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Exploiting the π-Acceptor Properties of Carbene-Stabilized Phosphorus Centered Trications $[L_3P]^{3+}$: Applications in Pt(II) Catalysis

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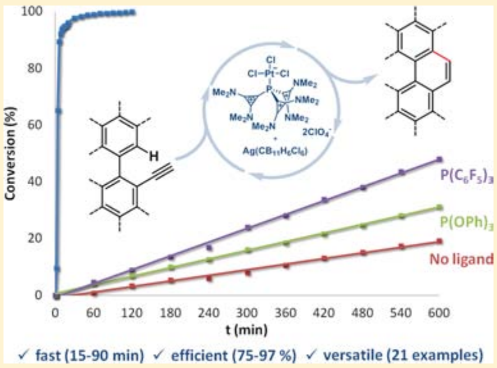
Supporting Information

ABSTRACT: Reaction of tris(dimethylaminocyclopropenium) substituted phosphine **1** with K_2PtCl_4 afforded the bench stable complex **3** which upon treatment with $Ag[CB_{11}H_6Cl_6]$ turned out to be an excellent catalyst for the transformation of a variety of *ortho*-biaryl substituted alkynes into polycyclic homo- and heteroarenes of different size, shape, and curvature through a 6-*endo*-dig cyclization. This constitutes the first example ever reported of using a P_1-centered trication as ligand in catalysis. The strong π-acceptor character of **1** that derives from its three positive charges substantially increases the intrinsic π-acidity of Pt in complex $\mathbf{1}\cdot PtCl_2$ and dramatically enhances its ability to activate π-systems toward nucleophilic attack. As a consequence, a remarkable acceleration of the model transformation is observed when compared with other classical π-acceptor ligands such as $P(OPh)_3$ or $P(C_6F_5)_3$. Moreover, the employment of **1** as ligand also expands the scope of this reaction to previously inaccessible substitution patterns. Kinetic studies and deuterium labeling experiments as well as density functional theory (DFT) calculations were performed in order to explain these findings.



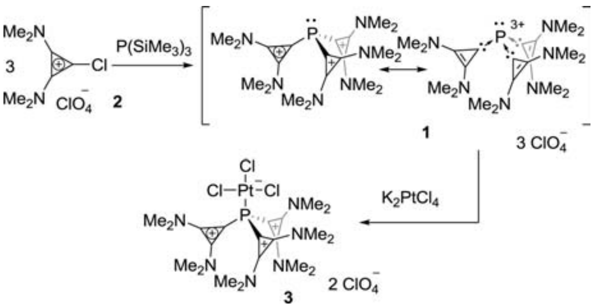
✓ fast (15-90 min) ✓ efficient (75-97 %) ✓ versatile (21 examples)

1. INTRODUCTION

π-Acid catalysis, mainly with Au(I) and Pt(II) based species, has emerged in the past decade as one of the most efficient tools for the promotion of rearrangements in unsaturated organic substrates, which provide an exquisite entry for the synthesis of intricate skeletons that may be otherwise difficult to prepare.[1] The generally accepted mechanism that governs most of these transformations involves three main steps: (i) coordination of the π-acid metal to the alkyne or allene moiety present in the starting material, (ii) nucleophilic intra- or intermolecular attack to the thus activated substrate forming a vinyl-metal species, and (iii) protodemetalation of the vinyl intermediate with concomitant regeneration of the active catalyst.[2] It seems reasonable to expect that the first two of these steps may be accelerated by strong π-acceptor ancillary ligands, which should increase the Lewis acidity of the metal center they coordinate. In striking contrast, potent σ-donating ligands will weaken the M−C bond in the vinyl intermediates by their *trans* influence and thus facilitate the third protodemetalation step. Hence, the selection of the most appropriate ligand for a particular transformation of this type can only be done on the basis of an in-depth understanding of the nature of the rate-determining step.[3]

Very recently, we reported the synthesis of the first ever isolated carbene-stabilized P_1-centered trication $[L_3P]^{3+}$ (L = 2,3-dialkylamino-cyclopropenyl-1-ylidene) **1** by reaction of the 1-chloro-2,3-dimethylamino)cyclopropenium salt **2** and $P(SiMe_3)_3$.[4] Despite the three positive charges on the groups directly attached to the P atom, this compound can still serve as a ligand for π-acidic metals such as Pt. Thus, when **1** is treated with K_2PtCl_4 in acetonitrile, the bench stable complex **3** is formed (Scheme 1). More interestingly, charge decomposition analysis of the metal−ligand interaction in **3** gave the surprising result that the total L→M σ-donation (0.31 e) is lower than the M→L π-back-donation (0.43 e) into the very low-lying LUMO of **1**, which must hence be regarded as the main interaction in **3**. This unconventional situation in which the P-ligand removes net electron density from the metal suggests that compound **1** increases the natural π-acidity of Pt(II) centers. It should thus accelerate known reactions, or even permit new reactions, in

Scheme 1. Synthesis of $[L_3P]^{+3}$ Cation 1, its Pt Complex 3, and Molecular Structure of 3 in the Solid State



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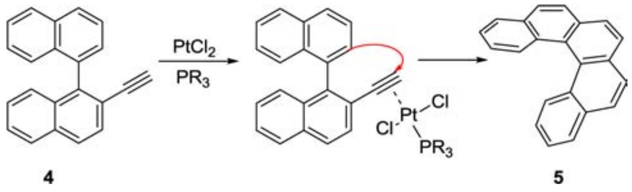
which either the coordination of the substrate or the nucleophilic attack to the already activated substrate is the rate-determining step.[5]

Herein, we report the first practical application of cation **1** as ligand in a catalytic process, the Pt-catalyzed cyclization of *ortho*-biaryl substituted alkynes into polycyclic homo- and heteroarenes, and describe the advantages derived from its employment in terms of higher reactivity and broader substrate scope. Moreover, we also present kinetic, isotope labeling, and DFT computational studies on the reaction mechanism governing this transformation in order to precisely ascertain the role of ligand **1**.[6]

2. RESULTS AND DISCUSSION

2.1. Selection of a Model Reaction. The Pt-catalyzed 6-*endo*-dig cyclization of 2-ethinyl-1,1′-binaphtalene **4** into pentahelicene **5**, first reported by Fürstner and co-workers,[7] was chosen as model reaction for two main reasons (Scheme 2): (a) The interest in polycyclic homo- and heteroarenes has been refueled in the last years due to their unique optoelectronic properties and their potential applications in organic electronic devices. The chosen cyclization is a very attractive entry for the preparation of these carbon-rich materials.[8] However, under the previously described conditions, quite long reaction times are necessary. Additionally, the development of a more reactive catalyst that broadens the scope of this transformation in terms of new substitution patterns is still necessary.[9] (b) Due to the relatively weak nucleophile that is employed (an aromatic ring), the nucleophilic attack is expected to be the rate-determining step for this reaction.[10] Hence, the use of strong π-acceptor ancillary ligands such as **1** should facilitate this transformation. Finally, it is likely that under the selected reaction conditions, with high substrate concentration and noncoordinating solvents, the coordination of the substrate to Pt is not a rate-relevant step.

Scheme 2. Cyclization of 2-Ethynyl-1,1′-binaphthalene 4 into Pentahelicene 5 as Model Reaction

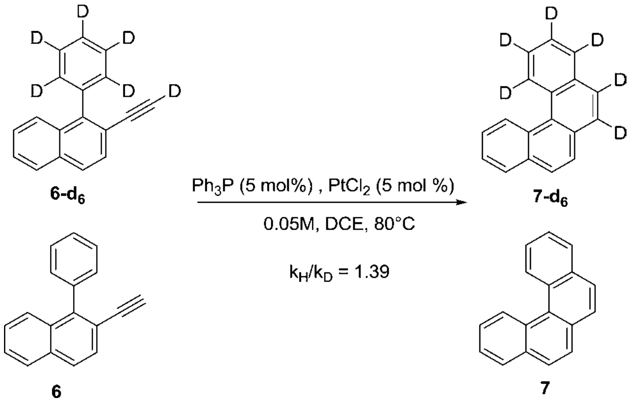


2.2. Kinetic Studies. In order to prove these assumptions, kinetic as well as computational studies were carried out to identify the rate-determining step for the catalytic reaction. Thus, we started by examining the order of this transformation in substrate. By monitoring by GC the reaction of **4** (50 mM), PPh_3 (2.5 mM), and $PtCl_2$ (2.5 mM) in dichloroethane at 80 °C, the cyclization was found to follow pseudo-zero-order kinetics in **4**. The measurements gave a linear plot of $(\Delta[\mathbf{5}]/\Delta t)/[\mathbf{4}]_0$; k_{obs} = 0.0274 h^{-1}, R^2 = 0.996 (Supporting Information, Figure S1), indicating (as expected) that coordination of **4** to the Pt center is not the rate-determining step.

The order in Pt was evaluated by measuring the rate constant for the reaction at different catalyst loadings (1−2.5 mM) keeping constant the concentration of alkyne **4** at 50 mM and the temperature at 80 °C (Supporting Information, Figure S2). A plot of the obtained rate constants k_{obs} versus $[Ph_3P\cdot PtCl_2]$ provided a straight line with a slope of 0.01 indicating an overall first order in Pt during the process (Supporting Information, Figure S3).

2.3. Deuterium Labeling Experiments. The nature of the intermediates involved in this catalytic cycle was also investigated by deuterium labeling experiments. The fact that no H/D scrambling occurs during the crossover cycloisomerization depicted in Scheme 3 strongly supports the intramolecular nature of any occurring proton shift. In addition, the small measured isotope effects suggest that none of the plausible transition states involving C−H bond cleavage are likely to be rate-determining (Supporting Information, Figure S3). Instead, the observed effect is probably derived from the hybridization change that must take place during an earlier cyclization step.

Scheme 3. Deuterium Labeling Crossover Experiment

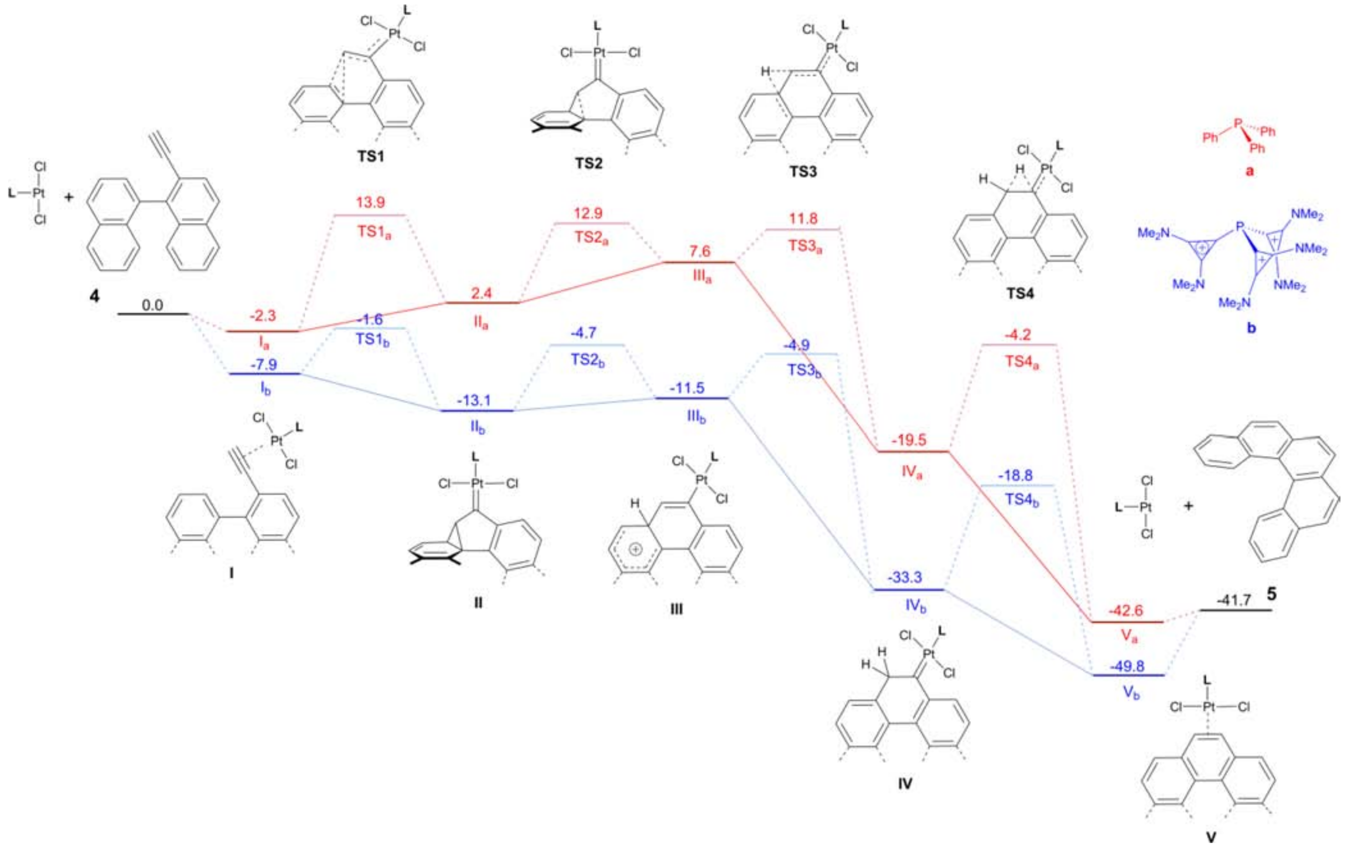


2.4. DFT Calculations on the Reaction Mechanism. The reaction mechanism was explored by means of hybrid DFT calculations. Geometry optimizations were performed using the B3LYP functional with the LANL2DZ effective core potential and the associated double-ζ basis set for Pt and the 6-31G* basis set for all other atoms (B3LYP-I level). Energies were determined from single-point calculations, in which the 6-31G* basis was replaced by the larger 6-31+G** basis whereas LANL2DZ was replaced by LANL2TZ(f) for Pt (B3LYP-II level). The reported free energies (Scheme 4) were obtained from the B3LYP-II energies by adding thermal and entropic corrections (B3LYP-I level) as well as dispersion and continuum solvation corrections (see Supporting Information for details). All calculations were done with the Gaussian09 suite of quantum chemical programs.[11]

We investigated the cycloisomerization of **4** into **5** using PPh_3 and the cation **1** as ancillary ligands.[12] As can be seen from Scheme 4, the free energy of coordination of alkyne **4** is computed to be −2.3 and −7.9 kcal/mol for $Ph_3P\cdot PtCl_2$ and $\mathbf{1}\cdot PtCl_2$, respectively, indicating exergonic formation of the intermediate complexes $\mathbf{I_a}$ and $\mathbf{I_b}$. The higher thermodynamic stability of $\mathbf{I_b}$ can be rationalized by inspection of the frontier orbitals of the actual catalysts (Figure 1). The LUMO has a similar shape in both cases (σ* P−Pt), but it lies much lower in the $\mathbf{1}\cdot PtCl_2$ complex and will therefore confer a much stronger Lewis acidity to this catalyst, thus favoring the coordination of the alkyne to Pt. This facile coordination is fully consistent with the observed pseudo-zero-order kinetics in substrate.

The next step along the reaction coordinate involves the nucleophilic attack of the arene ring to the activated alkyne

Scheme 4. Free Energy Profiles (kcal/mol) for the Cyclization of 2-Ethynyl-1,1′-binaphthalene 4 into Pentahelicene 5



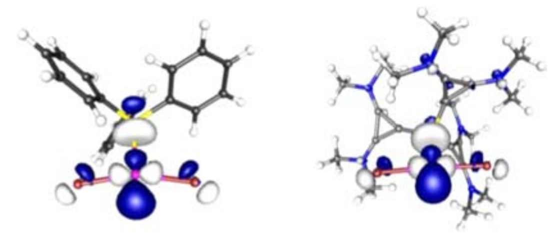


Figure 1. Left: LUMO of $Ph_3P·PtCl_2$, $E = -3.28$ eV. Right: LUMO of $1·PtCl_2$, $E = -11.69$ eV.

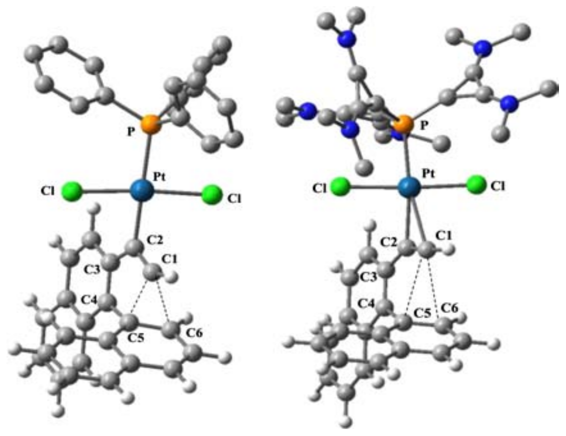


Figure 2. Left: calculated transition state **TS1**$_a$. Selected distances (Å): C(1)−C(2) 1.30, C(1)−C(5) 2.07, C(1)−C(6) 2.30. Right: calculated transition state **TS1**$_b$. Selected distances (Å): C(1)−C(2) 1.26, C(1)−C(5) 2.81, C(1)−C(6) 2.86. Hydrogen atoms on the ligands have been omitted for clarity.

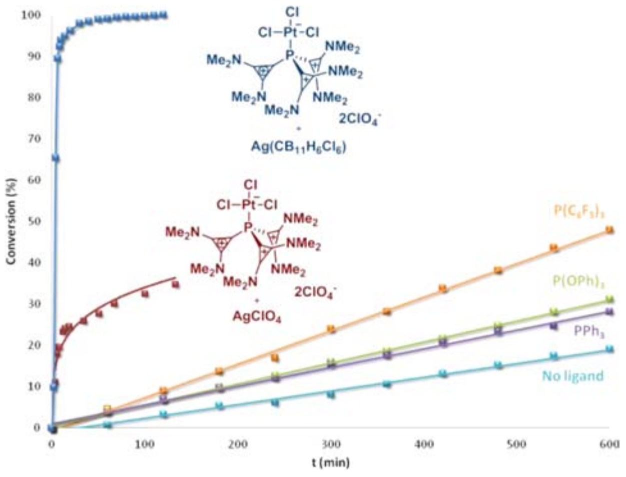
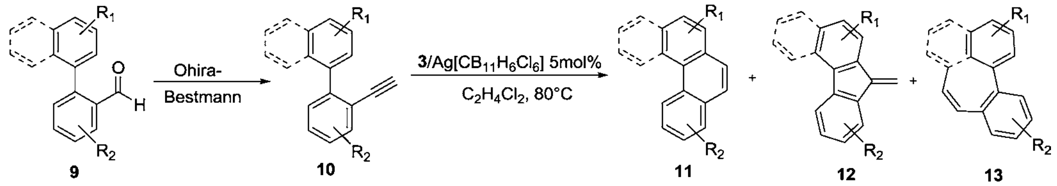
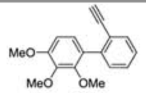
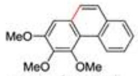
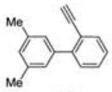
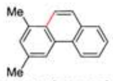
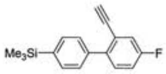
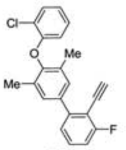
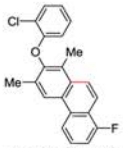
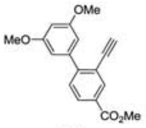
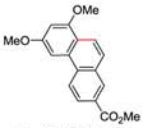
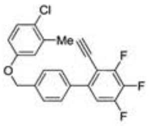
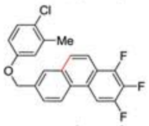
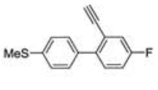
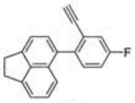
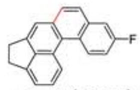
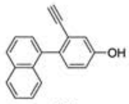
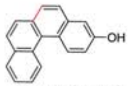
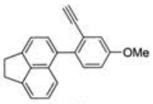
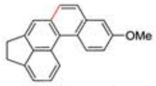
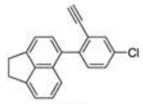
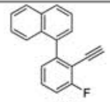
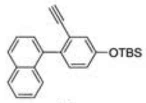
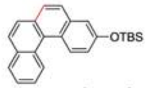
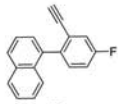
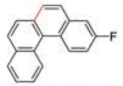
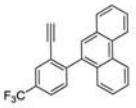
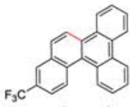
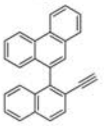
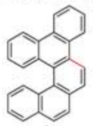
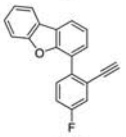
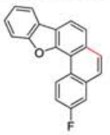
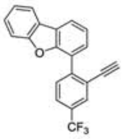
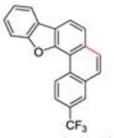
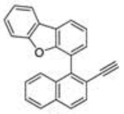
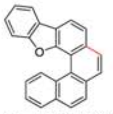
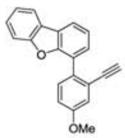
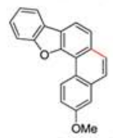
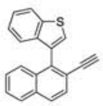
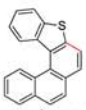
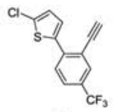
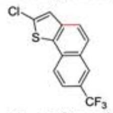


Figure 3. Ligand effect on the Pt-catalyzed cyclization of 2-ethynyl-1,1′-binaphthalene **4** into pentahelicene **5**. (a) Conditions for L = PPh_3, $P(OPh)_3$, $P(C_6F_5)_3$: **4** (0.05 M), $PtCl_2$ (5 mol %), and ligand (5 mol %), $Cl(CH_2)_2Cl$, 80 °C. (b) Conditions for precatalyst **3**: **4** (0.05 M), **3** (5 mol %), $AgClO_4$ or $Ag[CB_{11}H_6Cl_6]$ (5 mol %), $Cl(CH_2)_2Cl$, 80 °C.

to form the cyclopropyl intermediates **II**$_{a/b}$ through transition states **TS1**$_{a/b}$, respectively. Our calculations indicate that, regardless of the ancillary ligand used, these are the highest-energy transition states for both catalytic cycles (rate-determining in the framework of the energetic span model, see page S36 in the Supporting Information for a detailed discussion). Importantly, **TS1**$_b$ lies no less than 15 kcal/mol lower than **TS1**$_a$, suggesting that the use of **1** as ligand significantly fosters

Table 1. Scope of the Pt-Catalyzed Cycloisomerization of *ortho*-Alkynylated Biaryls Employing 1 as Ligand



Entry	Substrate	Time (min)	Product(s), yield %, (**11**:**12**:**13** ratio)
1	 **10a**	60	 **11a**, 75, (100:0:0)
2	 **10b**	15	 **11b**, 97, (82:18:0)
3[a]	 **10c**	90	 **11c**, 81, (100:0:0)
4	 **10d**	15	 **11d**, 87, (94:6:0)
5	 **10e**	20	 **11e**, 87, (93:7:0)
6	 **10f**	15	 **11f**, 89, (99:1:0)
7	 **10g**	90	n.r.
8	 **10h**	15	 **11h**, 91, (88:2:10)
9	 **10i**	15	 **11i**, 86, (95:3:2)
10	 **10j**	45	 **11j**, 88, (93:5:2)
11	 **10k**	15	 **11k**, 92, (91:7:2)
12	 **10l**	15	 **11l**, 94, (100:0:0)
13	 **10m**	15	 **11m**, 86, (95:4:1)
14	 **11n**	15	 **11n**, 95, (97:2:1)
15	 **10o**	15	 **11o**, 94, (94:5:1)
16	 **10p**	15	 **11p**, 95, (90:10:0)
17	 **10q**	15	 **11q**, 91, (93:7:0)
18	 **10r**	60	 **11r**, 87, (97:3:0)
19	 **10s**	60	 **11s**, 83, (99:1:0)
20	 **10t**	60	 **11t**, 77, (88:12:0)
21	 **10u**	30	 **11u**, 81, (80:20:0)
22[a]	 **10v**	90	 **11v**, 86, (98:2:0)

[a] Reaction initiated with a catalytic charge of 2.5 mol %. After 45 min a second portion of catalysts 2.5 mol % was added.

the whole process. The beneficial stabilizing effect of **1** can be easily rationalized by comparing the key C−C distances in transition states **TS1**$_a$ and **TS1**$_b$ (Figure 2). The calculated C1−C5 and C1−C6 distances are, respectively, 2.07 and 2.30 Å in **TS1**$_a$, but much longer in **TS1**$_b$ (2.81 and 2.86 Å) reflecting an earlier and therefore energetically lower transition state when **1** is used as ligand.

The subsequent opening of the cyclopropane ring requires moderate activation that does not depend much on the nature of the ancillary ligand (barriers of 9−10 kcal/mol) and leads to intermediates **III**$_{a/b}$, which evolve via a 1,2-H shift to form the Pt-carbenes **IV**$_{a/b}$ through transition states **TS3**$_{a/b}$. The two intermediates **IV**$_{a/b}$ are 22−27 kcal/mol more stable than their precursors **III**$_{a/b}$, and the energies of the following transition states **TS4**$_{a/b}$ are much lower than those of **TS3**$_{a/b}$, respectively. Thus, the formation of the Pt-carbenes **IV**$_{a/b}$ is likely to be irreversible. Finally, a second 1,2-H shift leads to the pentahelicene-Pt π-complexes **V**$_{a/b}$, which after dissociation regenerate the active catalysts and the desired product **5**. The two proposed intramolecular proton shifts are in agreement with the observations from deuterium labeling experiments.

2.5. Ligand Effect. The whole set of kinetic and calculated data suggests that (i) the rate-determining transition state must be **TS1**, and (ii) this step must be facilitated by the use of electron-poor ancillary ligands. Accordingly, we chose for our studies of ligand effects a series of phosphanes such as PPh_3, $P(OPh)_3$, $P(C_6F_5)_3$ and precatalyst **3** in combination with a silver salt.[13] As can be seen from Figure 3 the theoretical predictions were confirmed, and both $P(OPh)_3$ and $P(C_6F_5)_3$ performed better than PPh_3 in terms of reactivity. Interestingly, the mixture of **3** and $AgClO_4$ produces a much faster initial reaction surpassing any of the other π-acceptor ligands. However, the catalytic species rapidly decays and complete conversion of the substrate was not observed after two hours. To overcome this problem, the less coordinating and more soluble carborane-based anion $[CB_{11}H_6Cl_6]^-$ was evaluated.[14] We were glad to see that this new catalytic mixture was vastly superior to any other described, and complete conversion of the model substrate to pentahelicene **5** was achieved in less than 20 min under the standard reaction conditions.

With this optimized catalyst in hand we explored the scope of this methodology in detail. To this end a representative set of biaryl substituted alkynes was prepared and submitted to the newly developed procedure. Particular attention was paid to investigating the compatibility of the novel catalysts with different functional groups. The examples compiled in Table 1 clearly demonstrate the generality of this catalytic system for the synthesis of substituted phenanthrenes **11a−g**, benzophenanthrenes **11 h−n**, benzotriphenylenes **11o−p**, substituted benzofuranes **11q−t**, and thiophenes **11u−v**. Moreover, the functional group compatibility is outstanding. Ethers, free or silylated alcohols, esters, halogen substituents, silyl and trifluoromethyl groups, thiophenes, and furanes were well tolerated, and the cyclized products were obtained in few minutes with very good to excellent yields.[6] Only compounds containing strongly coordinating functionalities such as thioethers **10g** were found to interfere with the activity of the catalytic system (Table 1, entry 7). Also remarkable is the pronounced selectivity for the 6-*endo*-dig cyclization over the also conceivable 5-*endo*-dig mode. Single crystals suitable for X-ray analysis were grown for various representative products, and their structures are shown in Figure 4 (**11c**, **11p**) and in the Supporting Information (**11o**, **11t**).

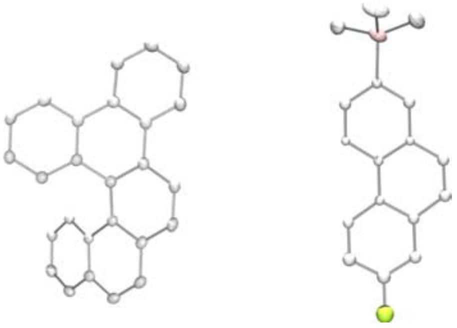


Figure 4. Molecular structures of compounds **11p** (left) and **11c** (right). Anisotropic displacement parameters shown at 50% probability level and hydrogen atoms omitted for clarity.

2.6. Conclusions. We report the first application of a P_1-centered trication as ligand in catalysis. Due to its high π-acceptor character, the trication **1** substantially enhances the intrinsic π-acidity of Pt and hence its ability to activate alkynes toward nucleophilic attack. Specifically, upon treatment with $Ag[CB_{11}H_6Cl_6]$, complex **3** turns out to be an extremely reactive catalyst for the hydroarylation of *ortho*-alkynylated biaryls, which clearly surpasses other known catalytic systems not only in terms of reactivity but also regarding functional group tolerance.

Moreover, the nonspecific mode of action of **1**, a simple reinforcement of metal-to-ligand back-donation, makes us think that the impact of this study may be limited neither to the particular transformation chosen as model reaction, nor to Pt(II) catalysis. Whether these or related P_1-centered mono- or polycations could find application as ligands in other metal-catalyzed transformations is currently under investigation in our laboratories and will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures including characterization data for all new compounds, additional deuterium labeling experiments, CIF files for **11c**, **11p**, **11o**, and **11t**, computational procedures, further computational results (structural parameters, charge distributions, and optimized Cartesian coordinates) as well as complete ref 11. NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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