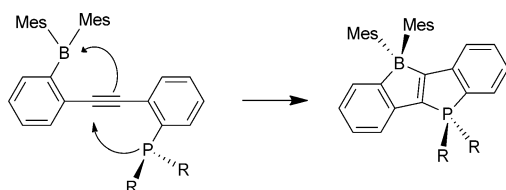


Double Cyclization/Aryl Migration Across an Alkyne Bond Enabled by Organoboryl and Diarylplatinum Groups**

Christina Sun, Zachary M. Hudson, Leanne D. Chen, and Suning Wang*

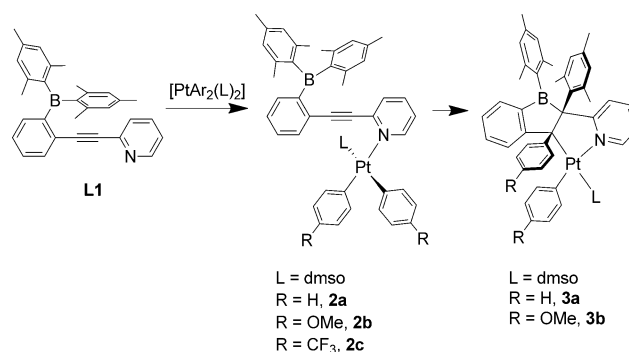
Organoboron compounds exhibit rich chemical reactivity, associated with the electron-accepting nature of the boron center, and this reactivity can lead to fascinating transformations and applications.^[1–4] In particular, molecules that contain both Lewis acidic boranes and Lewis basic amines or phosphines have unusual reactivity, which has been used in the activation of molecular hydrogen, alkenes, and alkynes.^[5–7] In a recent report, Yamaguchi and co-workers demonstrated that such a Lewis acid/base pair, specifically the boryl group, BMe₂ (Mes = 2,4,6-trimethylphenyl), and a phosphino group, can act synergistically to promote a double intramolecular cyclization of π -conjugated systems, containing an internal alkyne, to give a tetracyclic product (Scheme 1).^[5b] This reactivity has been exploited in a highly effective strategy for preparing a new class of zwitterionic π -conjugated materials that have unusual photonic and electronic properties.^[5] Stephan and co-workers have shown that the intermolecular addition of a phosphine and B(C₆F₅)₃ to an alkyne can also occur readily.^[6a,d]



Scheme 1. An intramolecular cyclization of a π -conjugated system involving an internal alkyne, a phosphine, and a borane.

Inspired by this previous work, we wanted to determine if similar cooperative reactivity, between an electron-rich metal center, such as Pt^{II}, and a BMe₂ group, could be used to construct metalocyclic π skeletons. We are interested in boron-containing Pt^{II} metalocyclic compounds because the presence of a BMe₂ group, for example, can greatly enhance the phosphorescence efficiency or the anion-sensing ability of Pt^{II} complexes.^[8] For this study, we designed ligand **L1**, which has a suitable handle for coordination of transition metal ions

to the BMe₂/alkyne scaffold. Furthermore, **L1** is known for its unusual reactivity: it undergoes facile hydration of the internal alkyne at ambient temperature, facilitated by the cooperation of the borane and the pyridine groups.^[9] We found that the coordination of **L1** to an electron-rich Pt^{II} center initiates a reaction sequence involving a spontaneous double cyclization of the π system, two aryl migrations, and a reduction of the internal alkyne to a C–C single bond (compound **3a** and **3b**, Scheme 2). The details of this remarkable transformation are reported herein.



Scheme 2. Spontaneous transformation of **2a** and **2b** involving two aryl migrations and two cyclizations.

The mixing of equimolar amounts of **L1** and [Pt(*p*-RC₆H₄)₂(dmsO)₂]^[10] in either CH₂Cl₂ or toluene at ambient temperature gave complexes **2a–c**, which were isolated in near quantitative yield and were fully characterized by ¹H NMR spectroscopy and elemental analysis (see the Supporting information). Compounds **2a–c** are air-stable light-yellow solids, however, upon prolonged standing in solution under N₂, using CH₂Cl₂ or toluene as solvent, **2a** and **2b** undergo gradual transformation into compounds **3a** and **3b**, respectively; **2c** remains unchanged. **3a** was isolated as block-shaped yellow crystals, and its structure was determined by single-crystal X-ray diffraction analysis (see the Supporting Information).^[11]

The crystal structure of **3a** reveals important information about the transformation (Figure 1). Firstly, one mesityl group from the boron center and one phenyl group from the Pt^{II} center have migrated to the C(2) and C(1) atoms, respectively. In addition, new σ bonds have been formed between the boron atom and the C(2) atom, and between the Pt^{II} center and the C(1) atom. As a consequence of this bond formation and migration, the C(1)–C(2) triple bond is transformed into a single bond, with a C–C bond length of 1.627(4) Å. Furthermore, the migrated aryl groups adopt

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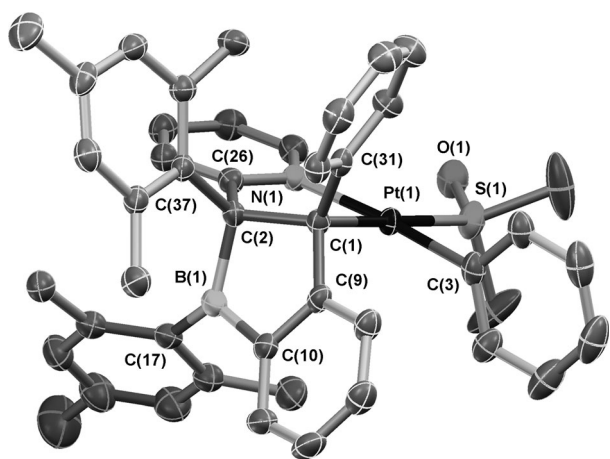


Figure 1. Crystal structure of compound **3a**. Thermal ellipsoids at drawn at 50% probability and hydrogen atoms are omitted for clarity. Important bond lengths [Å] and angles [°]: Pt(1)–C(1) 2.120(3), Pt(1)–C(3) 2.025(3), Pt(1)–N(1) 2.113(2), Pt(1)–S(1) 2.3026(9), B(1)–C(2) 1.656(4), B(1)–C(10) 1.528(5), B(1)–C(17) 1.587(5), C(1)–C(2) 1.627(4), C(1)–C(9) 1.514(4), C(1)–C(31) 1.529(4), C(2)–C(26) 1.515(4), C(2)–C(37) 1.558(4); C(3)–Pt(1)–N(1) 174.04(10), C(3)–Pt(1)–S(1) 177.69(8), C(2)–B(1)–C(10) 106.0(3), C(2)–B(1)–C(17) 127.1(3), C(10)–B(1)–C(17) 125.1(3).

a *syn* relationship in all crystals examined, and form significant π – π interactions with each other. Similar π – π interactions are also evident between the C(3) and the C(9) phenyl rings, as well as between the pyridyl and the C(17) mesityl ring. The C(1) and C(2) atoms both have distorted tetrahedral geometries, whereas the Pt^{II} center has a square planar geometry, in which the two Pt–C bonds are *cis* to each other. The boron center has a typical trigonal planar geometry and there is considerable B–C bond length variation, which is attributable to the steric environment of the molecule.

In the transformation of **2a** into **3a**, the alkyne carbon atoms, C(1) and C(2), become stereogenic centers, and both enantiomers of **3a** are found in the unit cell (space group $P\bar{1}$). Also, the magnetically equivalent methyl groups at the *ortho* positions of the mesityl groups of **2a** transform into two chemically inequivalent pairs of diastereotopic methyl groups in **3a**; these methyl groups together with the methyl groups at the *para* position, correspond to the six well-resolved methyl peaks in the ¹H NMR spectrum of **3a** (see the Supporting Information). Compound **3a** is air-stable in the solid state, despite the presence of a three-coordinate boron center bearing only one bulky mesityl group. NMR spectroscopic studies confirmed that compound **3b**, an air-stable yellow powder, is an analogue of **3a** (see the Supporting Information). In non-halogenated solvents, such as benzene or toluene, **3a** and **3b** are stable for days under air. However, in CH₂Cl₂, slow degradation of both compounds was observed when the solutions were exposed to air for a period of several days.

To establish whether compounds **3a** and **3b** are the major products from the transformation of the corresponding starting materials, **2a** and **2b**, we monitored the reaction by ¹H NMR spectroscopy at ambient temperature (see the Supporting Information). Conversion of both **2a** into **3a**,

and **2b** into **3b**, was observed within a few days in either CD₂Cl₂ or C₆D₆, although minor impurities associated with decomposition of the product or the presence of side reactions were observed after prolonged standing of the solution. NMR studies confirmed that for **2a** and **2b**, the desired products **3a** and **3b**, respectively, are the dominant products. Interestingly, we observed that the transformation of **2b** into **3b** proceeded much faster than that of **2a** into **3a**. For example, in CD₂Cl₂, whereas 37% conversion of **2b** into **3b** was observed after a period of seven days, only 18% conversion of **2a** into **3a** was observed after the same period of time. Longer reaction times led to higher conversions for both compounds, for example, up to 56% conversion of **2a** into **3a** can be observed after 4 weeks at ambient temperature. Conversion can be accelerated by warming the reaction mixture: when a solution of **2a** in C₆D₆ was maintained at 45 °C, a 50% conversion into **3a** was observed after a reaction time of one day (see the Supporting Information). In contrast to the facile transformation of **2a** and **2b**, compound **2c**, as a solution in CD₂Cl₂, which was maintained at ambient temperature, did not undergo any transformation within 17 days. These results suggest that the unusual transformation is promoted by the presence electron-rich aryl groups on the Pt^{II} center.

To determine the roles of both the boryl and the diaryl-platinum group in this unusual transformation, we synthesized control compounds **2d** and **2e** and examined their reactivity (Figure 2). In comparison to the initially studied compounds **2a** and **2b**, compound **2d** lacks the BMe₂ group, whereas compound **2e** contains a considerably more electron-deficient Pt^{II} center (PtCl₂). The structure of **2d** was determined by single-crystal X-ray diffraction analysis (Figure 2). The distances between the Pt^{II} center and the two carbon atoms of the alkyne moiety were 3.230(6) and 3.834(6) Å, and are similar to those of the computationally optimized structure of **2a**. However, when a solution of compound **2d** in CD₂Cl₂ was allowed to stand at ambient temperature, no reaction occurred after 10 days, as determined by ¹H NMR analysis, thus indicating that the presence of the boron acceptor is required for a reaction between the

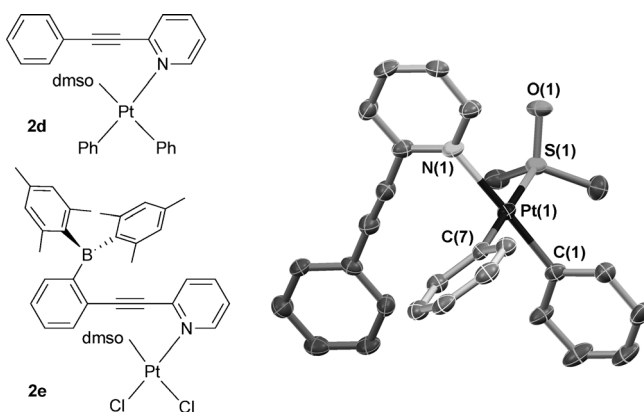


Figure 2. The structures of **2d** and **2e** (left) and the crystal structure of compound **2d**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity.

alkyne and the diarylplatinum center to occur. Similarly, **2e** does not undergo any transformation under the same conditions; this result indicates that the presence of the electron-rich diarylplatinum group is necessary for the transformation to occur. These results suggest that both of the aryl migrations and cyclizations for the formation of **3a** and **3b** require the synergistic action of the diarylplatinum and boryl groups.

Alkynyltriorganylborates with the general formula $\text{Li}[\text{R}'\text{-C}\equiv\text{C-BR}_3]$ undergo 1,2-migration reactions, in which upon electrophilic attack at the β -carbon atom of the triple bond, one R group migrates from the boron center to the α carbon atom of the alkyne.^[12a–g] However, the substrates for such migration reactions are typically terminal alkynes. The intermolecular addition of boranes to $\text{M-C}\equiv\text{C-R}'$ (M = main group or transition metal) have also been previously described.^[12h–j] More recently, Erker and co-workers have shown that a 1,2-alkyl and a 1,2-aryl migration reaction involving a $\text{B}(\text{CH}_3)(\text{C}_6\text{F}_5)_2$ and a $\text{B}(\text{C}_6\text{F}_5)_3$ group, respectively, and an internal alkyne are also possible.^[13] In contrast, a 1,4-migration of an aryl group from a boron center to a carbon center is highly unusual. To the best of our knowledge, the work described herein contains the first example of this type of migration, which is probably facilitated by the initial cyclization of the molecular backbone.

Based on the well-established mechanistic features of Pt^{II} facilitated alkyl migrations to alkyne bonds^[14] as well as the phosphine-borane cascade cyclization reported by Yamaguchi and co-workers,^[5] we propose a plausible mechanism for the transformation of **2a** into **3a** (and **2b** into **3b**) (Scheme 3). The proposed mechanism is supported by density functional theory (DFT) calculations (see the Supporting Information). The direct precursor for the transformation of **2a** into **3a** is species **A**, which is formed by dissociation of dimethyl sulfoxide from the Pt^{II} center. In **A**, the diphenylplatinum unit is much closer in space to the alkyne bond, with

calculated $\text{Pt}\cdots\text{C}$ distances of 2.91 and 3.41 Å; the corresponding distances in **2a** are 3.33 and 3.99 Å, respectively. This close proximity would activate the alkyne, thus promoting both the migration of a phenyl group from the Pt^{II} center to the π system and the cyclization upon formation of a bond between the π system and the boron center. We believe that the electron-deficient BMe_2 group and the electron-rich diphenylplatinum group thus act in synergy to promote this first step. DFT calculations support the hypothesis that the rate-determining step of the transformation of **2a** into **3a** involves the simultaneous formation of bonds between both the platinum and boron centers and the alkyne moiety, and the migration of the phenyl ring from the Pt^{II} center. This is consistent with the lack of reactivity of compound **2c** because it contains a relatively electron-poor diarylplatinum group, which would engender the aforementioned step with a relatively high activation barrier. Re-association of dimethyl sulfoxide would give species **B**, a key zwitterionic intermediate, which was identified by DFT calculations. In this species **B**, the electron-rich boryl group and the electrophilic Pt^{II} center enable a second migration step^[15]—a sigmatropic rearrangement involving the transfer of a boron-bound mesityl group to the proximate alkenyl carbon atom with concomitant formation of a Pt-C σ bond, thus yielding the final product **3a**.

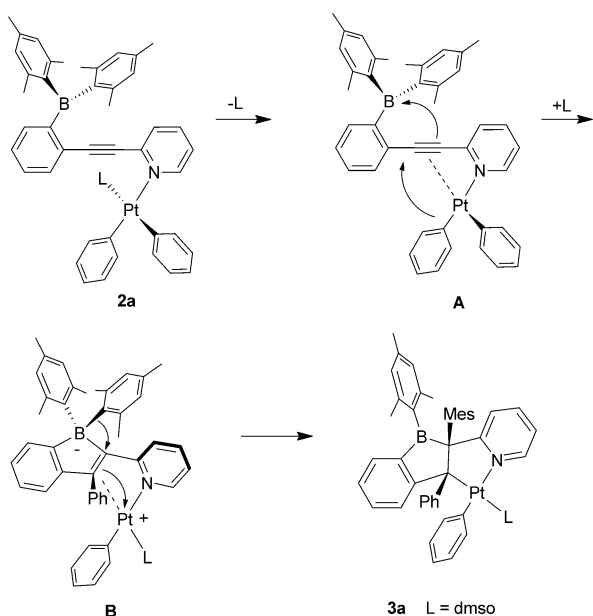
This mechanism also explains the diastereoselectivity of the transformation of **2a** into **3a**. As the Pt^{II} center in **B** blocks one face of the alkene, only the boron-bound mesityl group positioned near the other face of the alkene can migrate. This migration results in a final product wherein the two aryl groups that have undergone migration are *syn* to each other. Computational data also show that product **3a** is more stable than the starting material **2a** by approximately 36.8 kJ mol^{-1} .

In summary, we have demonstrated an unusual intramolecular reaction of **2a** and its analogue **2b**; this reaction involves two aryl migrations and two cyclizations and results in the formation of a unique bicyclic organometallic scaffold. Furthermore, the complementary electronic properties of the electron-deficient borane and electron-rich Pt^{II} centers were found to play a key role in this unprecedented transformation. Future work will involve the application of this strategy to the preparation of other polycyclic frameworks, as well as the incorporation of other electron-rich metal centers into boron-containing organometallic scaffolds.

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Scheme 3. Proposed mechanism for the transformation of **2a** into **3a**.

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