

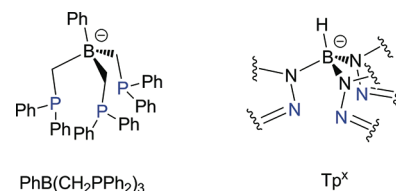
[(PhBP₃)Cu(PPh₃)] as a Surrogate of Tp^xCuL in Homogeneous Catalysis (PhBP₃ = PhB(CH₂PPh₂)₃; Tp^x = Hydrotrispyrazolylborate)

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ABSTRACT: The novel complexes [(PhBP₃)Cu(L)] (PhBP₃ = PhB(CH₂PPh₂)₃, L = PPh₃, **1**; L = tetrahydrofuran, **2**) have been synthesized and spectroscopically and, in the case of **1**, structurally characterized. Both complexes undergo dissociation of the PPh₃ or THF ligand in solution to deliver the (PhBP₃)Cu unit, similar in geometry to and isoelectronic with Tp^xCu (Tp^x = trispyrazolylborate ligand). A complete study of the catalytic properties of **1** has shown that it can be considered as a surrogate of Tp^xCu. The study includes (a) olefin cyclopropanation, cyclopropanation, cyclopropanation, aziridination, halocarbon addition, and radical polymerization, (b) X–H (X = O, N) functionalization by carbene insertion, and (c) furan conversion into dihydropyridines. Since the observed activity is quite comparable to that already described for Tp^xCu complexes, this new catalytic system could become an alternative to the latter.



INTRODUCTION

In the past decade, there has been a great development in the chemistry of trispyrazolylborate complexes (Figure 1) both in

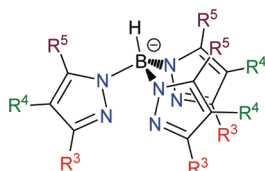


Figure 1. Trispyrazolylborate ligands (Tp^x).

the synthesis of new ligands with certain properties and in their use in catalytic transformations.¹ Among them, complexes of the type Tp^xM (M = Cu, Ag) have been found to promote a number of different transformations, such as the diazo decomposition and subsequent metal-catalyzed carbene transfer to olefins or alkynes to give cyclopropanes or cyclopropenes (Table 1, entries 1 and 2).^{2,3} Benzene has also been converted into cycloheptatrienes in the Tp^xM-catalyzed (M = Cu, Ag; Table 1, entry 3)⁴ Buchner reaction. The same methodology served to functionalize N–H and O–H (Table 1, entries 4 and 5)^{5,6} as well as an array of C–H bonds ranging from benzylic to alkylic in different substrates such as 2,3-dimethylbutane, pentane, and polyolefins (Table 1, entries 6–9).^{4,7,8} The culmination of this tool has consisted of the catalytic conversion of methane into ethyl propionate (Table 1, entry 10), recently described using Tp^xAg complexes as catalysts.⁹

Nitrene transfer from hypervalent iodine reagents (ArN=IPh) or Chloramine-T (NaCINTs) has also been described with Tp^xM as catalyst (M = Cu, Ag). The aziridination of plain olefins and a regio- and diastereoselective aziridination of allylic

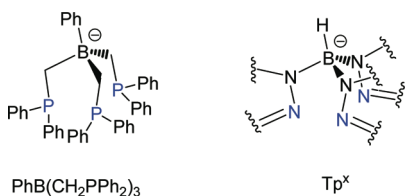
dienols have been achieved (Table 1, entries 11 and 12).^{10,11} The same complexes induced the amidation of C_{sp}²–H and C_{sp}³–H bonds by formal nitrene insertion reactions (Table 1, entries 13–15).^{12–14} In an unprecedented reaction that comprises four catalytic cycles in a one-pot fashion, furans and PhINTs were converted into 1,2-dihydropyridines, an example of concurrent catalysis catalyzed by both the copper and silver Tp^x-containing complexes (Table 1, entry 16).¹⁵

In a third type of transformation, Tp^xCu complexes have been employed as catalysts for atom transfer radical addition (ATRA) reactions (Table 1, entry 17),¹⁶ which consists of the addition of a C–Cl bond of a polyhalohydrocarbon to an olefin. The ATRP (atom transfer radical polymerization; Table 1, entry 18) process has also been promoted by Tp^xCu complexes.¹⁷

The availability of a large number of trispyrazolylborate ligands with tunable steric and electronic properties has been crucial for the success of the use of Tp^xCu complexes as catalysts for the above transformations. However, the synthetic route to these ligands, although simple (thermal reaction of pyrazoles with KBH₄),¹ often displays problems due to the formation of mixtures of products or unreacted starting materials, requiring a purification process that is also somewhat complex. It would be therefore useful to develop a similar system, electronically and sterically tunable as well, but easier from a preparative point of view. With this idea in mind, we have turned to the tris(phosphino)borate ligand^{18–20} [PhB(CH₂PPh₂)₃][–] (tris((diphenylphosphino)methyl)phenylborate, PhBP₃), which resembles the structure of trispyrazolylborate ligands to a certain extent. Thus, as shown in Figure 2, this PhBP₃ ligand

Table 1. Reactions Catalyzed by Tp^xM ($\text{M} = \text{Cu}, \text{Ag}$) Compounds

Entry	Reactant	Reactant	Product	Ref.	Entry	Reactant	Reactant	Product	Ref.
1				2	10	CH_4		$\text{CH}_3\text{CH}_2\text{CO}_2\text{Et}$	9
2	$\text{R}-\text{C}\equiv\text{C}-\text{R}'$			3	11		PhI=NTs NaCINTs		10
3				4	12		PhI=NTs		11
4	RNH_2		$\text{RNHCH}_2\text{CO}_2\text{Et}$	5	13		PhI=NTs		12
5	ROH		$\text{ROCH}_2\text{CO}_2\text{Et}$	6	14		PhI=NTs		12, 13
6				4	15		PhI=NTs		14
7				7	16		PhI=NTs		15
8				7	17	$\text{R}-\text{C}\equiv\text{C}-\text{R}$	CXCl_3		16
9				8	18	$\text{R}-\text{C}\equiv\text{C}-\text{R}$	Initiator		17

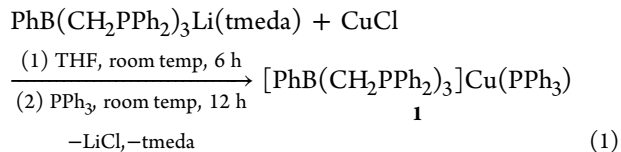

Figure 2. $\text{PhB}(\text{CH}_2\text{PPh}_2)_3$ and Tp^x ligands.

is also anionic in nature, with three donor atoms, and provides five electrons to the metal center (considering the neutral electron counting formalism). Although several transition-metal complexes bearing this PhBP_3 ligand have been independently reported by Tilley,¹⁹ Peters,²⁰ and Nocera,¹⁸ its coordination chemistry with copper is yet unknown, with the exception of the related, but bidentate, $\text{Ph}_2\text{BP}^t\text{Bu}_2$ ligand that afforded $\text{Ph}_2\text{BP}^t\text{Bu}_2\text{CuL}$ complexes.²¹ It is worth mentioning that Marks and co-workers have described a series of silver complexes of composition $\text{BP}_3\text{Ag}(\text{PR}_3)$.²² In this contribution we report the synthesis and structural characterization of the complexes $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]\text{Cu}(\text{PPh}_3)$ (**1**) and $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]\text{Cu}(\text{THF})$ (**2**) and the use of the former as a catalyst precursor for an array of transformations previously described with Tp^xCuL as the catalyst. The results obtained in this work allow us to propose that $\text{PhBP}_3\text{Cu}(\text{PPh}_3)$ serves as a surrogate for the latter, opening up the development of related complexes that could improve the catalytic performance in those transformations.

RESULTS AND DISCUSSION

Synthesis of the Complex $[(\text{PhBP}_3)\text{Cu}(\text{PPh}_3)]$ (1**).** This compound was prepared by direct reaction of $[(\text{PhBP}_3)]\text{Li}(\text{tmeda})$ ¹⁸ and CuCl in tetrahydrofuran as the solvent. After 6 h

of stirring at room temperature, 1 equiv of PPh_3 was added and the mixture stirred for an additional 12 h (eq 1). After workup, **1** was obtained as a colorless crystalline material.



The ^1H NMR spectrum showed the characteristic signals for both the $\text{PhB}(\text{CH}_2\text{PPh}_2)_3$ and PPh_3 ligands, evidencing a C_3 symmetry on the basis of the equivalency of the three arms of the tripod ligand. In addition, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consisted of two broad singlets centered at $\delta -4.81$ and -5.82 ppm, assigned respectively to the PPh_3 and PPh_2 groups of the ligands (see the Supporting Information). The lack of observance of coupling could be interpreted as a consequence of a fluxional process in which the PPh_3 ligand is undergoing a relatively fast coordination–decoordination process. In order to ascertain the exact structure of the molecules of **1**, an X-ray diffraction study was carried out with single, colorless crystals grown from THF solutions. As shown in Figure 3, the structure of complex **1** consists of a distorted-tetrahedral geometry with a P_4 copper unit, one P donor from the coordinated PPh_3 ligand and the other three from the tridentate ligand PhBP_3 , in the first example of a copper complex of this anionic PhBP_3 ligand. The distances $\text{Cu}-\text{P}(\text{PPh}_3)$ of 2.242(2) Å compares well with that of 2.241(3) Å in the cationic complex $[(\text{triphos})\text{Cu}(\text{PPh}_3)]\text{PF}_6$ (triphos = $\text{MeC}(\text{CH}_2\text{PPh}_2)_2$).²³ The same similarity is observed with the average of $\text{Cu}-\text{PPh}_2$ distances 2.32 and 2.36 Å, respectively, for **1** and the cationic complex.

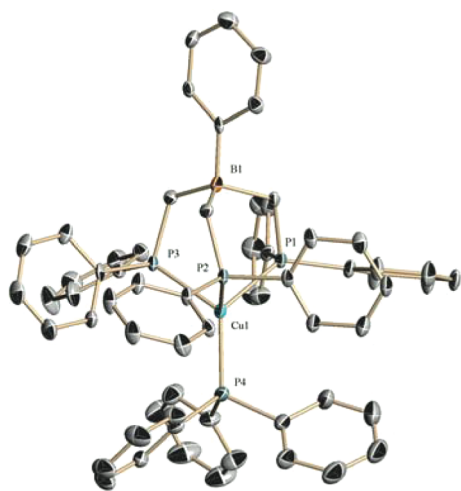


Figure 3. ORTEP view of the molecules of **1**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

A comparison of the structures of the PhBP_3Cu and $\text{Tp}^{\text{Me}_2}\text{Cu}$ fragments (obtained by removal of the PPh_3 ligand from the corresponding $\text{Tp}^{\text{Me}_2}\text{Cu}(\text{PPh}_3)^{24}$ and $\text{PhBP}_3\text{Cu}(\text{PPh}_3)$ X-ray structures) is shown in Figure 4. The relative

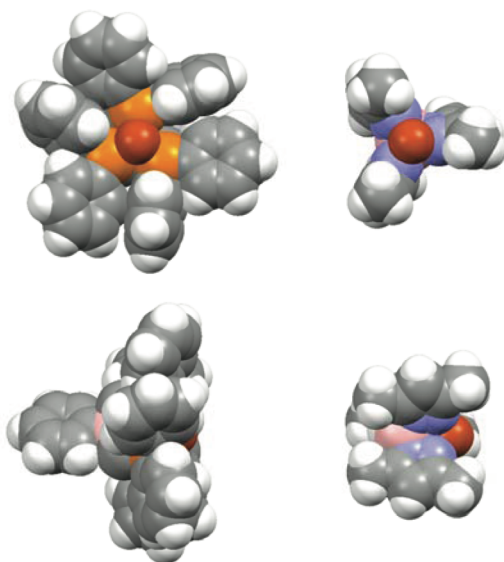
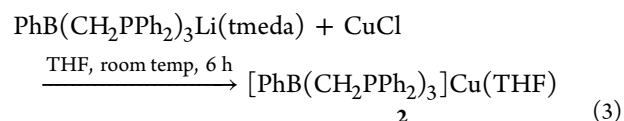
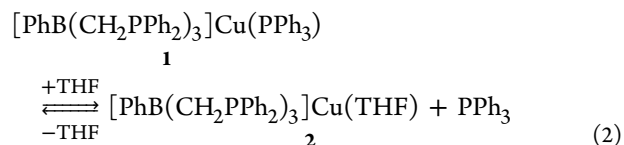


Figure 4. Front and side views of the $\text{PhB}(\text{CH}_2\text{PPh}_2)_3\text{Cu}$ (left) and $\text{Tp}^{\text{Me}_2}\text{Cu}$ (right) fragments obtained by removal of the PPh_3 ligand of the corresponding $\text{PhB}(\text{CH}_2\text{PPh}_2)_3\text{Cu}(\text{PPh}_3)$ and $\text{Tp}^{\text{Me}_2}\text{Cu}(\text{PPh}_3)$ X-ray structures.

position of the copper center with regard to the ancillary ligand differs from one case to the other. In the P-containing ligand, the metal center is somewhat aligned with the pendant phenyl groups. However, the copper ion is slightly embedded in the pocket originated by the pyrazolyl substituents. Therefore, the catalytic pocket seems to be larger in the former, and this feature should have the corresponding effect during catalysis.

During crystallization, white crystalline material was also obtained that gave a unique resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, very similar to that of complex **1**, but lacking in the PPh_3 resonance. The ^1H NMR spectrum displayed the resonances of the BP_3 ligand along with those expected for

one coordinated THF molecule. Elemental analyses confirmed the composition of $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]\text{Cu}(\text{THF})$ for this new complex. It seems that, in THF solution, a ligand exchange equilibrium takes place (eq 2), the PPh_3 ligand being replaced by the THF molecule. The synthesis of **1** was improved by dissolving the reaction residue in methylene chloride and crystallizing from this solvent. On the other hand, complex **2** can be prepared directly from $[(\text{PhBP}_3)]\text{Li}(\text{tmeda})$ and CuCl (eq 3), followed by further crystallization from THF.



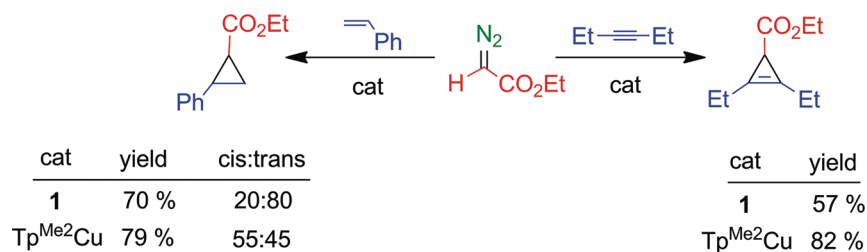
On the other hand, to gain information about the electronic properties of the PhBP_3 ligand, the carbonyl derivative $[(\text{PhBP}_3)\text{Cu}(\text{CO})]$ was generated upon bubbling of carbon monoxide through a solution of **1** or **2** at room temperature. Once the volatiles were removed, the IR of the resulting solid showed one absorption at 2055 cm^{-1} , a value slightly lower than that reported for $\text{Tp}^{\text{Me}_2}\text{Cu}(\text{CO})$ ($\nu(\text{CO})\ 2060\text{ cm}^{-1}$).²⁵ Therefore, the electron density of the BP_3 derivative seems to be slightly higher than in the $\text{Tp}^{\text{Me}_2}\text{Cu}$ complex.

At this point, we could conclude that the complex $[(\text{PhBP}_3)\text{Cu}(\text{PPh}_3)]$ displays some differences compared to the $\text{Tp}^{\text{Me}_2}\text{Cu}$ complex. First, the potential catalytic pocket available at complex **1** seems to be larger than that of the $\text{Tp}^{\text{Me}_2}\text{Cu}$ unit. Second, from an electronic point of view, the copper center at **1** possesses a higher electron density than in $\text{Tp}^{\text{Me}_2}\text{Cu}$. These features should be somewhat reflected in the catalytic behavior, as discussed below.

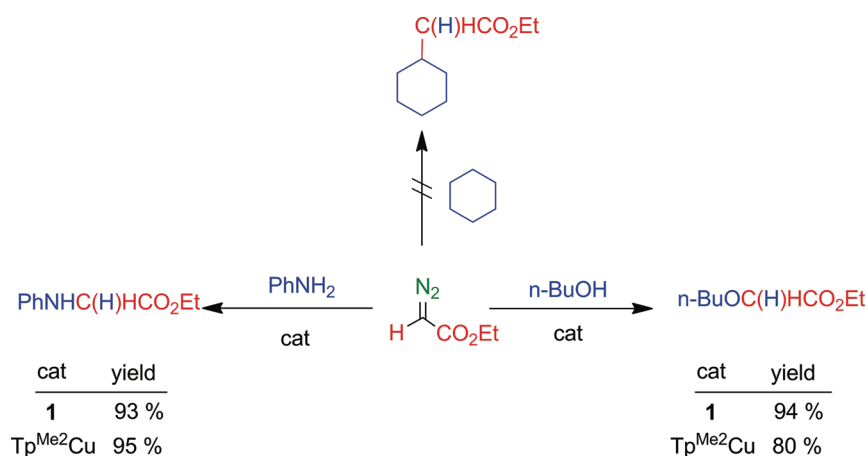
Catalytic Activity of $[(\text{PhBP}_3)\text{Cu}(\text{PPh}_3)]$ (1**).** (a). *Carbene Transfer Reactions.* Once the complex $[(\text{PhBP}_3)\text{Cu}(\text{PPh}_3)]$ was synthesized and characterized, it was employed as the catalyst precursor in some of the organic transformations shown in the Introduction (Table 1). On the basis of the electronic properties mentioned above, complex **1** should be a good catalyst for those reactions that do not require a somewhat electron deficient metal center. We should not therefore expect good results when employing this complex as the catalyst in carbene or nitrene insertion reactions into C–H bonds.^{7,12–14} On the other hand, those reactions in which a relatively electron rich metal center is preferred, such as ATRA or ATRP,^{16,17} should be induced catalytically by **1**. The addition of carbene or nitrene moieties to unsaturated substrates (olefins, alkynes)^{23,26} is not greatly affected by the electronic density (Tp^xCu complexes with an array of electron-deficient and electron-rich Tp^x ligands similarly catalyze those reactions), suggesting that **1** could also induce them.

The first group of reactions, where the catalytic ability of the new complex **1** was tested, was the addition of carbene units, from ethyl diazoacetate, to unsaturated hydrocarbons, resulting in the formation of cyclopropanes and cyclopropenes (Scheme 1). In the cyclopropanation reaction of styrene, the catalyst/EDA/styrene mixture (1/20/160 ratio) was stirred at room temperature until no EDA was detected by GC (8 h), with a 70% yield. In the case of the cyclopropanation reaction with 3-hexyne as

Scheme 1. Catalytic Carbene Transfer from Ethyl Diazoacetate Catalyzed by **1**

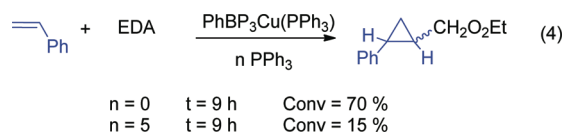


Scheme 2. Catalytic Carbene Insertion from EDA into N–H and O–H Bonds Catalyzed by **1**



substrate, the diazo compound was added slowly, with the aid of a syringe pump, for 15 h to avoid the formation of EDA-coupling products (diethyl fumarate and maleate)²⁷ to give cyclopropane in 57% yield. The lower catalytic activity is due to the high electron density at the metal center, since the diazo compound decomposition is favored by electrophilic metal catalysts.²⁸ The cis/trans diastereoselectivity provided in the cyclopropanation reaction was 20/80, opposite to that observed with Tp^xCu complexes, since complex **1** gave a trans selectivity higher than that for the Tp^{Me2}Cu complex.^{2b} This result must be related to the larger catalytic pocket in the PhBP₃Cu unit compared to that in Tp^{Me2}Cu shown in Figure 4. Thus, the formation of the bulkier *trans*-cyclopropane is more favored by complex **1**.

The above explanation is based on our assumption that the active species during catalysis is the 14-electron “PhBP₃Cu” unit. To test this, we carried out two twin experiments only differing in the amount of added excess of PPh₃, as shown in eq 4.



The yield in cyclopropanes drastically decreased in the presence of the large excess, indicating the decoordination of the PPh₃ ligand from **1** as the first step in this catalytic transformation.

We have also studied the potential of this system toward N–H and O–H functionalization (Scheme 2). Complex **1** catalyzed the insertion of the CHCO₂Et group, generated from EDA, into the N–H bond of aniline, using a [Cu]/[EDA]/[aniline] ratio of 1/40/100, respectively. In a similar manner, the use of *n*-butanol as substrate afforded the insertion product into the

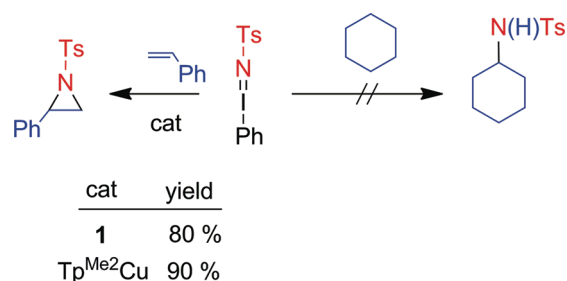
O–H bond (Scheme 2). The yields obtained in both reactions were at least comparable to those already reported for the Tp^{Me2}Cu complex.^{5a,6} Nevertheless, when the new complex **1** was employed as catalyst in the carbene insertion reaction into the C–H bonds of cyclohexane, no formation of the insertion product was detected, in good agreement with the electron-rich nature of the metal center. It is noteworthy that NMR spectra of the residue obtained at the end of the catalytic reactions showed the resonances of the initial catalyst, evidencing the lack of noticeable decomposition along the process.

We have also explored the potential of the THF adduct **2** as a catalyst for the above transformations. The results obtained were quite similar in terms of activities and selectivities, in good agreement with the proposal of a unique BP₃Cu core as responsible for the catalytic reaction. However, prolonged reaction times showed in some cases a certain bluish coloration of the reaction mixture, typical of copper oxidation. Therefore, we preferred to explore the catalytic potential with the phosphine adduct.

(b). *Nitrene Transfer Reactions.* A third group of reactions based on the addition or insertion of nitrene units, with PhINTs as the nitrene source, to unsaturated or saturated hydrocarbons has been studied (Scheme 3). In the styrene aziridination reaction, a [I]/[PhI=NTs]/[styrene] ratio of 1/20/100 gave the corresponding aziridine in 80% yield. Again, however, as observed in the carbene insertion reactions, we did not observe any product derived from nitrene insertion into the C–H bonds of cyclohexane when complex **1** was used as catalyst. It is worth mentioning that Tp^{Me2}Cu does not catalyze the latter reaction either.

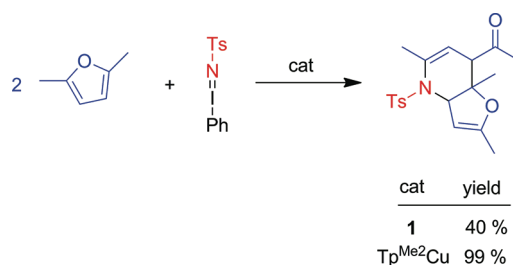
We have recently described a novel transformation where the Tp^{Me2}Cu complex catalyzes the conversion of furans into 1-(3a,4,7,7a-tetrahydro-2,5-dimethyl-4-tosylfuro[3,2-*b*]pyridin-7-yl)ethanone,¹⁵ the bicyclic compound shown in Scheme 4,

Scheme 3. Catalytic Nitrene Transfer Reactions from PhINTs Catalyzed by 1



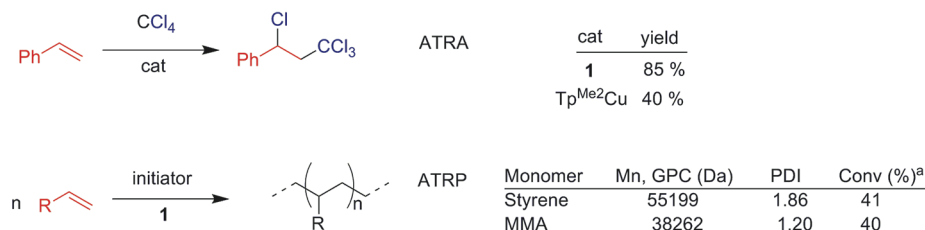
derived from two molecules of furan and one NTs fragment. The use of **1** as catalyst precursor also induced this transformation, in 40% yield (Scheme 4).

Scheme 4. Conversion of 2,5-Dimethylfuran into 1,2-Dihydropyridines Catalyzed by 1



(c). *Atom Transfer Radical Reactions.* Previous work from our laboratory has shown that atom transfer radical addition (ATRA) of polyhalogenated alkenes to olefins is catalyzed by Tp^xCu complexes.¹⁶ The best results were obtained with electron-donating Tp^x ligands. Consequently, the complex [(PhBP₃)Cu(PPh₃)] could be a good candidate to catalyze this reaction. In a typical procedure, a solution of complex **1** in CD₂Cl₂ containing 300 equiv of styrene and 1200 equiv of CCl₄ was maintained at 90 °C for 60 h. The final mixtures contained the desired product in 85% yield (Scheme 5), a conversion significantly higher than that already reported for Tp^{Me2}Cu as the catalyst.^{16a} We have also employed the complex [(PhBP₃)Cu(PPh₃)] as a catalyst in ATRP reactions with several olefins. As shown in Scheme 5, the conversions as well as the PDI values are moderate. Matyjaszewski and co-workers already described the use of Tp^{Me2}Cu as the catalyst for styrene polymerization.^{17b} At shorter reaction times (4 h), yields of 75% were obtained. However, the polydispersity value $M_w/M_n = 3.82$ was found, much higher than that obtained with **1**.

Scheme 5. Atom Transfer Radical Reactions Catalyzed by 1.



CONCLUSIONS

We have synthesized and characterized the novel copper complex [(PhBP₃)Cu(PPh₃)], containing a trisphosfinoborate ligand. The catalytic behavior of this complex toward a series of transformations already described with Tp^xCu has been established. Collected data allow describing **1** as a good surrogate of the Tp^xCu complexes for catalytic purposes. The preparation of other PhBP₃Cu complexes with the appropriate substituent at the P donors could provide the required electronic and/or steric properties to build a new family of catalysts for a number of transformations.

EXPERIMENTAL SECTION

General Procedures. 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 before their use. All the reagents were purchased from Aldrich and were used as received, with the exception of the olefins for the radical reactions, which were filtered through alumina before use. GC data were collected with a Varian 3900 instrument. NMR spectra were recorded on a Varian Mercury 400 MHz and gel permeation chromatography (GPC) on a Waters GPC system. [PhB(CH₂PPh₂)₃][Li(TMEDA)] was prepared according to literature methods.^{18–20} For all the reactions previously reported by our group, blank experiments in the absence of catalyst or ligand had already been performed.^{2–17,26,27}

Synthesis of [(PhBP₃)Cu(PPh₃)] (1**).** Copper(I) chloride (49.5 mg, 0.5 mmol) was added to a solution of [PhB(CH₂PPh₂)₃][Li(TMEDA)] (404 mg, 0.5 mmol) in tetrahydrofuran (10 mL). The mixture was stirred for 6 h. Then, 1 equiv of PPh₃ (131 mg, 0.5 mmol) was added and the mixture stirred overnight. 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 PPh₃ was added to disfavor the displacement of PPh₃ by THF. After concentration and cooling overnight at –20 °C, complex **1** was obtained as white crystals in 60% yield, some of them suitable for X-ray studies. Crystallization from dichloromethane was also successful, without the need of additional PPh₃, but no single crystals could be grown. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.52 (d, 2 H, *o*-PhB(CH₂PPh₂)₃), 7.25 (m, 21 H, PhB(CH₂PPh₂)₃CuPPh₃), 7.14 (m, 2 H, *m*-PhB(CH₂PPh₂)₃), 7.06 (m, 7 H, PhB(CH₂PPh₂)₃), 6.94 (t, 1 H, *p*-PhB(CH₂PPh₂)₃), 6.84 (m, 17 H, PhB(CH₂PPh₂)₃), 1.40 (br s, 6 H, PhB(CH₂PPh₂)₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ –4.81 (br s, –CuPPh₃), –5.82 (br s, PhB(CH₂PPh₂)₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 140.7 (m), 131.8, 127.4, 123.6 (PhB(CH₂PPh₂)₃), 134.6, 134.4, 132.9, 132.8, 132.7, 130.2, 129.1, 128.9, 128.4 (PhB(CH₂PPh₂)₃), 134.4, 134.2, 130.1, 129.1 (CuPPh₃), 18.5 (m, PhB(CH₂PPh₂)₃). Anal. Calcd for C₆₃H₅₆BCuOP₄: C, 74.82; H, 5.58. Found: C, 74.16; H, 5.86.

Synthesis of [(PhBP₃)Cu(THF)] (2**).** Copper(I) chloride (49.5 mg, 0.5 mmol) was added to a solution of [PhB(CH₂PPh₂)₃][Li(TMEDA)] (404 mg, 0.5 mmol) in tetrahydrofuran (10 mL). The mixture was stirred for 6 h. The solution was filtered, and the solvent was removed under vacuum to yield a white powder. The solid was crystallized from THF solution at –20 °C in 60% yield. ¹H NMR

^a Yield obtained by gravimetric analysis

(400 MHz, CD₂Cl₂): δ 7.52 (d, 2 H, *o*-PhB(CH₂PPh₂)₃), 7.25 (m, 6 H, PhB(CH₂PPh₂)₃), 7.14 (m, 2 H, *m*-PhB(CH₂PPh₂)₃), 7.06 (m, 7 H, PhB(CH₂PPh₂)₃), 6.94 (t, 1 H, *p*-PhB(CH₂PPh₂)₃), 6.84 (m, 17 H, PhB(CH₂PPh₂)₃), 3.70 (t, 2 H, -OCH₂CH₂), 1.83 (t, 2 H, -OCH₂CH₂-), 1.40 (br s, 6 H, PhB(CH₂PPh₂)₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ -5.82 (br s, PhB(CH₂PPh₂)₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 140.7 (m), 131.8, 127.4, 123.6 (*PhB*(CH₂PPh₂)₃), 134.6, 134.4, 132.9, 132.8, 132.7, 130.2, 129.1, 128.9, 128.4 (PhB(CH₂PPh₂)₃), 66.3 (-OCH₂CH₂), 22.9 (-OCH₂CH₂-), 18.5 (m, PhB(CH₂PPh₂)₃). Anal. Calcd for C₄₉H₄₉BCuOP₃: C, 71.67; H, 6.01. Found: C, 71.77; H, 5.66.

Structure Determination. Crystal data for [PhBP₃]₃Cu(PPh₃): C₆₃H₅₀BCuP₄C₄H₈O, *M*_r = 1077.36, orthorhombic, space group *Pbca*, *a* = 20.3770(19) Å, *b* = 17.9161(17) Å, *c* = 33.864(3) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *V* = 12362.9(19) Å³, *Z* = 8, *D*_{exptl} = 1.158 Mg/m³, μ (Mo *K* α) = 0.496 mm⁻¹. A crystal grown from THF, of size 0.40 × 0.06 × 0.05 mm³, coated with dry perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream (*T* = 173(2) K). X-ray diffraction data were collected on a Bruker-Nonius X8Apex-II CCD diffractometer, operating with graphite-monochromated Mo *K* α ₁ radiation, λ = 0.710 73 Å and a Kryoflex low-temperature device. A total of 87 281 reflections were measured, 12 636 of which were independent (*R*_{int} = 0.0802) and were used in all calculations. The data were reduced up to θ = 26.44° by the program SAINT²⁹ and corrected for Lorentz-polarization and absorption effects by a multiscan method applied by SADABS;²⁹ the structure was solved by direct methods (SIR-2002)³⁰ and refined against all *F*² data by full-matrix least-squares techniques (SHELXL97)³¹ minimizing $w[F_o^2 - F_c^2]^2$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and allowed to ride on the attached carbon atoms with the isotropic temperature factors (*U*_{iso} values) fixed at 1.2 times those *U*_{eq} values of the corresponding carbon atoms. For *F*² > 2 σ (*F*²), the final *R*₁ value was 0.0620 and the final *wR*(*F*²) value was 0.1453. For all data, the final *R*₁ value was 0.0938 and the final *wR*(*F*²) value was 0.1921. The goodness of fit on *F*² was 1.040, the largest difference peak and hole being 0.867 and -1.755 e Å⁻³, respectively.

General Catalytic Experiments. *Cyclopropanation of Styrene with Ethyl Diazoacetate.* Complex **1** (25.2 mg, 0.025 mmol) was dissolved in dichloromethane (10 mL), styrene (458 μ L, 4 mmol) and ethyl diazoacetate (52.6 μ L, 0.5 mmol) being added in one portion. The mixture was stirred for 8 h at room temperature. The consumption of ethyl diazoacetate was monitored by GC. Volatiles were removed under reduced pressure and the crude reaction product was dissolved in CDCl₃. 9-Anthracenecarboxaldehyde was added as internal standard (60 mg, 0.29 mmol), the conversion and yields being calculated by ¹H NMR.

Cyclopropanation of 3-Hexyne with Ethyl Diazoacetate. Complex **1** (25.2 mg, 0.025 mmol) was dissolved in dichloromethane (10 mL) along with 3-hexyne (284 μ L, 2.5 mmol). A solution of ethyl diazoacetate (105.2 μ L, 1 mmol) in dichloromethane (10 mL) was added slowly with the aid of a syringe pump over 15 h at room temperature. The consumption of ethyl diazoacetate was monitored by GC.

N-H and O-H Functionalizations by Carbene Insertion. (a) *N-H Bond Functionalization.* Complex **1** (25.2 mg, 0.025 mmol) was dissolved in dichloromethane (10 mL). Aniline (228 μ L, 2.5 mmol) and ethyl diazoacetate (105.2 μ L, 1 mmol) were added in one portion. After 12 h of stirring at room temperature, no ethyl diazoacetate was detected by GC. The solvent was removed under reduced pressure, and the residue was dissolved in CDCl₃ for analysis by ¹H NMR spectroscopy. 9-Anthracenecarboxaldehyde was added as internal standard (64 mg, 0.31 mmol), the conversion and yields being estimated by ¹H NMR.

(b) *O-H Bond Functionalization.* To a dichloromethane solution (10 mL) of complex **1** (25.2 mg, 0.025 mmol) was added *n*-butanol (229 μ L, 2.5 mmol). Then, a solution of ethyl diazoacetate (105.2 μ L, 1 mmol) in dichloromethane (10 mL) was added with the aid of a syringe pump for 12 h at room temperature. After that time, the

reaction mixture was analyzed by GC and no ethyl diazoacetate was detected.

Styrene Aziridination Reaction. Complex **1** (12.6 mg, 0.0125 mmol) and styrene (143.2 μ L, 1.25 mmol) were dissolved in dichloromethane (5 mL), before PhINTs (93 mg, 0.25 mmol) was added in one portion. The mixture was stirred for 8 h at room temperature; no solid PhINTs was observed after that time. The volatiles were removed under vacuum, and the residue was dissolved in CDCl₃. 9-Anthracenecarboxaldehyde was added as internal standard (12 mg, 0.06 mmol), the conversion and yields being calculated by ¹H NMR.

Reaction of 2,5-Dimethylfuran with PhINTs. Complex **1** (12.6 mg, 0.0125 mmol) and 2,5-dimethylfuran (1.07 mL, 10 mmol) were dissolved in dichloromethane (5 mL), and PhINTs (93 mg, 0.25 mmol) was added in one portion. After 8 h of stirring and removal of volatiles, the residue was dissolved in CDCl₃. 9-Anthracenecarboxaldehyde was added as internal standard (9.4 mg, 0.045 mmol), the conversion and yields being calculated by ¹H NMR.

Atom Transfer Radical Addition (ATRA) of CCl₄ to Styrene. A solution of complex **1** (5 mg, 0.005 mmol), styrene (172 μ L, 1.5 mmol), and CCl₄ (580 μ L, 6 mmol) was prepared in CD₂Cl₂ (0.4 mL). The solution was transferred into a pressure NMR tube with a Teflon cap. The tube was removed from the glovebox and placed into an oil bath at 90 °C. Biphenyl was added as internal standard (62 mg, 0.30 mmol); the conversion and yields were calculated by ¹H NMR at the end of the reaction.

Atom Transfer Radical Polymerization (ATRP) to Olefins. To a solution of complex **1** (30.3 mg, 0.03 mmol) in the corresponding olefin (9 mmol) was added *p*-toluenesulfonyl chloride (5.7 mg, 0.03 mmol), with toluene (1 mL) as the solvent. The reaction was heated to 80 °C for methyl methacrylate (MMA) or for styrene. The polymer was later precipitated with methanol and was separated from solution. The resulting solid was dried for 24 h. Conversions were determined by gravimetric analysis previous to the GPC analysis.

ASSOCIATED CONTENT

Supporting Information

Figures giving ¹H and ³¹P NMR spectra of [(PhB(CH₂CH₂PPh₂)₃)Cu(PPh₃)] and [(PhB(CH₂CH₂PPh₂)₃)Cu(THF)] and a CIF file giving X-ray data for the determination of the structure of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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