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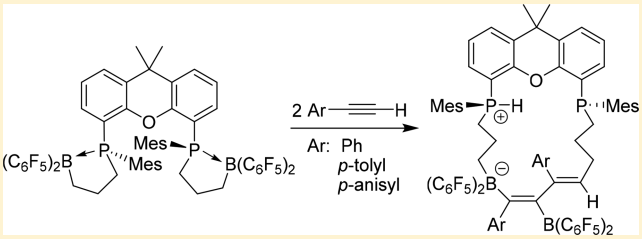
Macrocycle Formation by Cooperative Selection at a Double-Sited Frustrated Lewis Pair

Long Wang,[†] Dongsheng Deng,[†,‡] Karel Škoch, Constantin G. Daniliuc, Gerald Kehr, and Gerhard Erker*

Organisch-Chemisches Institut der Universität Münster, Corrensstr. 40, 48149 Münster, Germany

Supporting Information

ABSTRACT: Hydroboration of the 4,5-bis(allyl,mesityl)-phosphanyl xanthene derivative **2** with Piers' borane [HB-$(C_6F_5)_2$] gave the bis-P/B frustrated Lewis pair **3**. In this situation, the two symmetry-equivalent P/B FLP units featured markedly different reaction modes. With resorcinol, they formed the 20-membered macrocycle **11** by a sequence of −OH deprotonation/borane-induced tautomerization. With aryl acetylenes, the 18-membered macrocyclic products **15** (three examples) were formed in a unique sequence of carbon−carbon coupling reactions.



INTRODUCTION

Cooperativity is a powerful principle in biology and biological chemistry.[1] Many carrier proteins and enzymes contain two or more identical active sites, which may mutually influence their chemical behavior upon addition of reagents. If the reagent has been added to one site, then there are three options for the reactivity features of the second site: (a) the sites react independently—their behavior is additive; (b) the addition of the reagent to the second site is enhanced by the occupation of the first site (or the equilibrium constant is higher)—this marks cooperative behavior; (c) alternatively, the second site reacts slower. This is then termed anticooperative behavior (or marks negative cooperativity) (see Figure 1).[2]

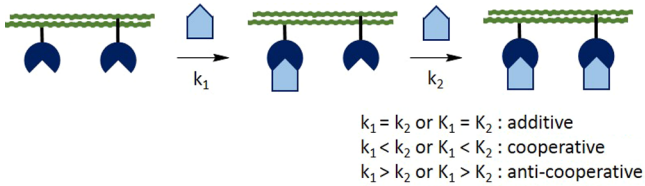


Figure 1. Cooperativity in biological systems.

We have now designed and prepared a completely artificial system for which such cooperative/anticooperative effects should be expected in its reactions. We chose frustrated Lewis pair (FLP) chemistry[3] for that purpose. Our system (see below) contained a pair of identical FLP units attached at a rigid organic backbone. Indeed, this led to cooperative behavior in some reactions, as expected, but surprisingly went beyond that in others: in some reactions, we recorded the consequences of an apparently new reaction principle, namely, "cooperative selection", between activated substrates at the pair of active sites which has caused reaction pathways to become favored that otherwise would probably not have been observed under other circumstances at all. Our observation may direct us toward using unusual methodical ways of finding new reactions. Two representative examples of this development are described in this account.

RESULTS AND DISCUSSION

Formation of the Double-Sited FLP System and Its Conventional Reaction with a Conjugated Ynone. We chose to prepare a double-sited P/B FLP system at the 9,9-dimethyl-9*H*-xanthene backbone.[4] We started our synthesis by metalation of 4,5-diiodo-9,9-dimethyl-9*H*-xanthene with *n*-butyl lithium in ether at −78 °C followed by two-fold phosphanylation with mesityl-PCl_2.[5] Subsequent reaction with 2 molar equiv of allyl magnesium chloride gave compound **2** as a white solid (Scheme 1). From the workup procedure, we obtained the *rac*-diastereomer **2** pure in 40% yield (δ^{31}P: −31.3). The X-ray crystal structure analysis as well as the NMR spectra identified it as the C_2-symmetric isomer (for details, see the Supporting Information). Compound **2** was then reacted with Piers' borane [$HB(C_6F_5)_2$] (2 equiv, 2 h, rt).[6] Workup gave the two-fold hydroboration product **3**, which we isolated as a white solid in 90% yield. Single crystals of compound **3** that were suitable for the X-ray crystal structure analysis were obtained from dichloromethane/pentane by the diffusion method.

The structure (Figure 2) shows near to (but not crystallographic) C_2-molecular symmetry. Each arene ring of the 9*H*-xanthene framework now bears a trimethylene-bridged P/B pair. We note that the boron atom of each unit binds to the phosphorus Lewis base [B1−P1 2.066(6), B2−P2

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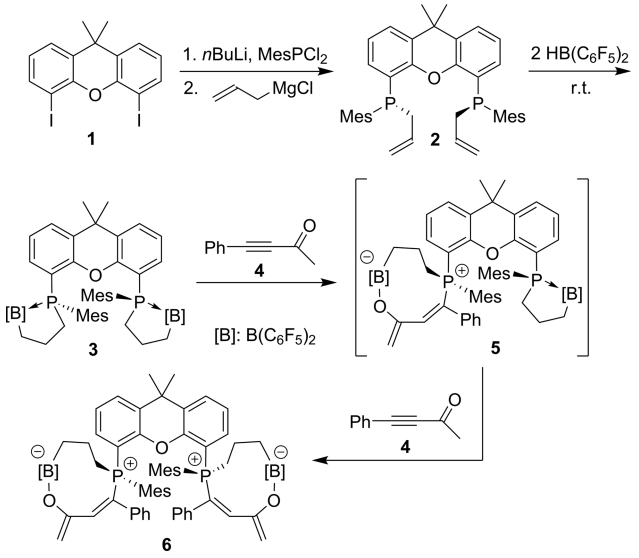
Scheme 1. Formation of the Double-Sited P/B FLP 3 and Its Reaction with the Conjugated Ynone 4



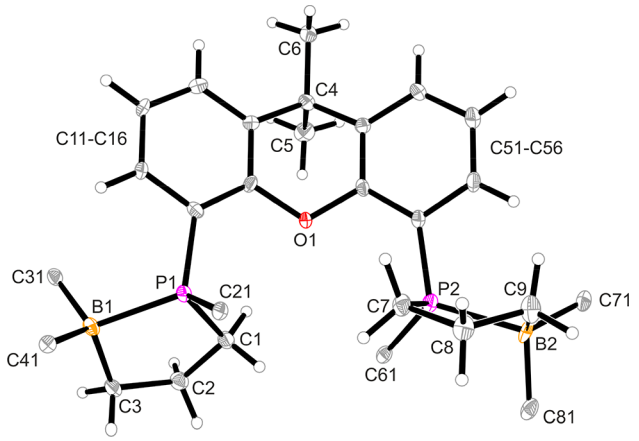


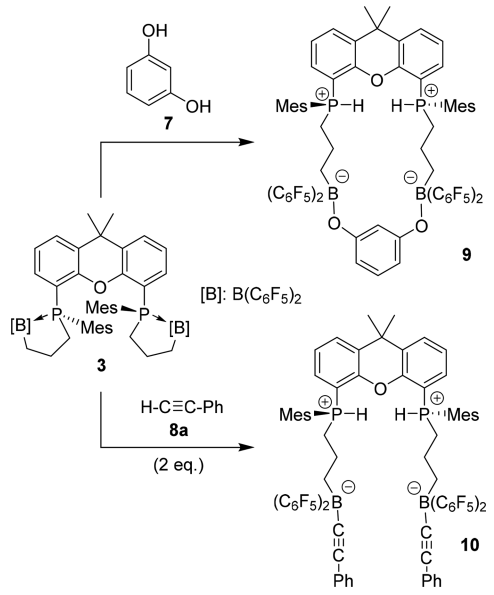
Figure 2. View of the molecular structure of the double-sited frustrated P/B pair *rac*-**3** (thermal ellipsoids are shown at 30% probability; substituents at P1/2 and B1/2 are omitted for clarity except their ipso-carbon atoms). Selected bond lengths (Å) and angles (deg): P1−B1 2.066(6), P2−B2 2.071(6), P1−C11 1.814(5), P2−C51 1.826(5), $\Sigma P1^{CCC}$ 326.6, $\Sigma P2^{CCC}$ 326.0, $\Sigma B1^{CCC}$ 336.8, $\Sigma B2^{CCC}$ 334.0, C12−C11−P1−B1−145.3(5), C52−C51−P2−B2−179.1(5), B1−P1···P2−B2 −82.5, C21−P1···P2−C61 125.9.

2.071(6) Å]. Compound **3** has retained its *rac*-^{P}R,^{P}R configuration. Consequently, compound **3** shows a single set of NMR data of the two symmetry-equivalent halves of the molecule in solution and a single resonance of the geminal dimethyl moiety at the backbone (CD_2Cl_2, 299 K): it shows a single ^{31}P NMR resonance at δ 26.5 and a ^{11}B NMR feature at δ −5.7. Due to the phosphorus chirality, the C_6F_5 groups of each $(C_6F_5)_2B$ unit are diastereotopic and there is hindered rotation around the B−C_6F_5 vectors at 258 K. Consequently, we observe a total of 10 ^{19}F NMR signals. Compound **3** show six ^{1}H NMR signals of the hydrogen atoms of the trimethylene bridge (for details, see the Supporting Information).

We first reacted the two-fold P/B FLP system **3** with the bifunctional conjugated ynone reagent **4**. The system **3** took up 2 molar equiv of **4**. Each five-membered P/B unit underwent 1,4-addition to the ynone unit followed by enolate rearrangement to give the pair of nine-membered heterocyclic units in product **6** (Scheme 1). We assume that the reaction proceeded via the mono-addition product **5** as an intermediate (see the Supporting Information for details, including the characterization of compound **6** by X-ray diffraction).[7]

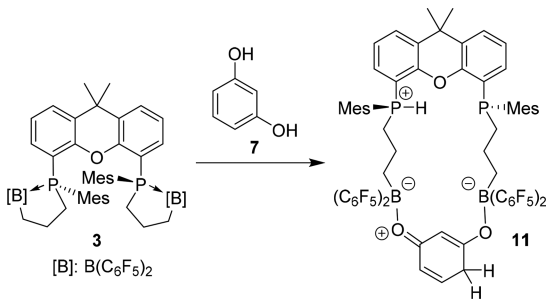
Reaction of the Bis-FLP 3 with Resorcinol and with 1-Alkynes: Unusual Cooperative Behavior. We next reacted the in situ generated double-sited FLP **3** with 1 equiv of resorcinol **7** or with 2 molar equiv of a small series of terminal aryl alkynes **8**. With terminal acetylenes, FLPs feature two prevailing competing reaction pathways, namely, cleavage of the terminal (sp)C−H bond in an acid/base reaction[8] or 1,2-addition of the FLP components to the carbon−carbon triple bond.[9] With Brønsted acidic ArO-H derivatives, P/B FLPs usually undergo protonation at phosphorus and formation of the respective boron phenolates. One might, therefore, have expected the formation of the conventional symmetric products **9** and **10**, respectively, from the reactions of the double-sited FLP **3** with these reagents (Scheme 2).

Scheme 2. Expected Reactions of the Two-Sited FLP 3 with Resorcinol or Two Phenyl Acetylene Equivalents



However, both of these reactions took a different course. The Brønsted acidic resorcinol reacted cleanly with **3** in a 1:1 molar ratio to give the macrocyclic product **11**, which we isolated as a white solid in 69% yield (Scheme 3). The X-ray crystal structure analysis showed that the boron atoms of both

Scheme 3. Reaction of the Twin FLP 3 with Resorcinol



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the FLP units had become bonded to the resorcinol oxygen atoms (Figure 3). One of the former resorcinol OH protons is

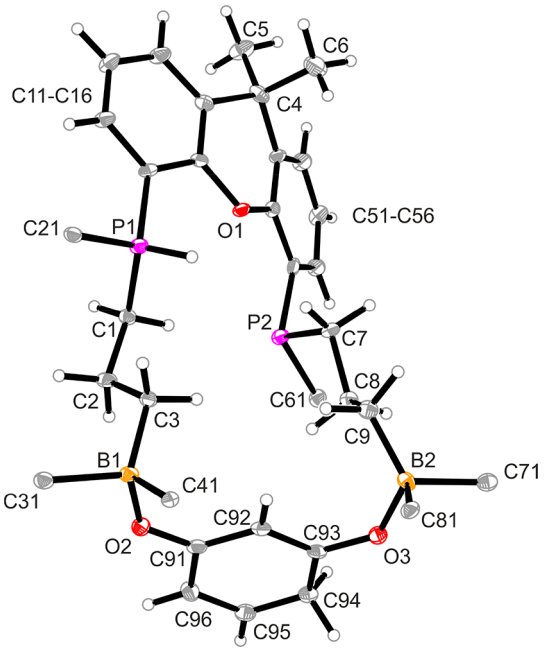


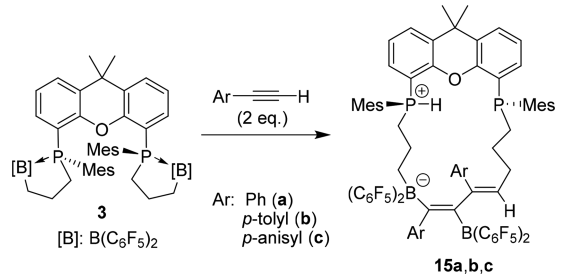
Figure 3. Molecular structure of the 20-membered macrocyclic product **11** (thermal ellipsoids are shown at 15% probability; substituents at P1/2 and B1/2 are omitted for clarity except for the arene ipso-carbon atoms). Selected bond lengths (Å) and angles (deg): P1···P2 4.466, P1−C11 1.799(5), P2−C51 1.823(6), B1−O2 1.528(7), B2−O3 1.547(7), O2−C91 1.277(7), O3−C93 1.295(6), C91−C92 1.402(8), C92−C93 1.408(8), C93−C94 1.462(8), C94−C95 1.401(8), C95−C96 1.391(8), C91−C96 1.459(8), $\sum P1^{CCC}$ 337.3, $\sum P2^{CCC}$ 315.8, B1−O2···O3−B2 −3.7.

found at the phosphorus atom P1 (to generate a phosphonium unit), whereas the other has been shifted in a boron Lewis-acid-induced dearomatization reaction[10] to the arene carbon atom C94 to generate a cyclohexadienone-type moiety (delocalized in the *β*-diketonate subunit). We found a bent conformation of the newly formed 20-membered macrocycle with the resorcinol-derived subunit oriented toward the side of the xanthene oxygen atom.

In solution (CD_2Cl_2, 299 K), we found a ca. 40:60 mixture of two isomers. We assume that they are persistent conformers that probably exhibit the resorcinol-derived unit oriented either toward the xanthene oxygen (as found in the crystal) or pointing away from it [^{31}P NMR: δ(major/minor) −14.1/−13.9 (PH^+), δ −37.5/−37.0 (P)]. The ^{19}F NMR spectrum shows four separate *o*-C_6F_5 signals of the pairs of diastereotopic C_6F_5 groups at the two boron atom for each of the isomers. The CH_2 group of the cyclohexadienone-derived backbone shows up at δ 3.19 and 2.37 (major isomer, minor isomer δ 3.37/3.30; both with $^2J_{HH}$ = 26.4 Hz) in the ^{1}H NMR spectrum of compound **11** (for further details, see the Supporting Information).

The reaction of the in situ generated bis-FLP **3** with phenyl acetylene (3 days, rt) also took an unexpected course. We isolated the unconventional 2:1 addition product **15a** as a white solid in 71% yield (Scheme 4). Single crystals suitable for the X-ray crystal structure analysis (Figure 4) were obtained from pentane/dichloromethane at rt by the diffusion method. It showed that two phenylacetylene units had been coupled

Scheme 4. Formation of the Macrocycles 15 by the Reaction of Bis-FLP 3 with Aryl Acetylenes



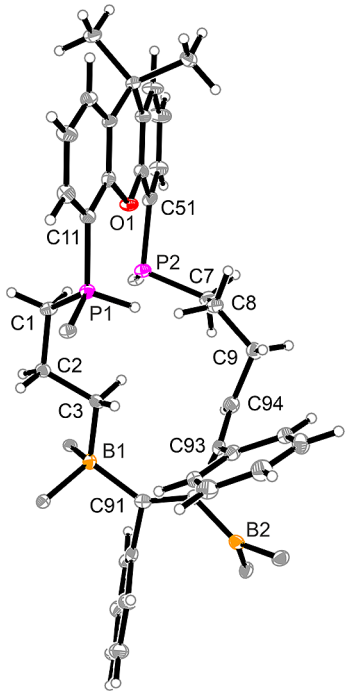


Figure 4. Molecular structure of the macrocyclic phenylacetylene coupling product **15a** (thermal ellipsoids are shown at 30% probability; substituents at P1/2 and B1/2 are omitted for clarity). Selected bond lengths (Å) and angles (deg): P1···P2 4.540, P1−C11 1.788(4), P2−C51 1.847(4), B1−C3 1.652(6), B1−C91 1.659(9), B2−C92 1.553(6), C91−C92 1.366(6), C92−C93 1.515(6), C93−C94 1.342(6), C94−C9 1.497(6), $\sum P1^{CCC}$ 338.6, $\sum P2^{CCC}$ 315.0, $\sum B1^{C3C31C41}$ 326.4, $\sum B2^{CCC}$ 359.5, B1−C91−C92−B2 175.1(4), C92−C93−C94−C9 177.2(4).

with rearrangement and involvement of both the P/B FLP units. We find the phosphorus atom P1 protonated. Its trimethylene linker still has the boron atom B1 attached. This $(C_6F_5)_2B$ moiety has now the −C91(Ph)=C92 group bonded to it, which originates from one phenylacetylene building block. Carbon atom C92 bears the $B(C_6F_5)_2$ substituent. It has become detached from its trimethylene chain, and it is found to be planar-tricoordinate. The pair of phenylacetylene building blocks has become head to tail coupled. Consequently, carbon atom C92 is found attached to the −C93(Ph)=C(94)H− unit, which is then found connected to the remaining trimethylene unit (C9−C7) which binds back it to the tricoordinate phosphorus atom P2. The newly formed conjugated diene unit (C91−C94) inside the resulting 18-membered macrocycle deviates markedly from coplanarity (θ C91−C92−C93−C94−72.9(6)°).

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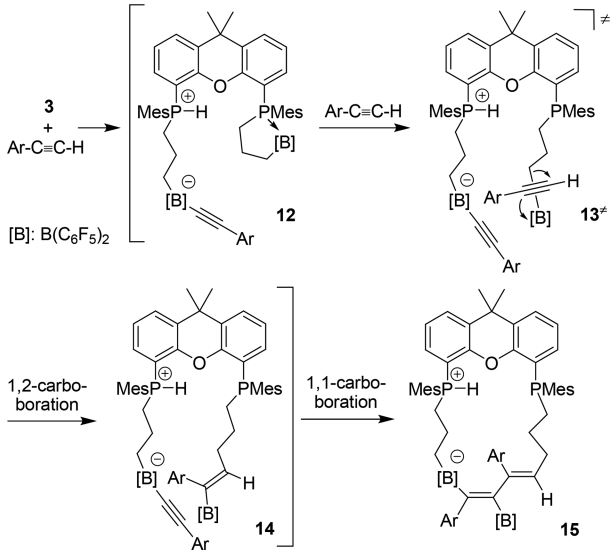
In solution (CD_2Cl_2, 299 K), compound **15a** shows six separate ^{1}H NMR CH signals and two methyl signals of the xanthene-derived framework. It features a broad ^{1}H NMR [P]H phosphonium doublet at δ 8.02 ($^1J_{PH}$ = 479.6 Hz) and a corresponding ^{31}P NMR doublet at δ −12.3 in addition to the P singlet at δ −32.3. We have monitored two very different ^{11}B NMR features, namely, a very broad signal of the planar-tricoordinate boron center at δ 61.0 and a rather sharp signal at δ −9.7 assigned to the tetracoordinate borate boron atom. The spectral information on the remaining cyclic moiety is rather complicated (see the Supporting Information for details), but we have located the =CH ^{1}H NMR resonance of the new 1,3-butadiene unit at δ 6.14 as a triplet ($^3J_{HH}$ = 7.1 Hz). We note that compound **15a** shows strongly temperature-dependent NMR spectra. Upon decreasing the temperature, we observed decoalescence to a double set of signals in most of the spectra (see the Supporting Information for the depicted spectra). We assume that this behavior originates from "freezing" a conformational equilibrium at low temperature on the respective NMR time scale. In view of the almost orthogonal geometry of the newly formed conjugated diene unit that we have observed in the solid-state structure of compound **15a**, it may be assumed that rotational "inversion" of the conformational chirality of this unit might be counted responsible for this observation.

The reaction of the in situ generated FLP **3** with *p*-tolylacetylene proceeded analogously (rt, 24 h, dichloromethane), and we isolated the 18-membered heterocyclic macrocycle **15b** as a white solid in 66% yield. It was characterized by C,H elemental analysis, spectroscopy, and X-ray diffraction. It shows structural (θ C91−C92−C93−C94 −73.2(8)°) and NMR features [^{31}P: δ −12.2 ($^1J_{PH}$ ∼ 480 Hz), δ −32.2; ^{11}B: δ 61.0 (very broad), δ −9.8] similar to those of **15a** (for details including the depicted spectra and a view of the molecular structure, see the Supporting Information). Like **15a**, compound **15b** also shows dynamic NMR spectra and features two probable conformational isomers at low temperature.

The reaction of compound **3** with *p*-anisyl acetylene was complete after 24 h at rt in dichloromethane. Crystallization from pentane/dichloromethane gave compound **15c** as white solid that we isolated in 71% yield. The X-ray crystal structure analysis shows the framework of the newly formed 18-membered macrocycle that was formed by carbon−carbon coupling of the two aryl acetylene units at the pair of P/B FLP functionalities. Like in **15a** and **15b**, the newly formed dienyl unit in **15c** is markedly rotated from conjugation (θ C91−C92−C93−C94 79.2(5)°). In solution, compound **15c** shows NMR data similar to those of its congeners **15a,b** (see the Supporting Information for details).

The formation of the macrocyclic alkyne coupling products **15** requires some rearrangement steps on the way. The formation of compound **15** can potentially be rationalized by means of a rather short reaction sequence as it is schematically depicted in Scheme 5, although this pathway is not proven as yet. It starts with a conventional deprotonation/addition of the C−H acidic alkyne[8] by the FLP phosphane in a typical FLP reaction to generate the intermediate **12**. We have actually observed this type of an intermediate in the special case of the reaction of **3** with *o*-tolyl acetylene (see the Supporting Information for details). We then might assume that the carbon−carbon coupling of the B-trimethylene unit of the adjacent P/B FLP unit takes place with a terminal alkyne

Scheme 5. Potential Rationalization of the Formation of Macrocycles 15 by Unconventional Alkyne Carbon−Carbon Coupling at the Two-Sited FLP 3



equivalent. As seen from the composition of the final products **15**, this might proceed selectively by a *trans*-1,2-carboboration process,[11] as depicted schematically by the respective assumed transition state geometry **13**$^{\neq}$. We might assume that this step then is followed by a 1,1-carboboration at the stage of the intermediate **14** (with either boryl or aryl migration)[12] to directly give the observed products **15**.

CONCLUSIONS

The reaction of the double-sited FLP **3** with the ynone **4** follows a route that is conceptually equivalent to the behavior of the biological systems, as schematically depicted in Figure 1: both the intramolecular trimethylene-bridged FLPs react in an identical way, giving the same medium-sized ring product by 1,4-P/B FLP addition, but maybe with different individual reaction rates. The reaction of **3** with resorcinol has a different quality. It is known that phenolic O−H groups can be deprotonated by the FLP phosphanyl unit, and strongly electrophilic boranes were shown to induce tautomerization reactions.[7,10] The special quality of the formation of compound **11** is that these two very different reactions have become specifically coupled in this cooperative situation. It seems that B−O bonding on one side has caused the tautomerization reaction to become favored over a second deprotonation reaction on the other side (or vice versa). It means that a specific activation at one site not only induces a change in rate of a reaction at the other site, but leads to favoring a different reaction type out of a possible manifold of competing reactions.

The situation has become even more extreme in the case of the acetylene coupling/rearrangement processes that we have observed to take place at the double-sited FLP **3**: There is increasing evidence that boranes can effectively couple acetylene units. Usually this was observed in intramolecular cases where bis-alkynyl-containing substrates underwent sequences of 1,1-carboboration reactions, leading to heterocyclic or arene annulation products.[13] Recently, we observed an intermolecular halogenoborane-induced alkyne oligomerization reaction.[14] The alkyne/alkyne coupling reaction

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observed here is of a new quality. Here, each of the P/B FLP units activated an alkyne equivalent apparently in a different but highly specific way (possibly in an equilibrium situation), and then the two resulting units underwent a specific combined action to form the observed carbon−carbon coupled products, here, the 18-membered macrocycles **15**. In other words, the neighboring FLP units each have activated an alkyne unit in some way, and then one of these intermediate system has apparently selected another differently activated alkynyl-derived species at the other FLP moiety for a coupling reaction that had become favored in that specific situation. This "cooperative selection" bears a new quality in the cooperative/anticooperative manifold: we not only change the rates (or equilibrium constants) of the subreactions in this situation but also induce a fit that leads to a selection of reaction pathways that can lead to completely new reactions, which cannot be observed in other "conventional" situations. We will see how far this reaction principle will lead us. We hope that we can use it for finding synthetically useful new reaction types by applying such cooperative selection features of combinations of activating functionalities in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00002.

Full experimental procedures and characterization data (PDF)

Accession Codes

CCDC 1864103−1864109 and 1873800 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: erker@uni-muenster.de.

ORCID

Karel Škoch: 0000-0001-6406-989X

Gerald Kehr: 0000-0002-5196-2491

Gerhard Erker: 0000-0003-2488-3699

Author Contributions

†L.W. and D.D. contributed equally.

Notes

The authors declare no competing financial interest.

‡On leave from Henan Key Laboratory of Function-Oriented Porous Materials, College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471934, P.R. China.

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