

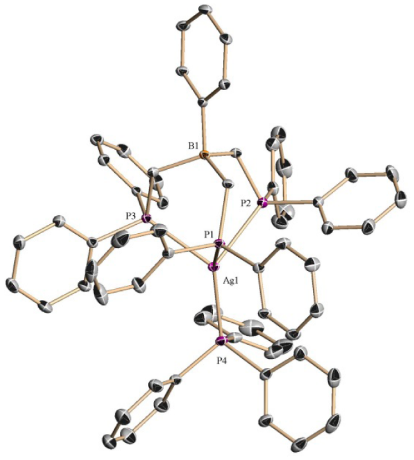


Figure 5. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **3**: Ag(1)−P(1) = 2.5432(6), Ag(1)−P(2) = 2.5522(6), Ag(1)−P(3) = 2.5210(6), Ag(1)−P(4) = 2.4380(6), P(1)−Ag(1)−P(2) = 92.660(18), P(1)−Ag(1)−P(3) = 88.164(18), P(1)−Ag(1)−P(4) = 128.166(19), P(2)−Ag(1)−P(3) = 90.802(18), P(2)−Ag(1)−P(4) = 120.89(2), P(3)−Ag(1)−P(4) = 125.559(19).

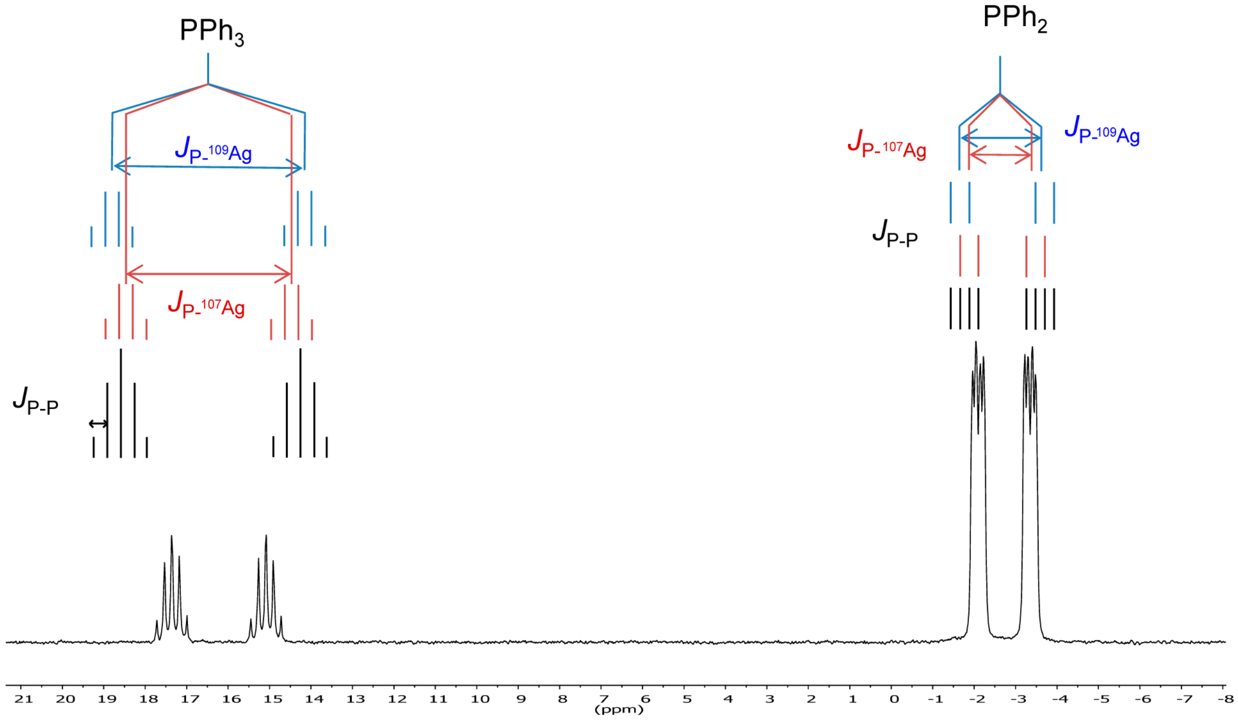


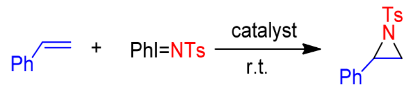
Figure 4. $^{31}P\{^1H\}$ NMR spectrum of complex **3**, showing the different P−P, P−^{107}Ag, and P−^{109}Ag coupling constants.

and the PPh_3 ligands) around the silver atom. The distances and angles also compared well: the P−Ag−P average value angle for the tripodal donor atoms of 90.5° is almost identical to that found for $[PhB\{CH_2P(Ph)_2\}_3]Ag(PEt_3)$ (89.3°), and the Ag−P distances averaged 2.44 Å (2.40 for $[PhB\{CH_2P(Ph)_2\}_3]Ag(PEt_3)$). The PPh_3 ligand deviates only slightly from the B−Ag axis (B−Ag−P angle of 178.24°) when compared with the copper analogue.

A final comment on the hydroscopic behavior of the compounds containing this new fluorinated ligand has to be noted. The three compounds with thallium, copper, or silver are isolated as crystalline materials, with NMR spectra showing the expected resonances. However, in all cases those spectra (see Supporting Information) showed the presence of water due to that hydroscopic nature. Even under extreme dried and anhydrous handling, water was incorporated to the samples, precluding the achievement of good elemental analyses. We believe that the presence of the fluorinated groups must be related to this behavior, since the copper and silver complexes **1** and **3** with the parent BP_3 ligand provided such data within the appropriate experimental error.

Nitrene Transfer Reactions Catalyzed by $(PhBP_3^{p\text{-}CF3Ph})M(PPh_3)$ (M = Cu, 2; Ag, 4). (a) Olefin Aziridination Reactions. We first screened the catalytic activity of complexes **2** and **4** toward the aziridination of styrene using PhI=NTs as the nitrene source (Scheme 4).[13] The copper-based catalyst provided high yields of the expected aziridine whereas the silver analogue gave poor yields. This is in contrast with recent results from our laboratories with Tp^xM (M = Cu, Ag) complexes where both metals exhibited quite good catalytic activities for the aziridination of carbon−carbon double bonds, although with the assistance of directing groups in that case.[13d]

Scheme 4. Styrene Aziridination Catalyzed by Complexes 2 and 4

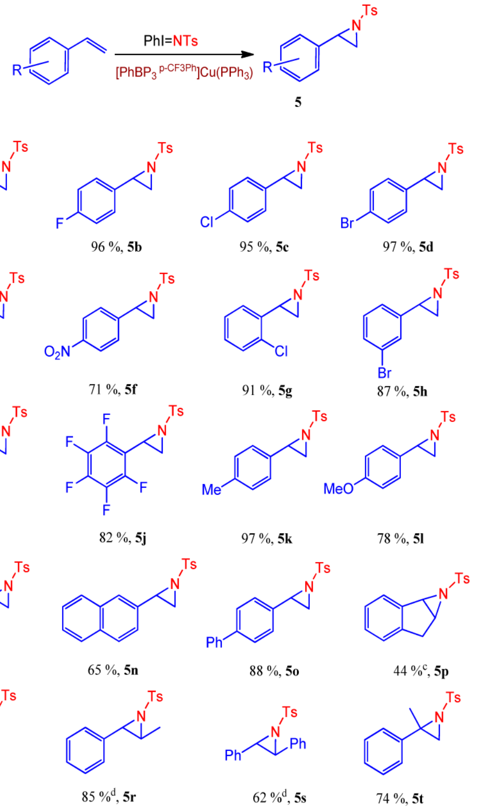


catalyst	yield
2	90 %
4	< 10 %

Therefore, we screened the use of catalyst **2** in the aziridination of alkenes (20 examples, Scheme 5). The standard conditions used were a 1:20:100 ratio of [**2**]:[PhI═NTs]:[olefin] stirred at room temperature for 5 h. A wide range of styrenes were aziridinated in good to excellent yields, *including some with electron-withdrawing groups* (**5a**−**5f**). Interestingly, there are very few examples in the literature of catalytic systems based on copper that induce the aziridination of electron-poor olefins to a similar extent compared to those found with electron-rich olefins. And this is in spite of the seminal work by Evans and co-workers, nearly 20 years ago, that demonstrated that the bis(oxazoline)-copper catalyst could convert cinnamates into the aziridines derivatives.[14] Lebel and co-workers have recently applied a similar system to *p*-nitrostyrene with good results.[15]

Different substitution patterns along the ring also provided good yields (**5g**−**5i**), with even the pentafluorostyrene derivative being converted with an 82% yield (**5j**). This feature is exclusive of complex **2**, since **1** does not provide such a reaction outcome.

Scheme 5. Aziridination of Styrenes Using Complex 2 as Catalyst[a,b]



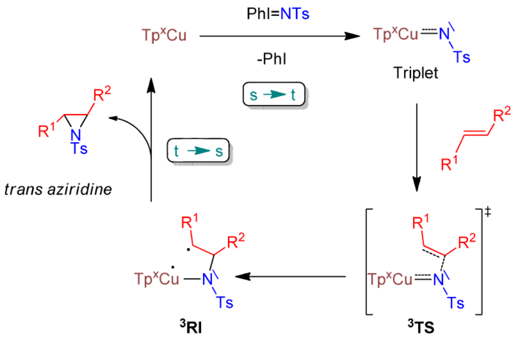
[a]General conditions: 5 mmol % Cu-complex, 0.1 mmol of PhI═NTs, 0.5 mmol of alkene, 5 mL of dichloromethane, 5 h, rt. [b]Isolated yields, average of at least two independent runs. [c]One mmol of alkene employed. [d]Only *trans*-aziridine observed.

In addition, electron-donating styrenes also provided moderate to good yields (**5k**−**5m**). Sterically hindered alkenes, such as 2-vinylnaphthalene and 4-vinylbiphenyl, were also aziridinated (products **5n**−**5o**).

Aziridines from indene and 1,2-dihydronaphthalene, however, were obtained in moderate yields, probably as a result of an increase in bulkiness (**5p**−**5q**). Interestingly, *trans*-*β*-methyl styrene and *trans*-stilbene (**5r**−**5s**) were stereoselectively aziridinated, with only *trans*-aziridines being observed in the ^1H NMR spectra of the reaction crudes. An experiment with *cis*-stilbene gave the *trans*-aziridine as the major product (*trans:cis* ratio = 4:1). Finally, substitution at the *α*-position of the alkene did not affect the reaction (**5t**).

We have recently proposed a general mechanism for the olefin aziridination reaction catalyzed by Tp^xCu complexes.[16] On the basis of an experimental and theoretical study, we proposed that this transformation is triggered by the formation of a triplet metallonitrene intermediate that reacts with the olefin to give a radical intermediate, also in the triplet state (Scheme 6). For aryl- or alkyl-substituted olefins, the pathway continues by spin crossing with the open shell singlet surface and ring closing to yield aziridine and revert $TpCu^I$ to restart the catalytic cycle. Thus, the observance of retention of the initial geometry of the olefin in the final aziridines is explained on the basis of that crossing, that takes place before rotation around the C−C bond might occur. The radical nature of the initial metallonitrene intermediate was assessed by the fitting of experimental data

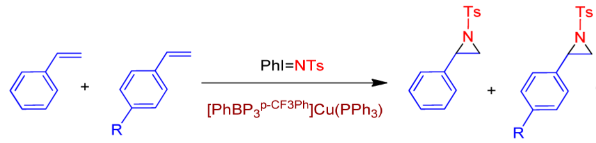
Scheme 6. Mechanism for the Olefin Aziridination Proposed with Trispyrazolylborate-Containing Copper Catalysts Involving Singlet and Triplet Pathways



from competition experiments with *p*-substituted styrenes to a double-parameter Hammett equation (eq 3).[17]

$$\log(K_X/K_H) = \sigma^+\rho^+ + \sigma^\bullet\rho^\bullet \tag{3}$$

Since most authors have frequently invoked that the mechanism of the metal-catalyzed aziridination reaction is system-dependent,[18] we have focused on providing data to extend our previous proposal to this catalytic system. A series of competition experiments with *p*-substituted styrenes (eq 4) were carried out. In a typical procedure, equimolar mixtures of styrene and the *p*-substituted styrene were reacted with PhI═NTs in the presence of **2** (1:20:100:100 ratio of **2**:PhINTs:*p*-substituted styrene:styrene). The relative ratios of the corresponding aziridines were determined by ^{1}H NMR spectroscopy. Data shown in Table 1 only fit into the dual-parameter Hammett equation (eq 3).[17] This equation has been previously employed to account for reactions involving both polar and radical effects of substituents.[13b,16,19] A good fit with eq 3 (and Jackson's constants)[17b] was obtained with $\rho^+ = -0.24$ and $\rho^\bullet = 0.11$ (Table 1 and Figure 6). The negative value of ρ^+ is consistent with the existence of an electrophilic transition state whereas the positive value of $\rho^\bullet$ indicates the intermediacy of radical contributions. The $\rho^+/\rho^\bullet$ value of 2.2 is higher than any of those recently reported for Tp^{x}Cu.[16] Moreover, the proposal of radical species is in agreement with the observance of the different reactivity of the *meta*- and *para*- substituted styrenes bearing nitro or bromo substituents. The well-known capabilities of these groups of stabilizing benzyl-radicals when located in the *para* position explains the observed decrease of the catalytic activities of the corresponding *meta*-isomers.



(4)

Table 1. Competition Experiments with *p*-Substituted Styrenes Using 2 as Catalyst

X	K_X/K_H	σ^+	$\sigma^\bullet$
OMe	1.86	−0.78	0.42
Me	1.38	−0.31	0.39
Cl	1.19	0.11	0.18
Ph	1.41	−0.18	0.42
F	1.17	−0.07	0.12
H	1	0	0
NO_2	0.83	0.79	0.76

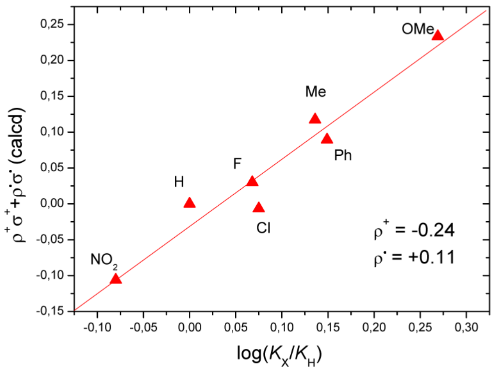
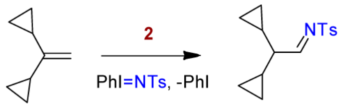


Figure 6. Plot of Experimental log (K_X/K_H) vs Calculated $\sigma^+\rho^+ + \sigma^\bullet\rho^\bullet$.

We have also carried out two additional experiments. First, a well-known radical trap such as BHT (2,6-bis(*tert*-butyl)-4-hydroxytoluene) was added to the reaction mixture, in an attempt to inhibit the reaction. However, we did not observe such inhibition, just a decrease from 80 to 50%, in line with our previous work with Tp^x ligands,[16] probably due to fast ring closing before BHT can trap the C-centered radical similar to ^{3}**RI** in Scheme 5. A second experiment consisted of the use of 1,1-dicyclopropylethylene, a radical clock, as the olefin, and **2** as the catalyst (eq 5). If C-centered radicals survive enough, then cyclopropyl-opening products should be observed to a certain extent in the reaction mixture. However, we did not detect any ring-opening products, but an imine derived from the copper-nitrene derivative, as also observed for the Tp^x-based system. The formation of this compound can be inferred to result from high steric induction by both cyclopropyl groups, thus preventing ring closing and aziridine formation.[17] Both results are in accord with a short-lived radical intermediate that undergoes ring-closing prior to C—C rotation.



(5)

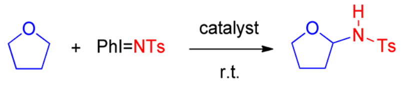
major product
(+ TsNH$_2$ as byproduct)

Therefore, data collected supports that this trisphosphinoborate copper(I) catalytic system seems to operate through similar stepwise pathways than those proposed for the related Tp^{x}Cu-based system, in which both the triplet and the singlet states are involved.

(b) C—H Amidation Reactions. We have also studied the catalytic capabilities of complexes **2** and **4** toward the insertion of nitrene moieties into carbon—hydrogen bonds. This reaction has been reported in a yet reduced number of cases.[20,21] In a probe reaction, we employed tetrahydrofuran as the substrate. As shown in Scheme 7, only complex **4** exhibited a successful catalytic performance. It is worth mentioning that the copper complex **1** did not catalyze this reaction, in contrast with other copper-based catalysts that we have previously reported to induce this transformation.[7,21,22]

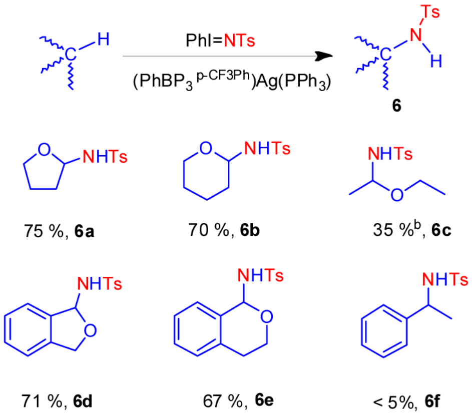
The capabilities of the silver complex toward this reaction were further exploited with a series of substrates bearing C—H bonds at benzylic positions or vicinal to O-atoms (Scheme 8). These substrates were functionalized in moderate to good yields.

Scheme 7. Nitrene Insertion into C−H Bonds of Tetrahydrofuran with PhINTs Induced by Complexes 2 and 4



catalyst	yield
2	< 5 %
4	75 %

Scheme 8. Nitrene Insertion into C−H Bonds with PhINTs Catalyzed by 4[a]



[a]General conditions: 5 mmol % Ag-complex, 0.1 mmol of PhINTs, 5 mL of substrate, 5 h, room temperature. Isolated yields. [b]Yield was calculated by adding pentafluorostyrene as an internal standard.

The use of silver as catalyst was first described by He and co-workers,[23] followed by work developed in our laboratories,[6,24] the catalytic activity displayed by **4** comparing well with those previous examples.

CONCLUSION

We have synthesized and characterized the novel triphosphinoborate ligand $[PhB(CH_2P(p\text{-}CF_3C_6H_4)_2)_3]^-$, containing fluorinated electron-withdrawing groups, as well as the corresponding Tl-, Cu-, and Ag-complexes, with the coinage metal derivatives containing PPh_3 as coligand. Our goal of enhancing electrophilicity at the metal center to improve the catalytic performance of the corresponding copper and silver derivatives has been achieved. Thus, these compounds have been used as catalysts in nitrene transfer reactions to saturated and unsaturated substrates with good results. Aziridination of both electron-rich and electron-deficient olefins has been achieved with the copper derivative, with the latter substrates being unaffected with parent complex **1**. Further, C−H bonds of several cyclic ethers were amidated with the silver complex as the catalyst, providing another example to the yet scarce number of catalytic systems which verify this transformation. We have demonstrated that substitution at distal positions in the P-aryl enhances the electrophilicity at the metal center, with virtually no incidence in the sterics of the metal complex, but improves significantly the catalytic properties.

EXPERIMENTAL SECTION

General Methods. All preparations and manipulations were carried out under an oxygen-free nitrogen atmosphere using conventional Schlenk techniques or inside a glovebox. The solvents were dried, distilled, and degassed using a standard procedure. Reagents were purchased from Aldrich and Alfa-Aesar and were used as received. Flash column chromatography was carried out using a forced flow of the indicated solvent on Merck silica gel 60 (230−400 mesh). Reactions were monitored by TLC carried out on 0.25 mm E. Merck silica gel 60 F_{254} glass or aluminum plates. Multinuclear NMR spectra were recorded on a Varian Mercury 400 MHz instrument. Chemical shift values for ^{1}H and ^{13}C were referred to internal $SiMe_4$ (0.0 ppm), and for ^{31}P, they were referred to H_3PO_4 (85% solution in D_2O, 0 ppm).

Synthesis of $MeP(p\text{-}CF_3C_6H_4)_2(BH_3)$. The Grignard reagent p-$CF_3PhMgBr$ was generated from p-CF_3PhBr and Mg in Et_2O. In a separate flask $MePCl_2$ (1.80 mL, 18 mmol) was dissolved in Et_2O (23 mL) and cooled to 0 °C. The solution of the aryl Grignard reagent was slowly added via cannula over the cold $MePCl_2$ solution. The reaction mixture was then stirred at rt for 2 h, before the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL). The organic layer was washed with water (2 × 20 mL) and dried over magnesium sulfate. Removal of the volatiles provided the $MeP(p\text{-}CF_3Ph)_2$ phosphine as a colorless oil. The crude was then dissolved in THF (4 mL), and $BH_3{\cdot}THF$ (23.5 mmol, 23.5 mL of a 1 M solution) was slowly added. The mixture was stirred overnight before adding EtOH (15 mL), with the resulting solution being concentrated under reduced pressure to give an oily residue that was purified by column chromatography applying hexanes:ethyl acetate (25:1). $MeP(p\text{-}CF_3C_6H_4)_2(BH_3)$ was isolated as a colorless oil (3.27 g, 52% yield (over 2 steps)). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.81{-}7.76$ (m, 4H, *p*-CF_3*Ph*), 7.73−7.71 (m, 4H, *p*-CF_3*Ph*), 1.94 (d, 3H, $J = 9.6$ Hz, C*H*$_3$-P), 1.50−0.50 (br, 3H, P−B*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): $\delta = 134.4$ (d, $J = 53$ Hz, *ipso*-P*Ph*), 133.6 (d, $J = 33$ Hz, *o*-P*Ph*), 132.4 (d, $J = 10$ Hz, *m*-P*Ph*), 126.0 (m, *p*-P*Ph*), 123.5 (q, $J = 272$ Hz, CF_3), 11.5 (d, $J = 39.5$ Hz, CH_3−P). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): $\delta = 12.5$ (d, $J = 62$ Hz). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): $\delta = -38.2$ (d, $J = 45$ Hz). ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz, δ in ppm): $\delta = -63.2$ (s). ESI-HRMS (m/z) $(2M\text{-}BH_3)^+$ calcd for $C_{30}H_{25}BF_{12}P_2$: 686.13, found: 686.13.

Synthesis of $[PhB\{CH_2P(p\text{-}CF_3C_6H_4)_2(BH_3)\}_3]Li(Et_2O)$. A diethyl ether solution (100 mL) of $MeP(p\text{-}CF_3C_6H_4)_2(BH_3)$ (1.41 g, 4.04 mmol) was placed into a Schlenk flask at −78 °C (dry ice/acetone bath). A solution of *sec*-BuLi (3.20 mL, 1.4 M, 3.20 mmol) was added by syringe, and the reaction mixture was stirred at that temperature for 3 h. Then, a toluene solution (5 mL) of $PhBCl_2$ (172 μL, 1.33 mmol) was added via cannula into the reaction flask at −78 °C. The resulting mixture was stirred and allowed to gradually warm up to room temperature over 14 h. Volatiles were removed under reduced pressure, and the residue was redissolved in Et_2O (20 mL). Filtration through a plug of Celite was carried out to eliminate LiCl. The filtrate was concentrated in vacuo, and the resulting foam was washed with hexanes (2 × 10 mL), affording the title compound as a colorless solid (3.93 g, 80% yield, 95% purity). ^{1}H NMR ($(CD_3)_2CO$, 400 MHz): $\delta = 7.72{-}7.68$ (m, 12H, *p*-CF_3*Ph*), 7.56−7.54 (m, 12H, *p*-CF_3*Ph*), 6.85 (d, 2H, $J = 6.8$ Hz, *o*-*Ph*B), 6.25 (t, 1H, $J = 7.4$ Hz, *p*-*Ph*B), 6.10 (m, 2H, *m*-*Ph*B), 3.39 (q, 4H, $J = 7.2$ Hz, $Li(CH_3CH_2O)_2$), 1.94 (br d, 6H, $J = 16.4$ Hz, -BC*H*$_2$P-), 1.14 (t, 6H, $J = 7.2$ Hz, $Li(CH_3CH_2O)_2$), 1.5−0.5 (br, 9H, (P−B*H*$_3$)$_3$). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 100.6 MHz): $\delta = 141.9$, 134.4, 126.5, 123.0 (*Ph*B-), 133.4 (d, $J = 8.7$ Hz, *ipso*-P*Ph*-CF_3), 131.4 (dq, $J = 32, 2$ Hz, *p*-P*Ph*-CF_3), 125.3 (d, $J = 4.0$ Hz, *o*-P*Ph*-CF_3), 125.2 (s, *m*-P*Ph*-CF_3), 125.0 (q, $J = 271$ Hz, -CF_3), 66.0 (Et_2O), 15.5 (Et_2O), 21.1 ($PhB\{CH_2P(p\text{-}CF_3Ph)_2(BH_3)\}_3$). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$, 162 MHz): $\delta = 19.5$ (br s). ^{11}B{^{1}H} NMR ($(CD_3)_2CO$, 128 MHz, δ in ppm): $\delta = -16.6$ (br s, Ph*B*CH_2P), −40.2 (br s, P-*B*H_3). ^{19}F{^{1}H} NMR ($(CD_3)_2CO$, 376 MHz): $\delta = -63.4$ (s). ESI-HRMS (m/z) $(M)^-$ (negative mode) calcd for $C_{51}H_{44}B_4F_{18}P_3$: 1135.27, found: 1135.33.

Synthesis of $Tl[PhB\{CH_2P(p\text{-}CF_3C_6H_4)_2\}_3]$. A Schlenk tube was charged with $[PhB\{CH_2P(p\text{-}CF_3C_6H_4)_2(BH_3)\}_3]Li(Et_2O)$ (1.21 g, 1 mmol), degassed diethylamine (4 mL), and 2 mL of THF. The reaction mixture was heated to 55 °C during 14 h. Examination of an aliquot by ^{31}P{^{1}H}NMR spectroscopy showed full conversion toward the free-borane ligand (singlet at −7.2 ppm). Volatiles were removed under reduced pressure, and the resulting foam was washed with hexanes (3 × 20 mL). Then, the crude material was dissolved in 30 mL of THF and slowly added with a cannula to another flask containing $TlNO_3$ (266 mg, 1 mmol). The mixture was stirred at room temperature during

2 h when volatiles were removed under reduced pressure and the resulting brownish foam was washed with hexanes (3 × 20 mL) to give $[\mathrm{PhB}\{\mathrm{CH_2P}(p\text{-}\mathrm{CF_3Ph})_2\}_3]$ as a white solid (843 mg, 65% yield (over 2 steps)). Single crystals were obtained by slow diffusion of hexane into a dichloromethane solution of the complex at −20 °C. ^{1}H NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 400 MHz): δ = 7.49–7.45 (m, 12H, *p*-CF$_3$*Ph*), 7.43–7.41 (m, 12H, *p*-CF$_3$*Ph*), 7.36 (d, 2H, J = 7.2 Hz, *o-Ph*B), 6.84 (t, 2H, J = 7.2 Hz, *m-Ph*B), 6.75 (t, 1H, J = 7.2 Hz, *p-Ph*B), 1.50 (br s, 6H, B-C*H*$_2$-P). ^{13}C{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 100.6 MHz): δ = 149.0 (br s, *ipso-Ph*B-), 133.3, 127.1, 123.5 (*Ph*B-), 133.8 (d, J = 18 Hz, *ipso*-P*Ph*-CF$_3$), 133.8 (d, J = 3.9 Hz, *o*-P*Ph*-CF$_3$), 129.9 (q, J = 32 Hz, *p*-P*Ph*-CF$_3$), 125.3 (d, J = 1.8 Hz, *m*-P*Ph*-CF$_3$), 125.3 (q, J = 271 Hz, -CF$_3$), 22.9 (m, $\mathrm{PhB}\{\mathrm{CH_2P}(p\text{-}\mathrm{CF_3Ph})_2\}_3$). ^{31}P{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 162 MHz): δ = 1.4 (br s). ^{11}B{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 128 MHz): δ = −12.6 (br s).^{19}F{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 376 MHz): δ = −63.2 (s). The crystalline material is highly hydroscopic, precluding appropriate values for elemental analysis.

Synthesis of $[\mathrm{PhB}\{\mathrm{CH_2P}(p\text{-}\mathrm{CF_3C_6H_4})_2\}_3]\mathrm{Cu}(\mathrm{PPh_3})$ (2). A Schlenk flask was charged with the Tl complex (150 mg, 0.115 mmol), CuI (22 mg, 0.115 mmol), PPh$_3$ (30 mg, 0.115 mmol), and 10 mL of THF. The mixture was stirred at room temperature for 20 min, and then it was filtered through a plug of Celite. The resulting solid was washed with hexanes (2 × 20 mL), affording the Cu-complex as an off-white solid (130 mg, 80% yield). Single crystals were obtained by cooling at −20 °C a concentrated THF solution of the complex. ^{1}H NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 400 MHz): δ = 7.63–7.58 (m, 6H, CuP*Ph*$_3$), 7.48–7.43 (m, 6H, CuP*Ph*$_3$), 7.37–7.26 (m, 29H, *p*-CF$_3$*Ph*, *o-Ph*B and CuP*Ph*$_3$), 7.20 (t, 2H, J = 7.6 Hz, *m-Ph*B), 7.04 (t, 1H, J = 7.2 Hz, *p-Ph*B), 1.63 (br s, 6H, -BC*H*$_2$P-). ^{13}C{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 100.6 MHz): δ = 143.8 (br s, *ipso-Ph*B), 127.0, 124.8, 124.1 (*Ph*B), 132.7 (d, J = 14.4 Hz, *ipso*-P*Ph*-CF$_3$), 132.7 (d, J = 4.4 Hz, *o*-P*Ph*-CF$_3$), 130.6 (d, J = 1.4 Hz, *m*-P*Ph*-CF$_3$), 130.2 (q, J = 32.1 Hz, *p*-P*Ph*-CF$_3$), 124.0 (q, J = 271 Hz, -CF$_3$), 133.7 (d, J = 14.1 Hz, CuP*Ph*$_3$), 131.0 (CuP*Ph*$_3$), 129.0 (d, J = 8.9 Hz, CuP*Ph*$_3$), 128.5 (d, J = 7.4 Hz, CuP*Ph*$_3$), 18.8 (m, $\mathrm{PhB}\{\mathrm{CH_2P}(p\text{-}\mathrm{CF_3Ph})_2\}_3$). ^{31}P{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 162 MHz): δ = −5.7 (br s, CuPPh$_3$), 11.1 (br s, $\mathrm{PhB}\{\mathrm{CH_2}P(p\text{-}\mathrm{CF_3Ph})_2\}_3$). ^{11}B{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 128 MHz): δ = −15.1 (s). ^{19}F{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 376 MHz): δ = −63.4 (s). The crystalline material is highly hydroscopic, precluding appropriate values for elemental analysis.

Synthesis of $[\mathrm{PhB}\{\mathrm{CH_2PPh_2}\}_3]\mathrm{Ag}(\mathrm{PPh_3})$ (3). Silver(I) chloride (57.3 mg, 0.4 mmol) was added to a solution of $[\mathrm{PhB}\{\mathrm{CH_2PPh_2}\}_3]$-Li(TMEDA) (323.5 mg, 0.4 mmol) in tetrahydrofuran (10 mL). The flask was covered with aluminum foil, and the mixture was stirred for 2.5 h. Then, 1 equiv of PPh$_3$ (105.0 mg, 0.4 mmol) was added and the reaction was stirred for 2.5 h. The solvent was removed under reduced pressure to give a white powder that was washed with petroleum ether (2 × 15 mL). The solid was dissolved in tetrahydrofuran (10 mL), and 3 equiv of PPh$_3$ was added to favor crystallization. After concentration and cooling overnight at −20 °C, $[\mathrm{PhB}\{\mathrm{CH_2PPh_2}\}_3]\mathrm{Ag}(\mathrm{PPh_3})$ was obtained as colorless crystals, some of them suitable for X-ray studies (0.29 g, 70% yield). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 7.61 (d, 2H, *o-Ph*B-), 7.58 (m, 6H, AgP*Ph*$_3$), 7.45 (t, 3H, AgP*Ph*$_3$), 7.24 (m, 8H, *m-Ph*B-, AgP*Ph*$_3$), 7.15 (t, 6H, P*Ph*$_2$), 7.05 (m, 12H, P*Ph*$_2$), 7.02 (t, 1H, *p-Ph*B-), 6.96 (t, 12H, P*Ph*$_2$), 1.43 (br s, 6 H, $\mathrm{PhB}\{C\mathrm{H_2PPh_2}\}_3$). ^{13}C{^{1}H} NMR (CD$_2Cl_2$, 100.6 MHz): δ 140.2 (br s, *ipso-Ph*B), 127.9 (m), 126.7, 122.9 (*Ph*B), 133.6 (d), 132.3 (m), 131.1, 130.0 (d), 128.7 (d), 127.9 (m), AgP*Ph*$_3$ and PhB{CH$_2$P*Ph*$_2$}$_3$, 18.8 (m, PhB-{CH$_2$PPh$_2$}$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 162 MHz): δ 16.2 (doublet of pseudoquintets, $^1J(P\text{–}^{109}Ag)$ = 397.4 Hz, $^1J(P\text{–}^{107}Ag)$ = 338.6 Hz, $^2J(P\text{–}P)$ = 30 Hz, Ag–*P*Ph$_3$), −2.7 (ddd, $^1J(P\text{–}^{109}Ag)$ = 215 Hz, $^1J(P\text{–}^{107}Ag)$ = 192.3 Hz, $^2J(P\text{–}P)$ = 30 Hz, PhB{CH$_2$*P*Ph$_2$}$_3$). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 128 MHz): δ −14.7. Anal. Calcd for $\mathrm{C_{63}H_{56}BAgP_4}$: C, 71.68; H, 5.35. Found: C, 70.87; H, 5.65.

Synthesis of $[\mathrm{PhB}\{\mathrm{CH_2P}(p\text{-}\mathrm{CF_3C_6H_4})_2\}_3]\mathrm{Ag}(\mathrm{PPh_3})$ (4). A Schlenk flask was charged with the Tl complex (200 mg, 0.154 mmol), AgOTf (40 mg, 0.154 mmol), PPh$_3$ (40 mg, 0.154 mmol), and 20 mL of THF. The mixture was stirred at room temperature for 20 min and then filtered with a plug of Celite. The resulting solid was washed with hexanes (2 × 20 mL), affording the title compound as an off-white solid (0.17 g, 75% yield). ^{1}H NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 400 MHz): δ = 7.71–7.61 (m, 10H, AgP*Ph*$_3$), 7.46–7.36 (m, 31H, AgP*Ph*$_3$, *o-Ph*B, *p*-CF$_3$*Ph*), 7.20 (t, 2H, J = 7.4 Hz, *m-Ph*B), 7.01 (t, 1H, J = 7.4 Hz, *p-Ph*B), 1.55 (br s, -BC*H*$_2$P-). ^{13}C{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 100.6 MHz): δ = 143.7 (br s, *ipso-Ph*B), 127.0, 125.04, 125.02 (*Ph*B), 132.6 (d, J = 17.0 Hz, *ipso*-P*Ph*-CF$_3$), 132.6 (d, J = 5.1 Hz, *o*-P*Ph*-CF$_3$), 130.8 (s, *m*-P*Ph*-CF$_3$), 130.2 (q, J = 32.3 Hz, *p*-P*Ph*-CF$_3$), 124.0 (q, J = 271 Hz, CF$_3$), 133.7 (d, J = 16.2 Hz, Ag–P*Ph*$_3$), 130.9 (d, J = 1.4 Hz, AgP*Ph*$_3$), 129.2 (d, J = 9.5 Hz, Ag–P*Ph*$_3$), 123.2 (s, AgP*Ph*$_3$), 18.8 (m, $\mathrm{PhB}\{\mathrm{CH_2P}(p\text{-}\mathrm{CF_3Ph})_2\}_3$). ^{31}P{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 162 MHz): δ = 16.7 (doublet of pseudoquintets, $^1J(P\text{-}^{109}Ag)$ = 416.5 Hz, $^1J(P\text{-}^{107}Ag)$ = 357.2 Hz, $^2J(P\text{–}P)$ = 29.4 Hz, Ag-*P*Ph$_3$), −2.6 (ddd, $^1J(P\text{-}^{109}Ag)$ = 210.2 Hz, $^1J(P\text{-}^{107}Ag)$ = 182.5 Hz, $^2J(P\text{–}P)$ = 29.4 Hz, $\mathrm{PhB}\{\mathrm{CH_2}P(p\text{-}\mathrm{CF_3Ph})_2\}_3$). ^{11}B{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 128 MHz): δ = −14.6 (s). ^{19}F{^{1}H} NMR ($(\mathrm{CD_3})_2\mathrm{CO}$, 376 MHz): δ = −63.4 (s). The crystalline material is highly hydroscopic, precluding appropriate values for elemental analysis.

General Procedure for Aziridination Reaction. A Schlenk flask was charged, under an argon atmosphere, with the catalyst (0.005 mmol, 5 mmol % catalyst loading), 5 mL of anhydrous CH$_2$Cl$_2$, and the substrate (0.5 mmol). The mixture was stirred for 5 min, and freshly prepared PhINTs (0.1 mmol) was added in two portions over 1 h, with the mixture being further stirred for an additional 4 h. Then, the reaction mixture was filtered through a plug of silica gel to remove the catalyst, eluted with CH$_2$Cl$_2$, and evaporated to dryness under vacuum. Conversions were calculated by ^{1}H NMR of the reaction crude, and purification was carried out by flash chromatography to provide isolated yields.

General Procedure for Competition Experiments. Following the above procedure, a mixture of styrene (0.5 mmol) and the corresponding *para*-substituted styrene (0.5 mmol) was employed. After 5 h of stirring, the catalyst was removed by filtration through a plug of silica gel. Elution with CH$_2$Cl$_2$ and concentration by rotary evaporation led to a residue that was investigated by ^{1}H NMR to provide the relative ratio of aziridines.

General Procedure for C–H Activation with PhINTs. A Schlenk flask was charged, under an argon atmosphere, with the catalyst (0.005 mmol, 5 mmol % catalyst loading) and the substrate (5 mL) as the solvent. Freshly prepared PhINTs (0.1 mmol) were added in one portion and the mixture stirred at room temperature for 5 h. Volatiles were removed under reduced pressure, and the crude was investigated by ^{1}H NMR. Purification was carried out by flash chromatography.

X-ray Crystal Determinations. A single crystal of $\mathrm{PhBP_3}^{p\text{-}\mathrm{CF3Ph}}\mathrm{Tl}$ (**2** or **3**) suitable for X-ray diffraction studies was coated with dry perfluoropolyether and mounted on a glass fiber and fixed in a cold nitrogen stream [T = 173(2) K] to the goniometer head. Data collection[25] was carried out on a Bruker-Nonius X8 kappa APEX II CCD area-detector diffractometer using graphite-monochromatic radiation λ(Mo Kα) = 0.71073 Å, by means of ω and φ scans with narrow frames. Data reduction was performed using SAINT,[25] and corrected for Lorentz polarization effects and absorption by the multiscan method applied by SADABS.[26] The structure was solved by direct methods (SIR-2002)[27] and refined against al F^2 data by full-matrix least-squares techniques with SHELXTL.[28] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. Data associated with the crystal structures of $\mathrm{PhBP_3}^{p\text{-}\mathrm{CF3Ph}}\mathrm{Tl}$ (**2 and 3**) are provided in the Supporting Information as cif files.

ASSOCIATED CONTENT

Supporting information

Spectroscopic data as a single pdf file as well as crystallographic information files in CIF format.

Notes

The authors declare no competing financial interest.

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