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Copper(I) Complexes derived from Mono- and Diphosphino-Boranes: Cu→B Interactions Supported by Arene Coordination

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The monophosphino-boranes o-iPr$_2$P(C$_6$H$_4$)BR$_2$ (**1**: R = Ph and **3**: R = Cy) and diphosphino-boranes [o-R$_2$P(C$_6$H$_4$)]$_2$BPh (**5**: R = Ph and **6**: R = iPr) readily react with CuCl to afford the corresponding complexes $\{[o\text{-}i\text{Pr}_2\text{P}(\text{C}_6\text{H}_4)\text{BPh}_2]\text{Cu}(\mu\text{-Cl})\}_2$ **2**, $\{[o\text{-}i\text{Pr}_2\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2]\text{Cu}(\mu\text{-Cl})\}_2$ **4**, $\{[o\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)]_2\text{BPh}\}\text{CuCl}$ **7**, and $\{[o\text{-}i\text{Pr}_2\text{P}(\text{C}_6\text{H}_4)]_2\text{BPh}\}\text{CuCl}$ **8**. The presence of Cu→B interactions supported by arene coordination within complexes **2**, **7**, and **8** has been unambiguously evidenced by NMR spectroscopy and X-ray diffraction studies. The unique η^2-BC coordination mode adopted by complexes **7** and **8** has been thoroughly analyzed by density-functional theory (DFT) calculations.

Introduction

Over the past few years, the ability of Lewis acids to act as σ-acceptor, Z-type[1] ligands has attracted growing interest.[2−4] In particular, the coordination of ambiphilic ligands combining phosphine and borane moieties has allowed significant advances in M→B interactions.[5−9] Indeed, we have shown that such M→B interactions (M = Rh, Ni, Pd, Pt, Cu, Ag, Au) are readily accessible by coordination of tri-, di-, and even monophosphino-boranes (complexes of type **A**−**C**).[7] In the mean time, Emslie et al. demonstrated that a rigid phosphino-thioether-borane ligand (PSB) is also prone to engage in M→B interactions (M = Rh, Pd, Pt) *via* the unprecedented η^3-BC$_{ipso}$C$_{ortho}$ coordination of a BPh

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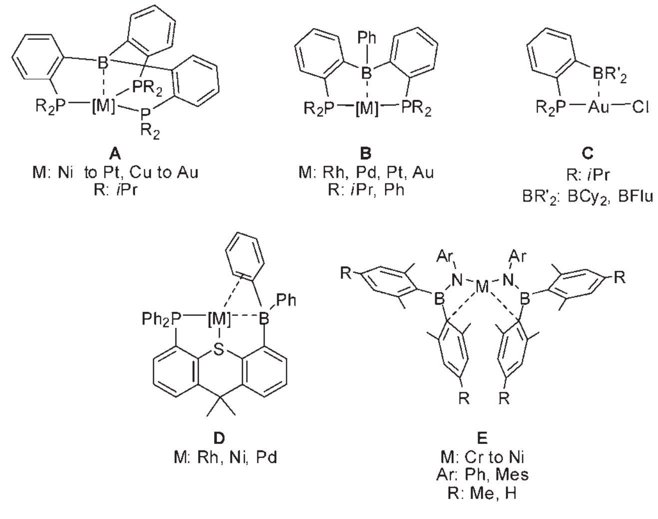
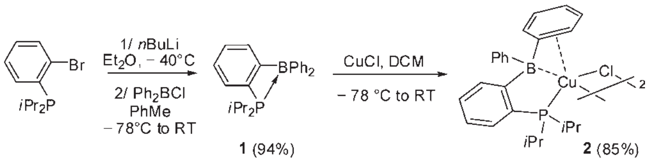


Figure 1. Structure of complexes **A**−**E** featuring η^1-B, η^3-BC$_{ipso}$C$_{ortho}$, and η^1-C$_{ipso}$ coordinated arylborane fragments.

fragment (complexes of type **D**).[8] The coordination of arylboranes to transition metals was at that time limited to weak η^1-C$_{ipso}$ coordination, as observed by Power et al. in the homoleptic complexes **E** featuring two borylamide ligands (Figure 1).[10,11]

To shed more light on the different coordination behaviors of the B(aryl) fragment in complexes **A**−**C** (η^1-B), **D** (η^3-BCC), and **E** (η^1-C), we recently became interested in copper complexes derived from mono- and diphosphino-boranes. To date, Cu→B interaction has only been authenticated when enforced in a metallaboratrane cage structure (complex of type **A**).[7f,12,13] Here, the related complexes of type **B** and **C** are shown to display Cu→B interactions that are supported by arene coordination. The original η^2-BC coordination mode evidenced in complexes of type **B** has been thoroughly investigated, both experimentally and theoretically.

Scheme 1. Synthesis and Coordination to Copper(I) of the Monophosphino-Borane **1**



Results and Discussion

Starting from (*o*-bromophenyl)diisopropylphosphine, the monophosphino-borane (MPB) **1** was obtained in 94% yield by bromine−lithium exchange followed by electrophilic trapping with chlorodiphenylborane (Scheme 1). The ^{31}P-{^{1}H} and ^{11}B{^{1}H} NMR chemical shifts for **1** (24.8 and 5 ppm, respectively) are similar to those observed in the solid state for the related triphosphino-borane [*o*-*i*Pr$_2$P(C$_6$H$_4$)]$_3$B (TPB) (δ^{31}P: 28.5 ppm and δ^{11}B: 13.0 ppm),[14] suggesting the presence of an intramolecular P→B interaction. Density-functional theory (DFT) calculations performed on the real molecule at the [B3PW91/SDD+pol(P),6-31G**(B,C,H)] level of theory confirmed this hypothesis.[15] Indeed, the experimental ^{31}P and ^{11}B NMR chemical shifts are in good agreement with those computed using the Gauge Including Atomic Orbitals (GIAO) method for the *closed* form of **1** (31.0 and 10.7 ppm, respectively), but differ significantly from those of the related *open* form (without P→B) that was found 1.5 kcal/mol higher in energy (δ^{31}P: 16.5 ppm and δ^{11}B: 61.8 ppm). The copper complex **2** was prepared by adding the monophosphino-borane **1** to a suspension of CuCl in dichloromethane (DCM) at −78 °C. Upon warming to room temperature (RT), the reaction mixture rapidly became homogeneous and turned pale yellow. After precipitation with diethyl ether, complex **2** was isolated in 85% yield. The ^{11}B{^{1}H} NMR resonance observed at 58 ppm is close to that exhibited by the (TPB)CuCl complex of type **A** (54 ppm), suggesting the presence of a weak Cu→B interaction in **2**.[7f]

To get more insight into the precise structure of **2**, single crystals suitable for X-ray diffraction (XRD) analysis were prepared from a saturated dichloromethane solution at RT (mp 138−140 °C). Complex **2** adopts a centrosymmetric chloro-bridged dimeric structure in the solid state (Figure 2). The copper center is surrounded by the phosphorus atom, two chlorine atoms, and a BPh moiety organized in a tetrahedral environment. The CuB distance in **2** [2.555(2) Å] is appreciably shorter than the sum of van der Waals radii (3.80 Å),[16] and very similar to that of the (TPB)CuCl complex of type **A** [2.508(2) Å].[7f] The C$_{ipso}$ and one of the C$_{ortho}$ atoms of a phenyl substituent at boron are also close to the copper center. The corresponding CCu distances [2.339(2) and 2.596(2) Å, respectively] are in the same range as those reported for η^2-CC arylborate copper complexes (CCu distances of 2.32−2.68 Å were found in the polymeric [Ph$_n$B(CH$_2$SR)$_{4-n}$Cu] complex).[17] This data indicates η^3-BCC coordination of the BPh moiety in **2**. This contrasts with the η^1-B coordination induced by the metallaboratrane

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(11) In complexes **E**, relatively short MB distances (2.50−2.85 Å) are imposed geometrically, but the orientation of the vacant 2p orbital at boron precludes direct M→B interaction.

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(13) The contribution of a weak Cu→B interaction has been pointed out in a copper(I) complex featuring an α-boroalkyl ligand: Laitar, D. S.; Tsui, E. Y.; Sadighi, J. P. *Organometallics* **2006**, *25*, 2405–2408.

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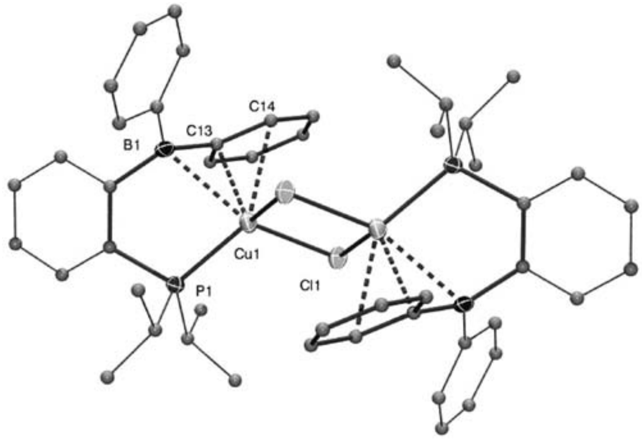
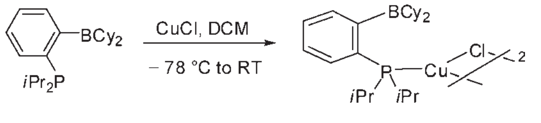


Figure 2. Molecular structure of **2** with hydrogen atoms and solvent molecules omitted. Selected bond distances (Å) and angles (deg): P1−Cu1 2.215(1), Cu1−Cl1 2.339(1), Cu1−Cl1A 2.353(1), Cu1−B1 2.555(2), Cu1−C13 2.339(2), Cu1−C14 2.596(2), P1−Cu1−Cl1 113.90(2), P1−Cu1−Cl1A 123.33(2) Cl1−Cu1−Cl1A 94.14(2).

Scheme 2. Synthesis of the Copper(I) Monophosphino-Borane Complex **4**



structure in the (TPB)CuCl complex of type **A**,[7f] but parallels what had been observed by Emslie et al. upon coordination of the rigid PSB ligand to rhodium, nickel, and palladium.[8] Notably, the geometry of the BPh fragment is almost unchanged upon coordination to copper: (*i*) the corresponding BC_{ipso} and $C_{ipso}C_{ortho}$ bond lengths are identical to those of the other phenyl substituent at boron, (*ii*) the C_{ipso} and C_{ortho} atoms are in perfectly planar environments, and (*iii*) the boron atom is only slightly pyramidalized [$\sum$(C−B−C) = 358.4°].[18] In addition, only three (respectively four) signals are observed for the BPh_2 fragment in the ^1H (respectively ^{13}C) NMR spectra of **2**. This indicates that the two phenyl substituents at boron rapidly exchange at the NMR time scale,[19] something that may occur either by decoordination/recoordination or by slippage of copper.

The phenyl substituents at boron were then replaced by cyclohexyl groups so as to ascertain the influence of the $C_{ipso}C_{ortho}$-coordination on the Cu→B interaction. The targeted complex **4** was prepared by reacting the previously reported monophosphino-borane *o*-$i Pr_2P(C_6H_4)BCy_2$ **3**[7b] with CuCl (Scheme 2). The $^{11}B\{^1H\}$ NMR resonance signal observed at 82.5 ppm is diagnostic for tricoordinate dialkylarylboranes,[20] suggesting the absence of significant Cu→B interaction in **4**. This was unambiguously confirmed by X-ray crystallography, single crystals being obtained from a saturated dichloromethane solution at −40 °C (mp 124−126 °C). Accordingly, complex **4** also adopts a centrosymmetric chloro-bridged dimeric structure in the solid state (Figure 3), but the copper center is essentially tricoordinate and its geometry tends to trigonal planar (the sum of P1Cu1Cl1, P1Cu1Cl1A, and Cl1Cu1Cl1A bond angles equals 358.3° in **4** vs 331.4° in **2**). The empty 2p(B) orbital points in the direction of the metal (the CuP and $C_{ipso}B$ vectors are almost parallel, with a torsion angle of only 8.0°), but the BCu distance (3.05 Å) significantly exceeds that of complex **2**, indicating negligible, if any, Cu→B interaction in **4**.[21,22] This argues in favor of cooperative coordination of the boron atom and π-system of the phenyl ring toward copper in complex **2**.

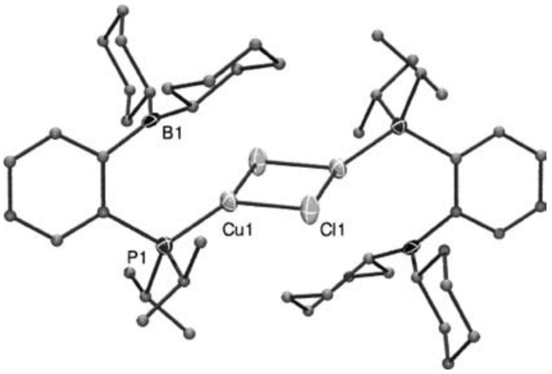


Figure 3. Molecular structure of **4** with hydrogen atoms and solvent molecules omitted. Selected bond distances (Å) and angles (deg): P1−Cu1 2.173(2), Cu1−Cl1 2.379(2), Cu1−Cl1A 2.237(2), P1−Cu1−Cl1 116.39(4), P1−Cu1−Cl1A 145.06(5), Cl1−Cu1−Cl1A 96.87(4).

Upon coordination to CuCl, the monophosphino-borane **1** and triphosphino-borane TPB lead to η^3-BCC and η^1-B complexes, respectively. To gain more insight into the precise influence of geometric constraints and stereoelectronic effects in these contrasting coordination behaviors, we then investigated the coordination of related diphosphino-borane (DPB) ligands. Because of the presence of two donating phosphine buttresses at boron, the copper center was expected to be less coordinatively and electronically unsaturated than in the monophosphino-borane complex **2**. Note that the AuCl complexes of type **B** derived from the DPB ligands **5** and **6** (featuring phenyl and isopropyl substituents at phosphorus, respectively) have been recently shown to adopt η^1-B coordination, leading to unprecedented square-planar geometry for tetracoordinate Au(I) complexes.[7c] The participation of the phenyl ring at boron to the coordination is more likely with copper, that tends to form complexes of higher coordination numbers than gold.[23] By allowing **5** and

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[18] M→B interactions with only slight boron pyramidalization have been observed in the [*o*-$i Pr_2P(C_6H_4)$BFlu]·AuCl complex[7b] and in the heterobimetallic rhodium-iron complex derived from the PSB ligand.[8a] Perfectly planar environments have even been found in unsymmetrically bridged boryl complexes: (a) Curtis, D.; Lesley, M. J. G.; Norman, N. C.; Orpen, A. G.; Starbuck, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1687–1694. (b) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Harlow, R. L.; Calabrese, J. C.; Lam, K. C.; Lin, Z. *Polyhedron* **2004**, *23*, 2665–2677.

[19] The very poor solubility of complex **2** prevents the study of this fluxional behavior at low temperature.

[20] For example, ^{11}B NMR chemical shifts of 77.6 ppm and 80.9 ppm have been reported for $PhBMe_2$ and PhBBN, respectively: (a) Wrackmeyer, B.; Nöth, H. *Chem. Ber.* **1976**, *109*, 1075–1088. (b) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1–15.

[21] For comparison, a weak Au→B interaction was found in the related gold complex (**3**) AuCl.[7b] This corroborates the strengthening of M→B interactions when going down group 11, as previously evidenced in TPB complexes of type **A**.[7f]

[22] The (μ-Cl)$_2$ bridge prevents M−Cl→B interaction, as observed previously in mononuclear Pd and Rh complexes derived from the phosphino-borane **3**. See ref 7b and (a) Bontemps, S.; Bouhadir, G.; Apperley, D. C.; Dyer, P. W.; Miqueu, K.; Bourissou, D. *Chem. Asian. J.* **2009**, *4*, 428–435.

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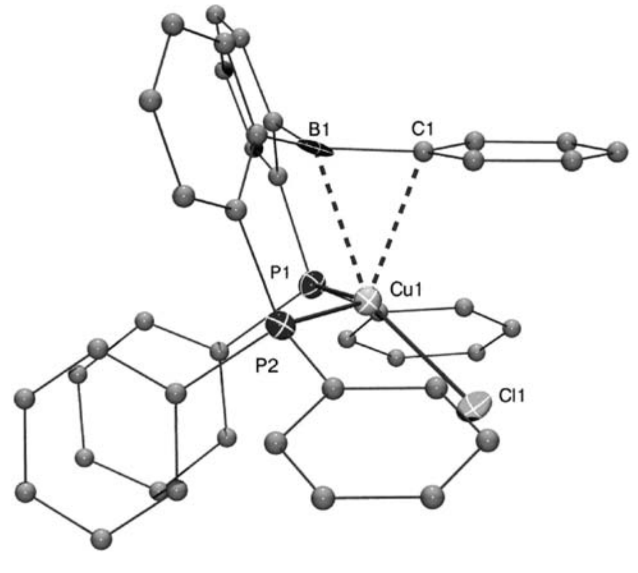
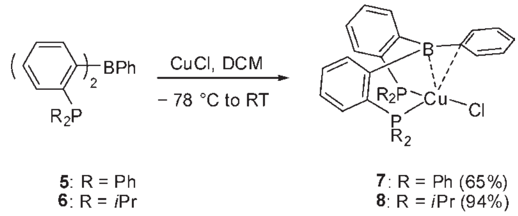


Figure 4. Molecular structure of **7** with hydrogen atoms and solvent molecules omitted.

Scheme 3. Synthesis of the Copper(I) Diphosphino-Borane Complexes **7** and **8**



6 to react with CuCl in DCM, the desired complexes **7** and **8** were obtained as yellow solids in 43 and 94% yield, respectively (Scheme 3). The $^{31}P\{^1H\}$ NMR spectra of **7** and **8** exhibit singlets at 3.4 and 21.5 ppm, respectively, indicating symmetric coordination of the two phosphorus atoms to the copper center. The $^{11}B\{^1H\}$ NMR chemical shifts for complexes **7** (56 ppm) and **8** (55 ppm) are very similar to those of **2** (58 ppm) and (TPB)CuCl (54 ppm),[7f] supporting the presence of weak Cu→B interactions. Notably, the ^{13}C NMR resonance signals associated with the C_{ipso} atom of the BPh fragment (δ = 132.7 ppm for **7** and 140.3 ppm for **8**) appear at significantly lower frequencies than those of the free ligands (~148 ppm)[7a,c] and related η^1-B gold complexes of type **B** (~151 ppm).[7c] The ^{13}C NMR signals of aryl rings are typically shifted to lower frequency upon coordination, shifts of 5 to 10 ppm being classically observed with copper.[24] The spectroscopic data thus suggest the participation of both B and C_{ipso} atoms upon coordination of the DPB ligands **5** and **6** to CuCl.

Single crystals of **7** (mp 259 °C) and **8** (mp 200−201 °C) were grown from saturated DCM solutions at RT, and XRD analyses were carried out. Both complexes adopt monomeric structures in the solid state, with the copper center being ligated by the two phosphorus atoms, the chlorine atom, and the BPh fragment. The metrical data for complex **7** will be discussed first (Figure 4). The CuB distance [2.396(5) Å] is shorter than in the MPB complex **2** [2.555(2) Å] and even than in the TPB complex of type **A** [2.508(2) Å],[7f] suggesting a rather strong interaction.[25] The CuC_{ipso} distance [2.364(4) Å] is very similar to that of **2** [2.339(2) Å]. This is the only short contact observed between the copper center and the phenyl ring at boron, the other carbon atoms standing at >2.9 Å. Thus, the BPh fragment in complex **7** adopts a η^2-BC coordination mode rather than η^3-BCC, as observed in complex **2**. We assume that the higher donating character of the second phosphino buttress in complex **7** compared with the chloride-bridge in complex **2** plays an important role in this feature. The participation of the BPh fragment in the coordination also induces in complex **7** a noticeable pyramidalization of the copper environment (sum of P1Cu1P2, P1Cu1Cl1 and P2Cu1Cl1 bond angles = 331.4°), but no elongation of the BC_{ipso} bond [1.566(3) Å compared to 1.585(3) and 1.571(3) Å for the BC_{ipso} bonds of the *o*-phenylene linkers]. Note also that two phenyl rings at the phosphorus atoms are almost parallel (the mean planes of the two rings are tilted by only 9°) and close enough (the distance between the two centroids is 3.63 Å) to suggest some $\pi-\pi$ interaction. The solid-state structure of **8** is composed of four crystallographically independent molecules. One of them, referred to as **8a**, resembles **7** (Figure 5). The CuB and CuC_{ipso} distances in **8a** (2.379(5) and 2.414(4) Å, respectively) are very similar to those of **7**, indicating here also symmetric η^2-BC coordination of the BPh fragment. The three other molecules present in the unit cell are almost identical (largest deviation in BCu, BC_{ipso}, CuC_{ipso} bond lengths of less than 0.1 Å)[15] and will be described here as an average form, referred to as **8b**. The CuB distance in **8b** (2.49 Å) exceeds that of **8a** by about 5%, while the CuC_{ipso} distance (2.66 Å) is elongated by 10%. Accordingly, the η^2-BC coordination is slightly weaker and dissymmetrized in **8b** compared to **8a**, suggesting some flexibility in the coordination of the BPh fragment to the metal center.

At this stage, it is interesting to note that, with copper(I), η^2-coordination of arenes is well-known,[26] but only a very few η^1-complexes have been reported to date.[27,28] In addition, η^2-BC coordination has only been authenticated in an iron complex featuring the methyleneborane Flu = BTmp (Flu: 9-fluorenylidene, Tmp: 2′,2′,6′,6′-tetramethylpiperidino),[29] and in a mixed cluster of palladium and rhenium capped by

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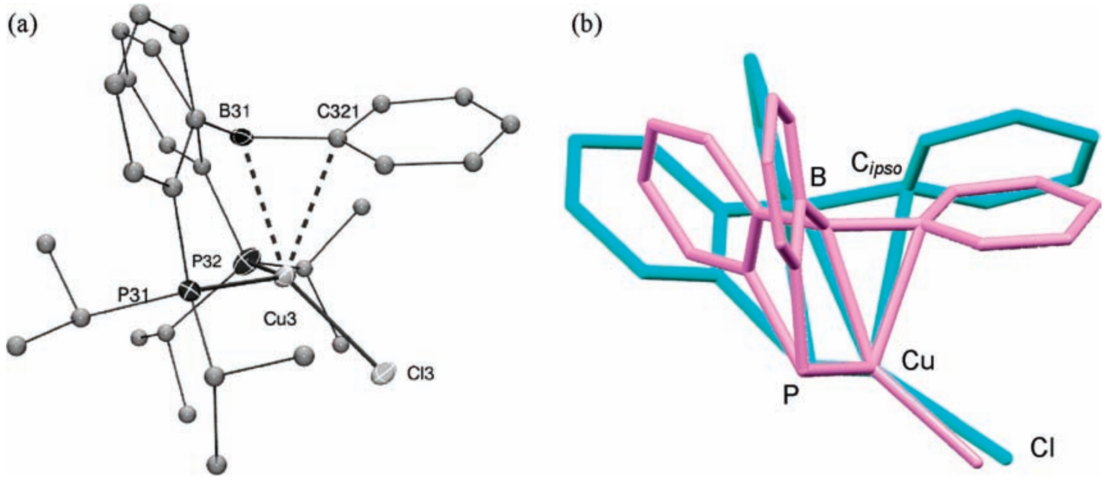

Figure 5. (a) Molecular structure of **8** with hydrogen atoms and solvent molecules omitted (only one of the four independent molecules of the unit cell, namely, **8a**, is shown for clarity). (b) Superposed side views of **8a** (pink) and **8b** (blue), the mean form of the three other molecules present in the unit cell (isopropyl substituents at phosphorus omitted for clarity).

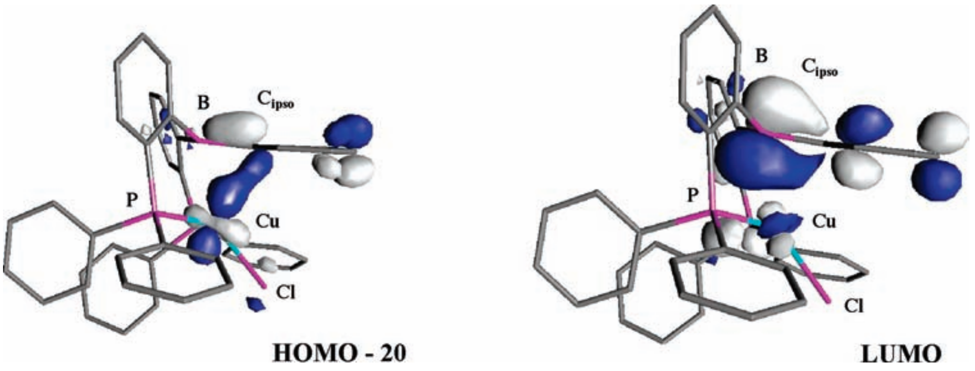

Figure 6. Molecular orbital plots associated with the three-center CuBC$_{ipso}$ interaction within **7***. For **8a***, see Supporting Information, Figure S1.[15]

two phenylboroles Ph−B(C_4H_4).[30] Thus, the complexes **7** and **8** derived from diphosphino-boranes provide the first examples of η^2-BC coordination involving a triarylborane, and bridge thereby the gap between the η^1-B and η^3-BCC coordination modes described previously.[7,8]

To further probe the η^2-BC coordination mode adopted by **7** and **8a**, DFT calculations were carried out on the real complexes. Calculations were performed at the B3PW91/SDD(Cu,P,Cl),6-31G**(other atoms) level of theory, that has already proved appropriate for transition metal complexes derived from ambiphilic ligands.[3e,7,31] The optimized geometries for **7***/**8a*** fit closely with those determined experimentally for **7**/**8a** (Table 1), and nicely reproduce the symmetric η^2-BC coordination (with computed CuB/CuC$_{ipso}$ distances of 2.43/2.46 Å for **7***, and 2.41/2.50 Å for **8a***).

Analysis of the molecular orbitals of **7*** and **8a*** indicated the presence of three-center CuBC$_{ipso}$ interactions. For both structures, the lowest unoccupied molecular orbital (LUMO) corresponds to the antibonding combination of a d orbital at Cu and a π(BC$_{ipso}$) orbital, whose bonding counterpart is associated with a low-lying filled orbital, HOMO-20 for **7*** and HOMO-12 for **8a*** (Figure 6). To shed more light on the bonding situation, Natural Bond Orbital (NBO) analyses were carried out. At the second-order perturbation level, several donor−acceptor interactions involving B, C$_{ipso}$, and Cu were found (Table 2). In particular, Cu→B donation arises from both s and d orbitals. The corresponding delocalization energy (12−13 kcal/mol) falls in the same range

Table 1. Experimental and Theoretical Data for Complexes **7** and **8**[a]

complex		PCu	CuB	CuC$_{ipso}$	CuCl	ΔG_{298}
7	X−ray	2.241(2) 2.244(2)	2.396(5)	2.364(4)	2.230(2)	
7*	DFT	2.296 2.293	2.434	2.459	2.261	
8a	X−ray	2.266(2) 2.274(2)	2.379(5)	2.414(4)	2.254(2)	
8a*	DFT	2.312 2.304	2.411	2.504	2.275	0
8b[b]	X−ray	2.250 2.264	2.489	2.655	2.267	
8b*	DFT	2.284 2.286	2.386	2.741	2.287	+3.0
8c*	DFT	2.292 2.290	2.574	2.890	2.279	−2.1
8d*	DFT	2.270 2.271	2.689	3.203	2.283	−3.0

[a] Bond lengths in Å, bond angles in deg, ΔG_{298} in kcal/mol. [b] Average value of the three very similar independent molecules present in the unit cell.

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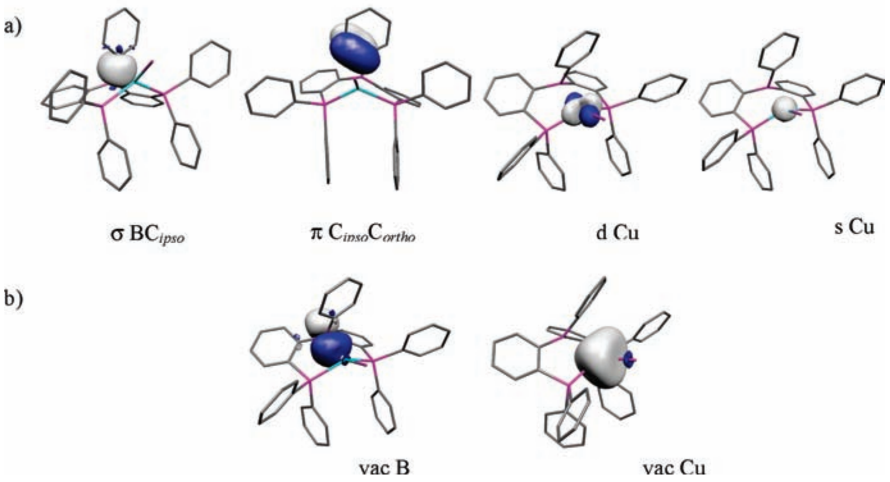
Table 2. Donor−Acceptor Interactions toward B and Cu Found by Second-Order Pertubative NBO Analysis of **7***;[a] Molekel Plots[b] for the Corresponding (a) Donor NBO and (b) Acceptor NBO[c]

s Cu → vac B	5.3
d Cu → vac B	7.3
π $C_{ipso}C_{ortho}$ → vac B	27.7
σ BC_{ipso} → vac Cu	5.7
π $C_{ipso}C_{ortho}$ → vac Cu	5.1



[a] Delocalization energies in kcal/mol. [b] Cutoff: 0.05. [c] For **8a***, see Supporting Information, Table S3.[15]

Table 3. Atomic Charges, As Derived from Natural Population Analyses (NPA), Computed for Complex **7***, the Free Ligand **5***, and the Related Boron-Free Complex $[(Ph_3P)_2CuCl]$[a]

	q Cu	*q* B	*q* P[b]	*q* C_{ipso}[c]	*q* Cl
complex **7***	0.77	0.64	1.00	−0.45 (−0.26)	−0.76
ligand **5***		0.87	0.99	−0.42 (−0.26)	
$(Ph_3P)_2CuCl$	0.63		0.95		−0.78

[a] For **8a***, **6*** and $[(iPr_2PhP)_2CuCl]$, see Supporting Information, Table S4.[15] [b] Mean value. [c] The value in parentheses is associated with the BPh fragment.

than that computed for the η^1-B complex of type **A** (7.9 kcal/mol).[7f] But here, the boron is also stabilized by the adjacent π system via a $\pi(C_{ipso}C_{ortho})$→2p(B) interaction, with a delocalization energy of 26−28 kcal/mol. In addition, a $\sigma(BC_{ipso})$ and a $\pi(C_{ipso}C_{ortho})$ orbitals were found to engage into donation toward Cu. The corresponding delocalization energy amounts to 9−11 kcal/mol.

The atomic charges, as derived from natural population analyses (Table 3), confirm the transfer of density from copper to boron. It was estimated by (*i*) the difference Δq_B between the charge at boron in the complexes and that in the related free ligands and (*ii*) the difference Δq_{Cu} between the charge at the copper in the complexes and that in the related boron-free copper complexes $(R_2PPh)_2CuCl$. The donor−acceptor Cu→B interaction resulted in negative values of Δq B (−0.22 for **7*** and −0.25 for **8a***) and positive values of Δq Cu (+0.14 for **7*** and +0.15 for **8a***). These values are similar in magnitude to those computed for the η^1-B complex of type **A** (Δq B = −0.24 and Δq Cu = +0.07).[7f]

Lastly, the presence of structures **8a** and **8b** in the crystallographic cell of complex **8** prompted us to scrutinize the potential energy surface to evaluate how flexible is the participation of the BPh fragment. In addition to **8a***, three energy minima differing essentially in the positioning of the BPh moiety were located. Structure **8b***, related to **8b**, displayed dissymmetric η^2-BC coordination. On going from **8a*** to **8b***, the CuB distance slightly shortens (from 2.411 to 2.386 Å), while the CuC_{ipso} distance increases by about 10% (from 2.504 to 2.741 Å). The two other minima, **8c*** and **8d***, correspond to further backward displacements of the BPh fragment. The corresponding CuB distances are elongated by 7% in **8c*** and 11.5% in **8d***, while the CuC_{ipso} distances reach 2.890 Å in **8c*** and 3.202 Å in **8d*** (corresponding to elongations of 15.5% and 28%, relative to **8a***). Structures **8c*** and **8d*** are thus better described as weak η^1-B coordination rather than η^2-BC coordination. This is consistent with the presence of the four independent molecules within the unit cell of **8** and further supports some flexible character for the coordination of the BPh fragment to copper.

Conclusion

In summary, a series of copper(I) complexes derived from mono- and diphosphino-boranes have been prepared and fully characterized. Compared with the previously reported TPB complex of type **A**, the presence of only two or even one phosphino buttresses imparts higher flexibility and favors thereby the participation of the aryl substituent at boron to the coordination. Accordingly, complex **2** derived from the monophosphino-borane ligand **1** adopts η^3-BCC coordination, drawing some parallel with that reported earlier by Emslie upon coordination of the PSB ligand to Rh, Ni, and Pd. In addition, the related complexes **7** and **8** derived from the diphosphino-borane ligands **5** and **6** adopt a unique

η^2-BC coordination mode that has been thoroughly investigated computationally. These results substantiate further the versatile coordination properties of arylborane fragments, and illustrate the ability of arene rings to support M→B interactions.

Experimental Section

Materials and Methods. All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Dry, oxygen−free solvents were employed. Diethyl ether and toluene were dried over sodium, CH_2Cl_2 and pentane were dried over CaH_2 and distilled prior to use. ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were recorded on Bruker Avance 300, 400, and 500 spectrometers. Chemical shifts are expressed with a positive sign, in parts per million, calibrated to residual ^{1}H (7.24 ppm) and ^{13}C (77.16 ppm) solvent signals, external $BF_3 \cdot OEt_2$ (0 ppm) and 85% H_3PO_4 (0 ppm), respectively. The N values corresponding to $1/2\ [J(AX)+J(A'X)]$ are provided for the second−order AA′X systems observed in ^{13}C NMR.[32] For the atom numbering used in the NMR assignment, see the Supporting Information. Mass spectra were recorded on a Waters LCT spectrometer. Diphenylchloroborane,[33] o-iPr$_2$P(C$_6$H$_4$)Br,[34] **3**,[7b] **5**,[7c] and **6**[7a] were synthesized as previously described.

o-iPr$_2$P(C$_6$H$_4$)BPh$_2$ Ligand 1. To a solution of o-iPr$_2$(C$_6$H$_4$)Br (188 mg, 6.88 mmol) in ether (1 mL) was added a solution of n-BuLi (1.6 M in hexanes, 0.43 mL, 6.88 mmol) at −40 °C. Following the apparition of a white precipitate, the suspension was further stirred for 20 min at the same temperature. The supernatant was then removed by filtration. The residue was dissolved in toluene (1.5 mL), and a solution of diphenylchloroborane (125 mg, 6.25 mmol) in toluene (1 mL) was added slowly at −78 °C. After warming to RT, the lithium chloride salts were removed by filtration. Ligand **1** (209 mg, 94%) was obtained as a white solid by evaporation of the solvent. X-ray quality crystals were grown from a saturated CH_2Cl_2/pentane solution at −30 °C. ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 298 K): $\delta = 24.8$; ^{11}B{^{1}H} NMR (160.5 MHz, $CDCl_3$, 298 K): $\delta = 5.0$; ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 7.41 (m, 4H, $H_{2,6}$), 7.38 (m, 2H, H_{arom}), 7.30 (m, 2H, H_{arom}), 7.23 (m, 4H, $H_{3,5}$), 7.14 (m, 2H, H_4), 2.67 (m, 2H, CH_{iPr}), 1.31 (d, 6H, ^{3}J(H,H) = 7.1 Hz, CH_{3iPr}), 1.10 (d, 6H, ^{3}J(H,H) = 7.3 Hz, CH_{3iPr}) ; HRMS (ESI$^+$) calcd for [MH$^+$,CH_3CN] $C_{26}H_{32}BNP$: 400.2365, found: 400.2351.

{[o-iPr$_2$P(C$_6$H$_4$)BPh$_2$]Cu(μ-Cl)}$_2$ Complex 2. To a suspension of CuCl (57 mg, 0.58 mmol) in CH_2Cl_2 (3 mL) was added a solution of **1** (209 mg, 0.58 mmol) in CH_2Cl_2 (6 mL) at −78 °C. After subsequent stirring for 15 min at −78 °C, the suspension was warmed to RT, and thus turned limpid pale yellow. Addition of 10 mL of ether allowed the apparition of a precipitate. After elimination of the supernatant by filtration, the resulting solid was dried under vacuum to afford **2** as a pale yellow powder (225 mg, 85%). X-ray quality crystals were grown from a saturated dichloromethane solution at RT; mp 138−140 °C. ^{11}B{^{1}H} NMR (128.2 MHz): $\delta = 53$. *Solution NMR:* ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 298 K): $\delta = 28.3$; ^{11}B{^{1}H} NMR (160.5 MHz, $CDCl_3$, 298 K): $\delta = 58$; ^{1}H NMR (500.3 MHz, $CDCl_3$, 298 K): δ = 7.88 (d br, 4H, ^{3}J(H,H) = 7.5 Hz, $H_{2,6}$), 7.60 (m, 3H, $H_{9,4}$), 7.55 (m, 1H, H_8), 7.53 (m, 1H, H_{11}), 7.49 (m, 5H, $H_{3,5,10}$), 2.25 (m, 2H, CH_{iPr}), 1.04 (m, 12 H, CH_{3iPr}) ; ^{13}C NMR (125.8 MHz, $CDCl_3$, 298 K): δ = 156.2 (m br, C_7), 138.4 (s, $C_{2,6}$), 137.2 (s br, C_1), 133.1 (s, C_4), 131.7 (d, ^{1}J(C,P) = 42.1 Hz, C_{12}), 131.1 (s, C_8), 131.0 (d, ^{2}J(C,P) = 19.1 Hz, C_{11}), 130.2 (d, ^{4}J(C,P) = 2.2 Hz, C_9), 128.7 (s, $C_{3,5}$), 127.8 (d, ^{3}J(C,P) = 6.0 Hz, C_{10}), 25.1 (s, CH_{iPr}), 24.9 (s, CH_{iPr}), 19.5 (d, ^{2}J(C,P) = 2.9 Hz, CH_{3iPr}), 18.9 (d, ^{2}J(C,P) = 5.3 Hz, CH_{3iPr}).

{[o-iPr$_2$P(C$_6$H$_4$)BCy$_2$]Cu(μ-Cl)}$_2$ Complex 4. To a suspension of CuCl (67 mg, 0.68 mmol) in CH_2Cl_2 (5 mL) was added a solution of (o-diisopropylphosphinophenyl)dicyclohexyl borane **3** (250 mg, 0.68 mmol) in CH_2Cl_2 (5 mL) at −50 °C. The suspension was warmed to RT, and the solvent was removed under vacuum. The residue was washed with 3 × 4 mL of pentane. X-ray quality colorless crystals were grown from a saturated dichloromethane solution at −40 °C (121 mg, 38%); mp 124−126 °C. ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 293 K): $\delta = 26.8$; ^{11}B{^{1}H} NMR (160.5 MHz, $CDCl_3$, 293 K): $\delta = 82.5$; ^{1}H NMR (500.3 MHz, $CDCl_3$, 293 K): δ = 7.43 (m, 2H, H_{Ar}), 7.30 (t, 1H, ^{3}J(H,H) = 8.1 Hz, H_{Ar}), 6.98 (d, 1H, ^{3}J(H,H) = 8.1 Hz, H_{Ar}), 2.38 (sept-d, 2H, ^{3}J(H,H) = 7.1 Hz, ^{2}J(H,P) = 9.5 Hz, CH_{iPr}), 2.18 (d, 2H, ^{3}J(H,H) = 12.3 Hz, H_{Cy}), 1.97 (pseudo-t, 2H, ^{3}J(H,H) = 12.1 Hz, H_{Cy}), 1.85 (d, 2H, ^{3}J(H,H) = 13.0 Hz, H_{Cy}), 1.80 (d, 2H, ^{3}J(H,H) = 12.8 Hz, H_{Cy}), 1.68 (d, 2H, ^{3}J(H,H) = 12.6 Hz, H_{Cy}), 1.63 (d, 2H, ^{3}J(H,H) = 12.8 Hz, H_{Cy}), 1.37 (m, 2H, H_{Cy}), 1.31 (dd, 6H, ^{3}J(H,H) = 7.1 Hz, ^{3}J(H,P) = 17.1 Hz, CH_{3iPr}), 1.23 (m, 6H, H_{Cy}), 1.14 (dd, 6H, ^{3}J(H,H) = 7.1 Hz, ^{3}J(H,P) = 15.8 Hz, CH_{3iPr}), 1.00 (m, 2H, H_{Cy}); ^{13}C NMR (125.8 MHz, $CDCl_3$, 293 K): δ = 157.5 (d, ^{2}J(C,P) = 29.9 Hz, C_1), 131.1 (d, J(C,P) = 1.4 Hz, C_{Ar}), 129.3 (d, J(C,P) = 2.2 Hz, C_{Ar}), 126.8 (d, ^{1}J(C,P) = 40.5 Hz, C_2), 126.6 (d, J(C,P) = 18.1 Hz, C_{Ar}), 126.0 (d, J(C,P) = 6.3 Hz, C_{Ar}), 39.5 (s, CH_{Cy}), 30.3 (s, C_{Cy}), 28.0 (s, C_{Cy}), 27.9 (s, C_{Cy}), 27.5 (s, C_{Cy}), 26.8 (s, C_{Cy}), 25.9 (d, ^{1}J(C,P) = 24.9 Hz, CH_{iPr}), 20.0 (d, ^{2}J(C,P) = 6.3 Hz, CH_{3iPr}), 19.9 (d, ^{2}J(C,P) = 2.8 Hz, CH_{3iPr}).

{[o-Ph$_2$P(C$_6$H$_4$)]$_2$BPh}CuCl Complex 7. To a suspension of CuCl (65 mg, 0.65 mmol) in CH_2Cl_2 (1 mL) was added a solution of **5** (400 mg, 0.65 mmol) in CH_2Cl_2 (10 mL) at −78 °C. After subsequent stirring for 15 min at −78 °C, the suspension was warmed to RT. The suspension turned bright yellow. After filtration, the solution was concentrated and addition of ether (25 mL) allowed a yellow solid to precipitate. Evaporation of the solvent from the residue afforded complex **7** as a bright yellow powder (200 mg, 65%). X-ray quality crystals were grown from a saturated dichloromethane solution at RT; mp 259 °C. ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 298 K): $\delta = 3.44$; ^{11}B{^{1}H} NMR (160.5 MHz, $CDCl_3$, 298 K): $\delta = 56$; ^{1}H NMR (500.3 MHz, $CDCl_3$, 298 K): δ = 7.89 (d, 2H, ^{3}J(H,H) = 7.7 Hz, H_{11}), 7.83 (m, 4H, PPh_2), 7.60 (t, 1H, ^{3}J(H,H) = 7.5 Hz, H_4), 7.57 (m, 2H, H_9), 7.48 (m, 2H, H_8), 7.43 (m, 10H, H_{Ar}), 7.21 (t, 2H, ^{3}J(H,H) = 7.5 Hz, $H_{3,5}$), 7.10 (t, 2H, ^{3}J(H,H) = 7.8 Hz, PPh_2), 6.90 (t, 4H, ^{3}J(H,H) = 7.8 Hz, PPh_2), 6.80 (m, 4H, PPh_2); ^{13}C NMR (125.8 MHz, $CDCl_3$, 298 K): δ = 155.3 (AA′X, N = 22.5 Hz, C_7), 139.6 (s br, $C_{2,6}$), 135.3 (AA′X, N = 19.8 Hz, C_{12}), 134.8 (AA′X, N = 7,1 Hz, PPh_2), 134.5 (s br, C_4), 133.5 (s, C_8), 133.4 (AA′X, N = 16.0 Hz, C_{ipso} PPh_2), 132.9 (AA′X, N = 20.1 Hz, C_{ipso} PPh_2), 132.7 (m br, C_1), 131.8 (AA′X, N = 6.2 Hz, PPh_2), 130.4 (AA′X, N = 11.7 Hz, C_{11}), 130.3 (s, PPh_2), 130.2, (s, C_9), 128.8 (s br, PPh_2), 128.5 (AA′X, N = 5.1 Hz, PPh_2), 128.3 (AA′X, N = 4.4 Hz, PPh_2), 128.1 (AA′X, N = 2.7 Hz, C_{10}), 128.0 (s, $C_{3,5}$).

{[o-iPr$_2$P(C$_6$H$_4$)]$_2$BPh}CuCl Complex 8. To a suspension of CuCl (42 mg, 0.42 mmol) in CH_2Cl_2 (1 mL) was added a solution of ligand **6** (200 mg, 0.42 mmol) in CH_2Cl_2 (2 mL) at −78 °C. After stirring for 15 min, the suspension was warmed to RT. The suspension turned limpid bright yellow. Evaporation of the solvent afforded complex **8** as a bright yellow solid (226 mg, 94%). X-ray quality crystals were grown from a saturated dichloromethane/ether solution at RT; mp 200−201 °C. ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 298 K): $\delta = 21.52$; ^{11}B{^{1}H} NMR (160.5 MHz, $CDCl_3$, 298 K): $\delta = 55$; ^{1}H NMR (500.3 MHz, $CDCl_3$, 298 K): δ = 7.57 (d br, 4H, ^{3}J(H,H) = 8.0 Hz, $H_{8,11}$), 7.46 (t br, 2H, ^{3}J(H,H) = 8.0 Hz, H_9), 7.43

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(m, 1H, H_4), 7.41 (t, 2H, ^3J(H,H) = 8.0 Hz, H_{10}), 7.30 (d, 2H, ^3J(H,H) = 7.0 Hz, $H_{2,6}$), 7.25 (m, 2H, $H_{3,5}$), 2.59 (m, 2H, CH_{iPr}), 2.35 (m, 2H, CH_{iPr}), 1.44 (m, 6H, CH_{3iPr}), 1.31(m, 6H, CH_{3iPr}), 1.14 (m, 6H, CH_{3iPr}), 1.02 (m, 6H, CH_{3iPr}); ^{13}C NMR (125.8 MHz, $CDCl_3$, 298 K): δ = 157.0 (m br, C_7), 140.3 (s br, C_1), 136.8 (s, $C_{2,6}$), 134.5 (AA′X, N = 16.6 Hz, C_{12}), 132.2 (s, C_4), 131.0 (AA′X, N = 10.9 Hz, C_{11}), 130.6 (s, C_8), 129.8 (s, C_{10}), 127.8 (s, $C_{3,5}$), 127.2 (AA′X, N = 2.5 Hz, C_9), 25.3 (AA′X, N = 10.7 Hz, CH_{iPr}), 24.7 (AA′X, N = 7.3 Hz, CH_{iPr}), 19.6 (m, CH_{3iPr}), 19.4 (s, CH_{3iPr}), 17.6 (s, CH_{3iPr}) ; HRMS (ESI^+) calcd for $[M-Cl]^+$ $C_{30}H_{41}BP_2Cu$: 537.2073, found: 537.2091.

XRD Studies. Data were collected using an oil-coated shock-cooled crystal on Bruker-SMART APEX II (**2**), Bruker−SMART APEX II (**4**, **7**) and Bruker X8 Kappa APEXII (**8**) diffractometers (λ = 0.71073 Å) at 180 (**2**), 193 (**4**, **7**), or 100 K (**8**). Semiempirical absorption corrections were employed for **2**, **4**, and **8**.[35] The structures were solved by direct methods (SHELXS-97),[36] and refined using the least−squares method on F^2.[37] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC−749019 (**2**), 749020 (**4**), 749021 (**7**) and 749022 (**8**). These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223−336−033; or deposit@ccdc.cam.ac.uk).

Computational Methods. Copper, Phosphorus, and Chlorine were treated with a Stuttgart-Dresden pseudopotential in combination with their adapted basis set.[38,39] The basis set has been augmented by a set of polarization function (d for P and Cl).[40] Boron, Carbon and Hydrogen atoms have been described with a 6-31G(d,p) double-ζ basis set.[41] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[42,43] Geometry optimizations were carried out without any symmetry restrictions, and the nature of the minima was verified with analytical frequency calculations. All these computations have been performed with the Gaussian 03[44] suite of programs. The electronic structure was studied using NBO analysis,[45] second−order perturbation theory being particularly adapted to the description of metal→Lewis acid interactions. Molecular orbitals and NBOs were drawn with Molekel 4.3. ^{31}P and ^{11}B NMR chemical shifts were evaluated by employing the direct implementation of the GIAO method[46] at the B3PW91/SDD+pol(P),6-31G**(B,C,H)//B3PW91/6-31G**(P,B,C,H) level of theory, using as reference the corresponding PMe_3 ($\delta^{31}P$ = −63.5 ppm) and BF_3-Et_2O ($\delta^{11}B$ = 0 ppm) shielding constants calculated at the same level of theory.

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Supporting Information Available: Computational results including the Cartesian coordinates for the optimized structures (PDF); X−ray crystallographic data for complexes **2**/**4**/**7**/**8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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