Inorg. Chem. **2009**, *48*, 16−18

Inorganic Chemistry

Communication

Strong Coordination of Tetraphenylborate Anion to Copper(I) Bipyridine and Phenanthroline-Based Complexes and Its Effect on Catalytic Activity in the Cyclopropanation of Styrene

Carolynne Ricardo, Lauren M. Matosziuk, Jeffrey D. Evanseck, and Tomislav Pintauer*

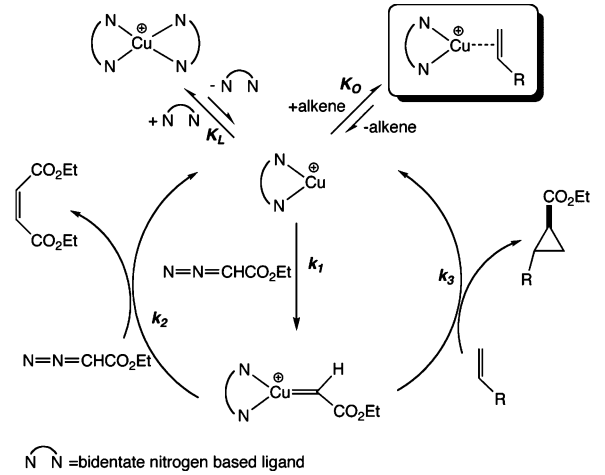
Department of Chemistry and Biochemistry, Duquesne University, 600 Forbes Avenue, 308 Mellon Hall, Pittsburgh, Pennsylvania 15282

Received September 18, 2008

The synthesis, characterization, and cyclopropanation activity of tetrahedral copper(I) complexes with bipyridine- and phenanthroline-based ligands containing strongly coordinated tetraphenylborate anions are reported. $Cu^I(bpy)(BPh_4)$, $Cu^I(phen)(BPh_4)$, and $Cu^I(3,4,7,8\text{-}Me_4phen)(BPh_4)$ complexes are the first examples in which the BPh_4^- counterion chelates a transition metal center in bidentate fashion through η^2 π interactions with two of its phenyl rings.

The asymmetric transition-metal-catalyzed transfer of carbene moieties generated from diazo reagents onto the prochiral face of an olefin to form a cyclopropane ring is a widely used reaction in organic synthesis.[1,2] Effective catalytic systems for this reaction require the use of a transition metal complex which facilitates the loss of N_2 from the diazo reagent as well as stabilizes intermediate carbene species against competing carbene dimerization. A variety of transition metal complexes have been found to be active in cyclopropanation reactions, and they include the complexes of Fe, Rh, Ru, and Cu. Copper appears to be particularly attractive because of its low cost relative to other transition metal complexes. So far, cationic and neutral copper(I) complexes in conjunction with a C_2-symmetric nitrogen-based ligands have been successfully used in cyclopropanation reactions.[3] However, despite a tremendous effort directed toward empirical catalyst development, the mechanism of this very important synthetic reaction is still not fully understood. It is generally accepted that copper-catalyzed cyclopropanation reactions proceed via a copper−carbene intermediate, as indicated in Scheme 1. However, the details of this process are not well-known. Only very recently, copper−carbene complexes have been detected as reaction intermediates in cyclopropanation reactions utilizing low-temperature NMR measurements and X-ray diffraction.[4,5] Another key mechanistic feature of this reaction includes the role of the monomer and counterion, both of which are poorly understood. Mechanistic and computational studies have indicated that copper(I)/olefin complexes in these systems might act as either catalytically active species or resting states.[6] Furthermore, the reactivity of cationic copper(I) complexes is strongly influenced by the counterion. Triflates and hexafluorophosphates were found to be highly effective catalysts, whereas halides, cyanides, acetates, and perchlorate showed little or no catalytic activity.[6]

Scheme 1. Proposed Mechanism for Copper(I) Catalyzed Cyclopropanation of Alkenes



In a recent study, our research group reported on the synthesis, characterization, and cyclopropanation activity of a series of well-defined $[Cu^I(2,2'\text{-bpy})(\pi\text{-M})][A]$ (M = styrene and methyl acrylate; A = ClO_4^-, PF_6^-, and $CF_3SO_3^-$) com-

---

* Author to whom correspondence should be addressed. Tel: +412-396-1626, Fax: 412-396-5683, Email: pintauert@duq.edu

(1) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley: New York, 1998.

(2) Pfaltz, A. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999; Vol. *II*.

(3) Chelucci, G.; Thummel, R. P. *Chem. Rev.* **2002**, *102*, 3129–3170.

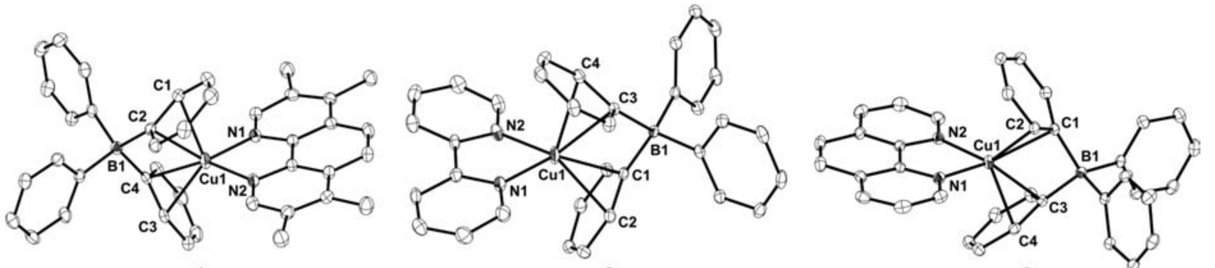
(4) Dai, X.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 10085–10094.

(5) Straub, B. F.; Hofmann, P. *Angew. Chem., Int. Ed.* **2001**, *113*, 1328–1330.

(6) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742–2753.

10.1021/ic801783r CCC: $40.75

© 2009 American Chemical Society
Published on Web 12/09/2008



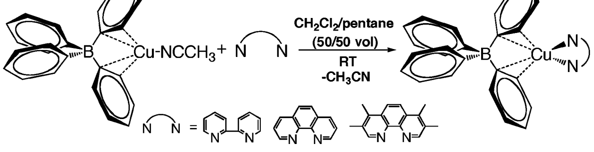
1 2 3

Figure 1. Molecular structures of [Cu^I(3,4,7,8-Me_4phen)(BPh_4)]·3CH_2Cl_2 (**1**), Cu^I(bpy)(BPh_4) (**2**), and Cu^I(phen)(BPh_4) (**3**) shown with thermal ellipsoids at 50% probability. H atoms and solvent molecules have been omitted for clarity.

plexes.[7,8] In the solid state, all complexes were distorted trigonal pyramidal in geometry, and the copper(I) atom was coordinated by two nitrogen atoms of the bpy ligand, two olefinic carbon atoms of alkene in the equatorial position, and a weakly coordinated counterion in the axial position. Moreover, in the case of styrene, the axial coordination of the counterion observed in the solid state was found to have a small effect on the binding constant of styrene to [Cu^I(bpy)]$^+$ cations in solution, resulting in similar cyclopropanation activities. In our effort to isolate and structurally characterize copper(I)/styrene complexes with much weaker coordinating anions, we observed a novel mode of coordination of BPh_4^- anions to copper(I) complexes with neutral bidentate nitrogen-based ligands. In this article, we report on the synthesis, characterization, and cyclopropanation activity of tetrahedral copper(I) complexes with bipyridine- and phenanthroline-based ligands containing strongly coordinated BPh_4^- anions.

The starting copper(I) complex for the syntheses of Cu^I(3,4,7,8-Me_4phen)(BPh_4) (**1**), Cu^I(bpy)(BPh_4) (**2**), and Cu^I(phen)(BPh_4) (**3**) was obtained by methathesis of the perchlorate salt [Cu^I(CH_3CN)$_4$][ClO_4] with $NaBPh_4$ in CH_3CN/H_2O, according to a modified literature procedure.[9] This reaction did not yield the expected [Cu^I(CH_3CN)$_4$][BPh_4] complex, but rather [Cu^I(CH_3CN)][BPh_4], the composition of which was confirmed by elemental analysis and ^{1}H NMR. The loss of CH_3CN after prolonged in vacuo treatment has been observed previously in [Cu^I(CH_3CN)$_4$][BF_4] and [Cu^I(CH_3CN)$_4$][B(C_6H_5)$_4$] complexes.[10] We were unable to obtain crystals of [Cu^I(CH_3CN)][BPh_4] suitable for X-ray diffraction studies; however, on the basis of the molecular structures of **1**, **2**, and **3** (Figure 1), one possibility would include a tricoordinated copper(I) complex, as indicated in Scheme 1. The reaction of [Cu^I(CH_3CN)][BPh_4] with a stoichiometric amount of bipyridine- or phenanthroline-based ligand in CH_2Cl_2, followed by slow diffusion of pentane, afforded crystals of **1**, **2**, and **3** in 92%, 55%, and 40% yield, respectively (Scheme 2).

Scheme 2. Synthesis of Copper(I) Complexes **1−3**



Shown in Figure 1 are the molecular structures of **1−3**. In all three complexes, bidentate coordination of the nitrogen ligand was observed (Cu^I−N_{av} = 2.047(3) Å (**1**), 2.062(3) Å (**2**), and 2.055(2) Å (**3**)) and the distorted tetrahedral coordination around the Cu^I atom was completed by two π interactions with a C═C double bond of the adjacent phenyl rings in the BPh_4^- anion (Cu^I−$C_{mid,1-2}$ = 2.289(5) Å (**1**), 2.148(3) Å (**2**), 2.121(**3**) Å (**3**); Cu^I−$C_{mid,3-4}$ = 2.073(4) Å (**1**), 2.236(6) Å (**2**), 2.203(3) Å (**3**)). On the basis of extensive literature and CCDB searches, such coordination of the BPh_4^- anion to transition metal complexes has never been observed before. With the exception of one example of η^2-coordination (Cu^I($NH_2CH_2CH_2NH_2$)(CO)(η^2-BPh_4)), all of the structures reported so far exhibit η^6-coordination (e.g., Ru(Cp)(η^6-BPh_4) and Rh(P(OMe$_3$)$_2$(η^6-BPh_4)).[11]

The coordination of BPh_4^- to the copper(I) center in **1−3** did not result in a significant change in the geometry of the anion. The bent angle between the B atom and adjacent C atoms in the coordinated phenyl rings (104.3(2)° (**1**), 103.1(2)° (**2**), and 101.92(11)° (**3**)) was slightly smaller than the corresponding angle for the uncoordinated ones (112.3(2)° (**1**), 111.3(**2**)° (**2**), and 113.84(11)° (**3**)). In copper(I) complexes with noncoordinating BPh_4^- anions, these two angles are also different (101−105° and 110−114°).[12] Furthermore, Cu^I−C bond distances for π-coordinated C═C bonds in phenyl rings (1.412(3) and 1.415(4) Å (**1**); 1.412(3) and 1.413(4) Å (**2**); 1.410(2) and 1.4118(18) Å (**3**)) did not change significantly upon coordination.

The coordination of the BPh_4^- anion to the copper(I) center can be suppressed using sterically more-hindered 2,9-Me_2phen. In the case of this ligand, we observed a quantitative formation of the [Cu^I(2,9-Me_2phen)(CH_3CN)][BPh_4] complex (see the Supporting Information). In [Cu^I(2,9-Me_2phen)(CH_3CN)][BPh_4], the counterion was found to be noncoordinating. Additionally, the crystal structure was stabilized by a series of short C−H···C contacts between the BPh_4^- anion and coordinated CH_3CN (2.841(2)−2.867(4) Å), as well as 2,9-Me_2phen (2.866(3)−2.894(4) Å; see the Supporting Information). Short contacts were also observed in the structurally similar [Cu^I(2,9-Me_2phen)(CH_3CN)][PF_6] complex (see the Supporting Information).

---

(7) Pintauer, T. *J. Organomet. Chem.* **2006**, *691*, 3948–3953.

(8) Ricardo, C.; Pintauer, T. *J. Organomet. Chem.* **2007**, *692*, 5165–5172.

(9) Liang, H.-C.; Kim, E.; Incarvito, C. D.; Rheingold, A. L.; Karlin, K. D. *Inorg. Chem.* **2003**, *41*, 2209–2212.

(10) Ogura, T. *Trans. Met. Chem.* **1976**, *1*, 179–182.

(11) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927–942.

(12) Braunecker, W. A.; Pintauer, T.; Tsarevsky, N. V.; Kickelbick, G.; Matyjaszewski, K. *J. Organomet. Chem.* **2005**, *690*, 916–924.

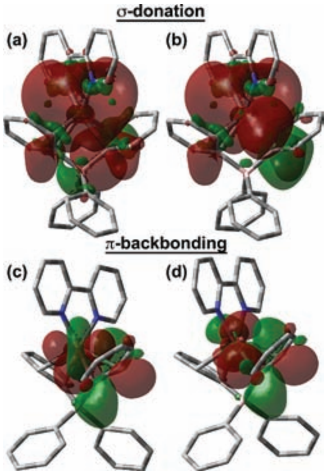
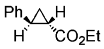
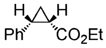
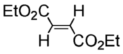
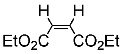


Figure 2. NBO orbital interactions between C−C π bonds (a) and B−C σ bonds (b) of the BPh_4^- counterion and n* orbital of copper (>99% s character) and between filled d orbitals of copper ((c) LP(4) and (d) LP(5)) and empty C−C π* orbitals of phenyl rings.

Table 1. Cyclopropanation of Styrene in the Presence of EDA Catalyzed by **1**−**3**[a]

Catalyst	**1**	**2**	**3**	$[ClO_4]$[b]	$[PF_6]$[b]	$[CF_3SO_3]$[b]
Products						
	72.4	68.2	73.5	66.9	58.7	58.0
	18.1	18.4	18.9	14.7	25.3	27.0
	4.5	7.0	5.2	6.7	9.9	8.0
	5.0	3.3	2.4	11.7	6.1	7.0

[a] $[Cu^I]_0/[EDA]_0/[Sty]_0 = 1{:}50{:}500$, $[Cu^I]_0 = 1.7 \times 10^{-3}$ M, (CH_2Cl_2, 3 h, 25 °C). The % yield is based on ^1H NMR (rel. err. are ± 10%). [b] Results from previous study with $[Cu^I(bpy)(\pi\text{-styrene})][A]$ complexes, ref 8.

The ^1H NMR spectrum of **1** in CD_2Cl_2 appeared relatively sharp at 22 °C and was fully consistent with the solid-state X-ray structure. The corresponding spectra of **2** and **3** were significantly broadened, indicating a fluxional system, which was presumably induced by ligand or anion association or dissociation. In all three complexes, the proton resonances associated with the BPh_4^- anion were identical to those of $NaBPh_4$. In the presence of as much as 15 equiv of alkene (styrene, methyl acrylate, and 1-octene), the ^1H NMR spectra of **1**−**3** remained unchanged. In other words, no visible shielding of vinyl protons upon coordination was observed, which is typical for copper(I)/alkene complexes.[12] These results clearly indicate that BPh_4^- anions strongly coordinate to the copper(I) center.

In order to further examine the nature of bonding of BPh_4^- to Cu^I in **1**−**3**, particularly with respect to σ donation from coordinated C═C bonds in BPh_4^- and π-backbonding from Cu^I, we have conducted additional density functional theory and natural bond order (NBO) calculations (see Supporting Information). The results obtained for **1** and **2** using three different basis sets (6−31+G(d), 6-31G(2d,p), and 6-311++G(2d,p)) indicated that σ donation from the BPh_4^- anion to copper(I) is the dominant interaction (approximately 75%), with the remaining 25% being attributed to classical π-backbonding from copper(I). Also, the NBO calculations indicated that B−C $\sigma \rightarrow$ n*(Cu) interactions were quite significant, with the charge transfer of the interaction totaling approximately half of the typical C═C π−n*(Cu) interaction. Representative orbital interactions are shown in Figure 2.

In order to further investigate the effect of BPh_4^- coordination in **1**−**3** on catalytic activity, cyclopropanation of styrene in the presence of ethyldiazoacetate (EDA) was conducted. The reactions were performed in CH_2Cl_2 at room temperature using standard reaction conditions $[Cu^I]_0/[Sty]_0/[EDA]_0 = 1{:}500{:}50$. The product distribution was determined by ^1H NMR, and the results are summarized in Table 1. For all three complexes, the relative amounts of EDA decomposition products ranged between 2.4 and 7.0%. Furthermore, the mole percents of *trans*- and *cis*-cyclopropane were very similar. Also, when compared to our previous results using well-defined $[Cu^I(bpy)(\pi\text{-sty})][A]$ complexes, **1**−**3** appear to be more selective toward *trans*-cyclopropane.[8]

The observed rate constants (k_{obs}) for the decomposition of EDA in the presence of externally added styrene were determined to be $k_{obs} = (1.5 \pm 0.12) \times 10^{-3}$ min^{-1} (**1**), $(6.8 \pm 0.30) \times 10^{-3}$ min^{-1} (**2**), and $(5.1 \pm 0.19) \times 10^{-3}$ min^{-1} (**3**). These rates should depend on the equilibrium constants K_O and K_L, corresponding to the formation of $[Cu^I(NN)(\pi\text{-olefin})][A]$ and $[Cu^I(NN)_2][A]$ complexes, respectively (Scheme 1). However, our previous results using $[Cu^I(bpy)(\pi\text{-Sty})][A]$ complexes indicated that k_{obs} and K_O were relatively independent of the nature of counterion ($(1.4 \pm 0.041) \times 10^{-2}$ min^{-1} and 4.3×10^3 M^{-1} ($A = CF_3SO_3^-$) and $(1.0 \pm 0.025) \times 10^{-2}$ min^{-1} and 4.4×10^3 M^{-1} ($A = PF_6^-$), respectively).[8] Therefore, assuming a constant value for K_L, the most reasonable explanation for the decrease in the observed rate constant for the decomposition of EDA in the case of **1**−**3** can be attributed to relatively strong coordination of the BPh_4^- anion. Furthermore, these data also indicate that the binding constant of BPh_4^- in **1** is stronger than in **2** or **3**, which is presumably induced by the stronger coordination of 3,4,7,8-Me_4phen ($pK_a = 6.58$), relative to bpy ($pK_a = 4.60$) or phen ($pK_a = 4.80$). Detailed kinetic, mechanistic, and computational studies of the catalytic activity of copper(I) complexes **1**−**3** in cyclopropanation are subject to further investigation in our laboratories.

In conclusion, the synthesis, characterization, and cyclopropanation activity of tetrahedral copper(I) complexes with bipyridine- and phenanthroline-based ligands containing strongly coordinated BPh_4^- counterions were reported. These complexes are the first examples in which the BPh_4^- anion chelates a transition metal center in bidentate fashion through η^2 π interactions with two of its phenyl rings.

Acknowledgment. T.P. acknowledges financial support from Duquesne University (startup fund and faculty development grant), NSF X-ray facility grant (CRIF 0234872), NSF NMR grant (CHE 0614785), and PRF fund (44542-G7).

Supporting Information Available: Synthetic procedures and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801783R