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Cationic Ligands

Coordination Chemistry of Cyclopropenylidene-Stabilized Phosphenium Cations: Synthesis and Reactivity of Pd and Pt Complexes

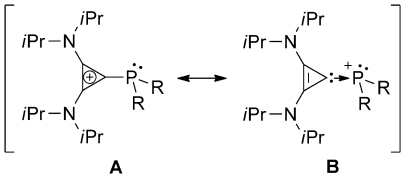
Ágnes Kozma, Tobias Deden, Javier Carreras, Christian Wille, Jekaterina Petuškova, Jörg Rust, and Manuel Alcarazo*[a]

Abstract: A straightforward synthesis of cyclopropenylidene-stabilized phosphenium cations **1a**–**g** through the reaction of $[(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{C}_3{}^{+}\mathrm{Cl}]\mathrm{BF}_4$ with secondary phosphines is described. Their donor ability was evaluated by analysis of the CO stretching frequency in Rh complexes $[\mathrm{RhCl(CO)L}_2](\mathrm{BF}_4)_2$ and electrochemical methods. The cyclopropenium ring induces a phosphite-type behavior that can be tuned by the other two substituents attached to the phosphorus atom. Despite of the positive charge that they bear, phosphenium cations **1a**–**g** still act as two-electron donor ligands, forming adducts with Pd^{II} and Pt^{II} precursors. Conversely, in the presence of Pd^0 species, an oxidative insertion of the Pd atom into the $C_{carbene}$–phosphorus bond takes place, providing dimeric structures in which each Pd atom is bonded to a cyclopropenyl carbene while two dialkyl/diaryl phosphide ligands serve as bridges between the two Pd centers. The catalytic performance of the resulting library of Pt^{II} complexes was tested; all of the cationic phosphines accelerated the prototype 6-*endo*-dig cyclization of 2-ethynyl-1,1′-biphenyl to afford pentahelicene. The best ligand **1g** was used in the synthesis of two natural products, chrysotoxene and epimedoicarisoside A.

Introduction

The ability to adjust finely the donor properties and steric demand of the ligands attached to a metal center is crucial in metal catalysis because it allows a dramatic control on the catalyst reactivity and product selectivity. For this reason, phosphines, which can be readily modulated by just changing the nature and size of the substituents on phosphorus, are probably the most employed and versatile ancillary ligands in the catalysis arena.[1] Specifically, when high Lewis acidity is required at a metal center to promote a transformation, poor donating phosphites or polyfluorinated phosphines are the traditional ligands of choice.

Recently, an alternative approach for the design of weak donor phosphines has emerged that makes use of cationic substituents directly attached to the phosphorus atom.[2] The positive charge thus introduced lowers the energy of all of the orbitals of the phosphine, including those responsible for the σ-donation and the π-back donation. This results in cationic phosphines depicting weaker neat electron-releasing properties than their neutral counterparts. In this context, our group has actively studied the synthesis and reactivity of cyclopropenium-substituted phosphines.[3] These compounds can be formally described as intermediates between two mesomeric forms: a phosphine containing a positively charged cyclopropenium substituent **A**,[4,5] or a phosphenium cation $[PR_2]^+$ stabilized by donation from a cyclopropenylidene internal ligand **B** (Scheme 1).



Scheme 1. Conceivable resonance extremes for cyclopropenylidene-stabilized phosphenium cations.

Herein, we describe a general procedure for the synthesis of these ligands, the evaluation of their donor ability by spectroscopic and electrochemical methods, and our studies on their reactivity towards Pd and Pt centers. These experiments indicate that both mesomeric forms **A** and **B** are in fact necessary to rationalize their reactivity. Moreover, the catalytic activity of a library of Pt complexes was tested on the model cycloisomerization of *ortho*-biaryl substituted alkynes into phenanthrenes. These results defined **6g**/$AgBF_4$ as the most efficient catalytic

[a] Á. Kozma, T. Deden, Dr. J. Carreras, C. Wille, Dr. J. Petuškova, J. Rust, Dr. M. Alcarazo
Max-Planck-Institut für Kohlenforschung
Kaiser Wilhelm Platz 1
45470-Mülheim an der Ruhr (Germany)
Fax: (+49) 208-306-2994
E-mail: alcarazo@mpi-muelheim.mpg.de

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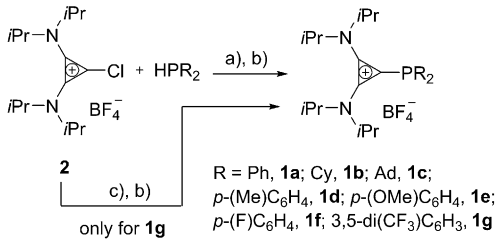
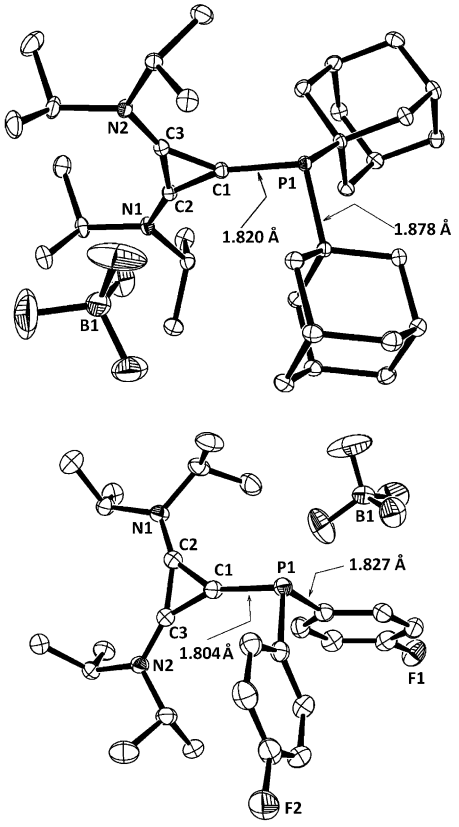
system for this reaction. Finally, the impact of this catalytic mixture was also demonstrated through the synthesis of phenanthrene-derived natural occurring products, namely chrysotoxene and epimedoicarisoside A.

Results and Discussion

We recently targeted the synthesis of cyclopropenium-substituted phosphines **1a**–**f** by condensation of the readily available 1-chloro-2,3-bis(diisopropylamino)cyclopropenium tetrafluoroborate **2** with an array of secondary phosphines. Thus, the desired salts **1a**–**f** could be obtained in good to excellent yields as air-stable white solids (Scheme 2).[3a] Furthermore, to further increase the range of electronic properties of cyclopropenium-substituted phosphines, we have now prepared compound **1g**, containing two very electron-withdrawing 3,5-bis(trifluoromethyl)phenyl substituents. This phosphine could not be synthesized following the general procedure because the low nucleophilicity of bis(trifluoromethyl)phenyl phosphine prevents its direct condensation with **2**. However, after basic treatment with *n*BuLi, the phosphide generated in situ does in fact react with salt **2**, affording the desired **1g** in moderate yield.





Scheme 2. Synthesis of **1a**–**f** and X-ray structure of **1c** and **1f**.[6] Hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability. Reagents and conditions (product yields in parentheses): a) phosphine, 2 equiv, THF, reflux, 24 h; b) $NaBF_4$ excess; **1a** (90%); **1b** (86%), **1c** (79%); **1d** (96%); **1e** (76%); **1f** (80%); c) $[3,5\text{-bis}(CF_3)C_6H_3]_2PH$, (1 equiv), −78 °C, THF, *n*BuLi (1 equiv) and then **2** (1 equiv), 60 °C, 48 h, **1g** (38%).

Scheme 2 also shows the X-ray structures of compounds **1c** and **1f**. Interestingly, both C1–P1 bond distances (C1–P1 1.820 Å in **1c** and 1.804 Å in **1f**) are slightly shorter than the other C–P single bonds present in the same molecules (C4–P1, 1.878 Å in **1c** and 1.827 Å in **1f**), indicating a weak but still measurable interaction between the phosphorus lone pair and the π-system of the cyclopropenium cation. This delocalization of the non-shared pair at phosphorus along the positively charged substituent, which can be understood as a back-donation from phosphorus, is common in onium-substituted phosphines, and in extreme cases, may preclude the efficient overlap between the lone pair at P and the orbitals of a metal avoiding the formation of the corresponding complexes.

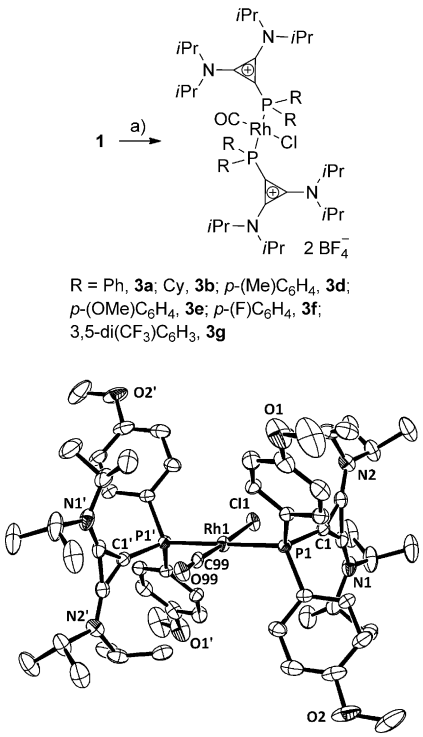
Donor-releasing properties

The donor abilities of phosphines **1a**–**g** were then evaluated by classical analysis of the CO stretching frequencies in Rh carbonyl complexes **3a**–**g**. These preliminary data indicated that ligands **1a**–**f** share with aryl phosphines the same area of the Tolman stereoelectronic map, whereas **1g** more closely approaches the values measured for phosphites (Scheme 3 and Table 1). It is of note that these results are counterintuitive given the cationic nature of our ligands and they certainly should be taken with caution. It is known that in Rh complexes the IR frequencies of the *cis*-located CO ligand may not be only sensitive to electronic effects but also reflect geometrical distortions around the metal center owing to steric hindrance or through-space interactions between the CO and the other ligands. For these reasons, electrochemical methods were

Table 1. Carbonyl stretching frequencies in $[RhCl(CO)L_2](BF_4)_2$ complexes in the solid state and electrochemical redox potential of the ligands. The values of commonly used phosphorus ligands are also included for comparison.

Ligand	$\tilde{\nu}_{CO}$[a] $[RhCl(CO)L_2](BF_4)_2$	E_p ox[b]
1a	1971	1.207
1c	–[c]	1.185
1d	1969	–[c]
1e	1969	1.040
1f	1976	1.246
1g	1991	1.548
Ph_3P	1979	0.697
$(MeO)_3P$	2011	1.287

[a] Values in cm^{-1}. [b] Oxidation peak potentials reported in V. Calibrated versus ferrocene/ferrocenium ($E_{1/2}$ = 0.00 V), Bu_4NPF_6 (0.1 M) in CH_2Cl_2. [c] Not determined.



Scheme 3. Synthesis of **3a–g** and X-ray structure of **3e**.[6] Hydrogen atoms and tetrafluoroborate counteranions are omitted for clarity; ellipsoids are set at 50% probablility. Reagents and conditions (product yields in parentheses): a) phosphine (2 equiv), [{RhCl(CO)}$_2$], (1 equiv) THF, −20 °C→RT, **3a** (93%); **3b** (98%), **3d** (98%); **3e** (98%); **3f** (97%); **3g** (93%).

chosen as a more reliable procedure to rank the donor properties of cyclopropenium-substituted phosphines.[7,8]

In sharp contrast to IR spectroscopy, the oxidation potentials E_p (ox) of phosphines **1a–g**, determined by cyclic voltammetry are indicative of weak neat donations that are similar or even poorer than those shown by phosphites (Table 1). This ranking is now in complete agreement with our experiments on the catalytic activity of Pt complexes bearing ligands **1a–g** described below. To conclude the stereoelectronic characterization, the Tolman cone angle for ligands **1a**,**c–g** has been determined from X-ray structures to be around 174°, which indicates a steric demand similar to PCy_3.[9]

Coordination chemistry

We then decided to study the coordination chemistry of these cationic phosphines towards Pd^{II} and Pt^{II} species. Thus, reaction of **1a** and **1f** with a half equivalent of [{PdCl(allyl)}$_2$] in THF led to quantitative yields of the corresponding adducts **4a** and **4f**. The coordination of phosphorus to the palladium atom was initially reflected by a significant shift of the ^{31}P NMR resonance signals from $\delta = -23.6$ and -24.6 ppm in **1a** and **1f** to $\delta = 26.9$ and 25.5 ppm in **4a** and **4f**, respectively. Moreover, crystals of **4f** were obtained and its structure determined unambiguously by X-ray diffraction, confirming the expected connectivity (Scheme 4). A similar procedure, but using 0.25 equiv of [{PtCl(allyl)}$_4$] instead, was also a viable way to obtain the corresponding Pt allyl analogue **5a**. In this case, the diagnostic appearance of satellite signals in the ^{31}P NMR spectrum ($^1J_{P-Pt} = 2188.0$ Hz) confirmed the formation of a Pt–P bond.

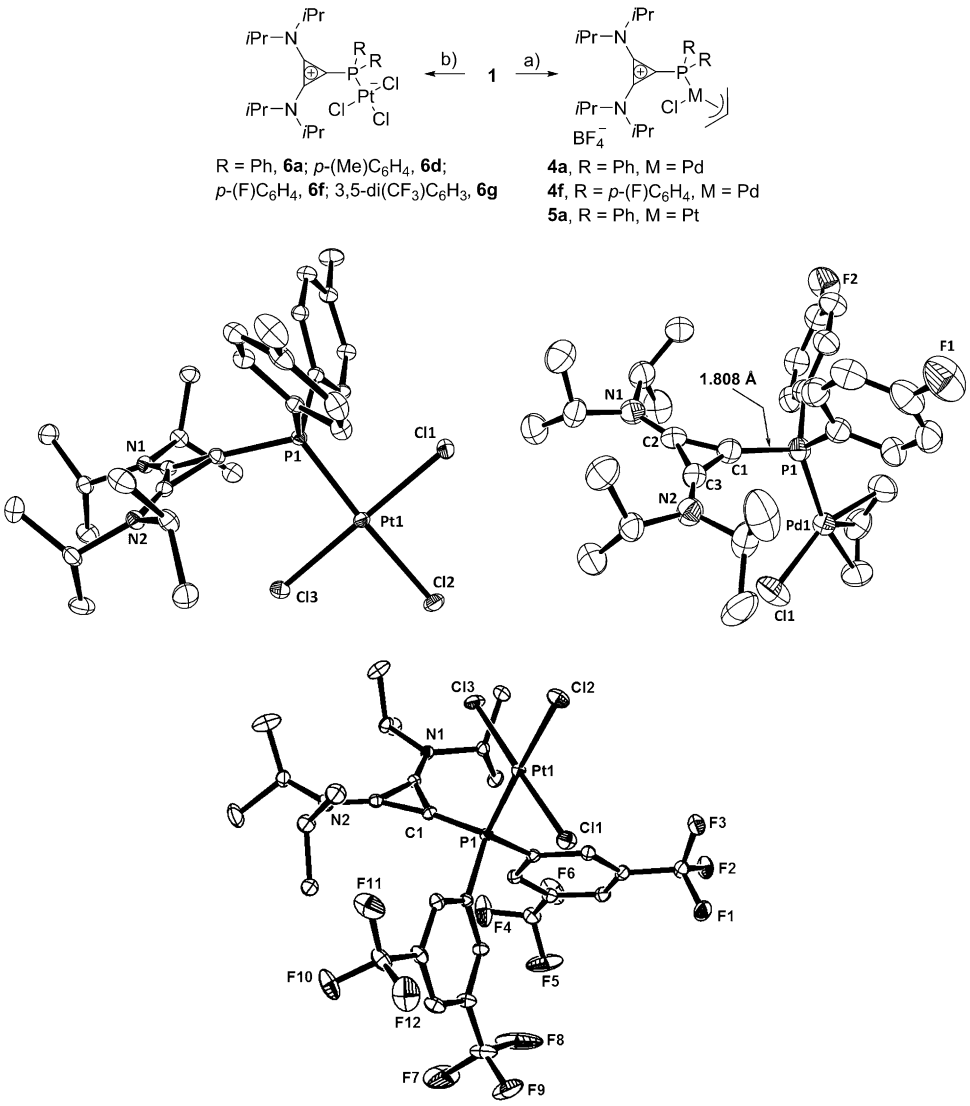
Furthermore, compounds **1a**, **1d**, **1f**, and **1g** were reacted with $K_2[PtCl_4]$, affording the trichloroplatinate complexes **6a**, **6d**, **6f**, and **6g**, respectively, as intensely yellow solids. In these cases again the presence of satellite signals in the ^{31}P NMR spectrum with $^1J_{P-Pt} = 2011.0$ Hz (**6a**), 2000.8 Hz (**6d**), 2016.8 Hz (**6f**), and 2037.3 Hz (**6g**) indicated the formation of the desired adducts, an extreme that could be later confirmed by crystallographic analysis in the case of **6d**. As expected, coordination of the P atom to a metal center cancels any possible back-donation from the phosphorous to the cyclopropenium ring. Thus, a slight elongation of the C1–P1 bond is observed in the coordinated phosphine moieties when compared to the free ligands.

In an attempt to further study the reactivity of cyclopropenium-substituted phosphines, we allowed a solution of **1a** in dichloromethane to react with [$Pd_2(dba)_3$] at room temperature. Under these conditions a characteristic yellow color gradually appeared together with the concomitant release of dba. After work up, the newly formed compound exhibited a very indicative ^{31}P NMR upfield signal at ($\delta = -130.6$ ppm), which cannot be attributed to the phosphorus atom of any of our phosphines; in fact, that is the region where anionic phosphide ligands $[R_2P]^-$ appear. Furthermore, the ESI mass spectrometry indicated that the newly formed complex is a salt whose cationic part contains two Pd atoms. Fortunately, after several attempts, crystallization from acetonitrile afforded single crystals of **7a**,**b** that where suitable for a crystallographic analysis and allowed the determination of their connectivity (Scheme 5). Interestingly, an oxidative insertion of Pd^0 into the C–P bond of **1a** had taken place, providing a Pd^{II}-cyclopropenylidene complex. Furthermore, two phosphide moieties act as bridging ligands between the two Pd centers and the remaining coordination position on each Pd^{II} is occupied by a molecule of acetonitrile used as solvent for crystallization. From the distance between the two Pd atoms (3.540 Å) any significant interaction between them can be ruled out. Their coordination is planar with a sum of the angles around each Pd of exactly 360.0°.

If [$Pd(PPh_3)_4$] is employed as Pd^0 source instead of [$Pd_2(dba)_3$], more forcing conditions are necessary (toluene, reflux) to observe the same kind of products. Note however that now PPh_3 instead of acetonitrile occupies the coordination vacancy created at each Pd atom of **8a**. It should be mentioned that the oxidative insertion of low-valent metals into C–Cl bonds of appropriate halo-imidinium salts is a well-known process; however, to the best of our knowledge, the insertion into the C–P bond of cyclopropenium salts is unprecedented.[10]

Catalysis

To compare the catalytic performance of our cationic ligands against standard phosphines, the platinum-catalyzed 6-*endo*-dig cyclization of 2-ethynyl-1,1′-binaphtalene **9** into pentaheli-



Scheme 4. Synthesis of **4a**, **4f**, **5a**, **6a**, **6d**, **6f**, and **6g** and X-ray structure of **4f**, **6d**, and **6g**.[6] Hydrogen atoms, tetrafluoroborate anions, and solvent molecules are omitted for clarity; ellipsoids are set at 50% probability. Reagents and conditions (product yields in parentheses): a) phosphine, (1 equiv), [{PdCl(allyl)}$_2$] (0.5 equiv) or [{PtCl-(allyl)}$_4$] (0.25 equiv), THF, −20 °C→RT, 30 min, **4a** (98%); **4e** (98%), **5a** (94%); b) phosphine, (1 equiv), $K_2[PtCl_4]$ (1.1 equiv), CH_3CN, RT, 24 h, **6a** (78%); **6d** (88%); **6f** (68%), **6g** (95%).

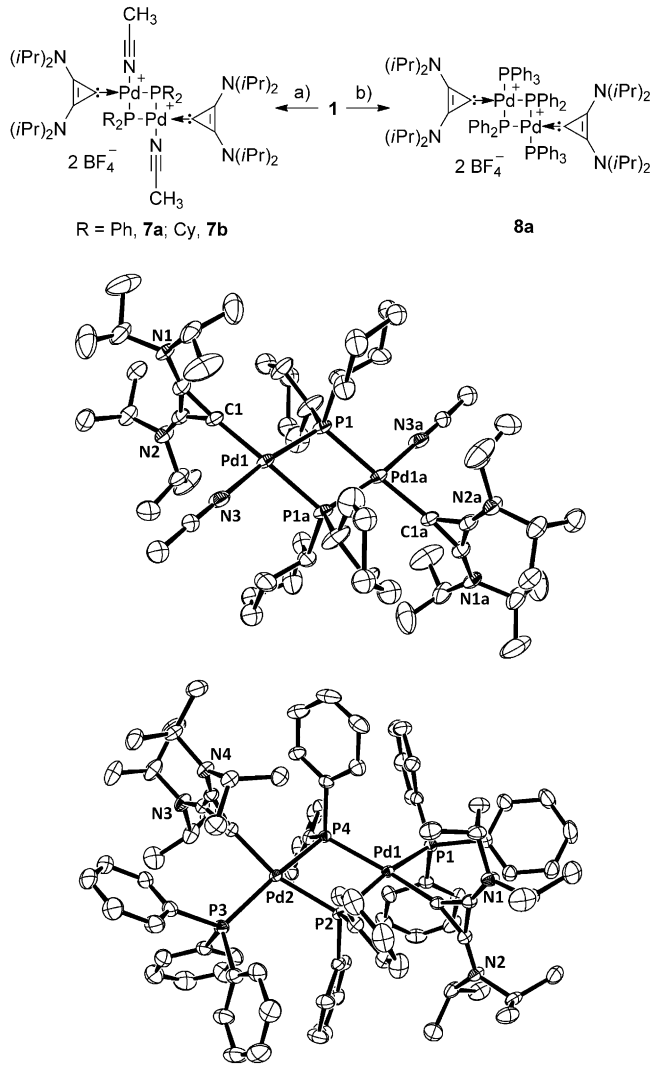
cene **10** was chosen as model reaction because the nucleophilic attack of the aryl ring to the activated alkyne is known to be the rate-determining step.[11] This makes this transformation ideal to evaluate strong π-acceptor ancillary ligands.[12] Figure 1 depicts the conversion versus time plot for Ph_3P (blue), $(PhO)_3P$ (yellow), $(C_6F_5)_3P$ (green) and precatalysts **6a** (red), **6f** (violet), and **6g** (light blue) under otherwise identical conditions. As expected, both $(PhO)_3P$ and $(C_6F_5)_3P$ performed better than Ph_3P in terms of reactivity, while combinations of **6a** or **6f** with $AgBF_4$ induced much faster reactions than any of the neutral π-acceptor ligands tested.

The outstanding catalytic performance of precatalysts **6g** deserves to be discussed separately. In combination with $AgBF_4$, it was able to promote complete conversion of **9** into pentahelicene **10** after only two minutes under the standard reaction conditions, exceeding any other catalyst system for this hydroarylation. This remarkable behavior can be probably ascribed to the synergic effect of the cyclopropenium substituent and the four CF_3 groups that simultaneously withdraw electron density from the Pt atom, and the higher solubility of **6g** in dichloroethane when compared with polycationic precatalysts.[3c]

Synthetic applications

In view of the excellent catalytic activity depicted by **6g**, its relevance on the synthesis of naturally occurring phenantrene derivatives isolated from plants belonging to the *Orchidaceae* family was explored. In particular, we focused our attention on the synthesis of two compounds, 7-hydroxy-2,3,4,8-tetramethoxy phenanthrene **11**, also known as chrisotoxene and 2-hydroxy-3,4,6,7-tetramethoxy-9,10-dihydrophenanthrene-2-*O*-β-D-glucopyranoside **12**, named epimedoicarisoside A after being isolated from the aerial parts of *Epimedium koreanum*.[13]

Chrisotoxene has been isolated from *Dendrobium aurantiacum* var. *denneanum* and *Tamus communis* and displayed moderate cytotoxicities (IC_{50} = 8.52 μM) against the HeLa cell line.[14,15] Our synthesis of this product started with the Suzuki coupling between the previously described 6-bromo-3-hydroxy-2-methoxybenzaldehyde **13**[16] and 2,3,4-trimethoxyphenylboronic acid **14** to afford the corresponding biphenyl **15**. Subsequently, the Ohira–Bestmann reaction produced the expected alkyne **16** although contaminated with substantial amounts of a second product that after NMR and X-ray analyses was probed to be benzofurane **17**. In line with our expectations, when **16** was treated with precatalyst **6g**, the key platinum-catalyzed hydroarylation took place cleanly, affording crysotoxene in excellent yield after only ten minutes. This compound crystallized quite readily, and thus its expected connectivity could be confirmed by X-ray diffraction analysis (Scheme 6). The detailed 1D and 2D NMR spectra and crystallographic analysis leaves no doubt that our synthetic material corresponds to structure **11**. However, comparison of the ^{13}C NMR spectrum of the synthetic and natural samples shows a significant mismatch for the resonance assigned to C2, which appears at δ =



Scheme 5. Synthesis of **7a**, **7b**, and **8a** and X-ray structure of **7b** and **8a**.[6] Hydrogen atoms and tetrafluoroborate anions were omitted for clarity; ellipsoids are set at 50% probability. Reagents and conditions (product yields in parentheses): a) phosphine, 1 equiv, $[Pd_2(dba)_3]$ 0.5 equiv, CH_2Cl_2, RT; **7a** (44%); **7b** (38%), b) phosphine, 1 equiv, $[Pd(PPh_3)_4]$, 1 equiv; toluene, reflux **8a** (73%).

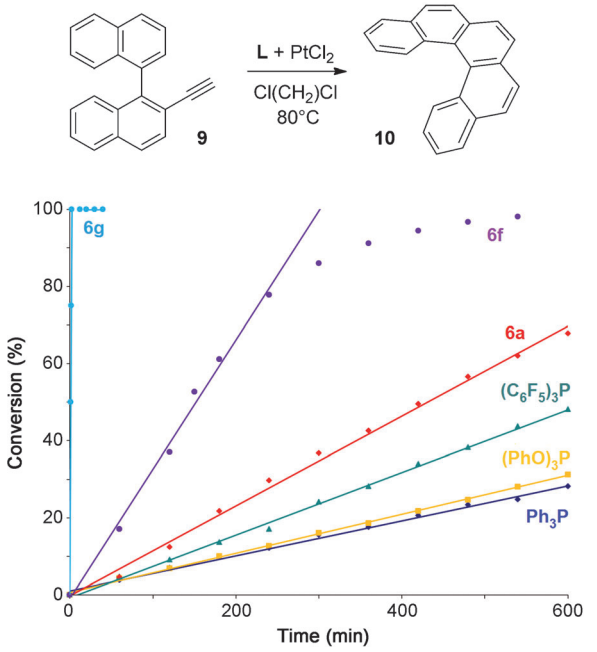
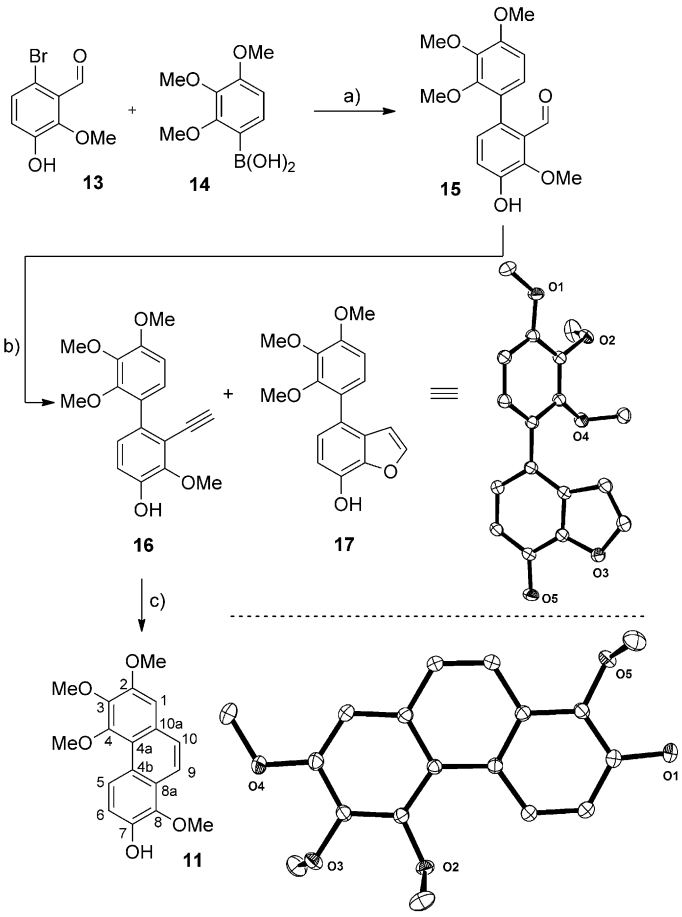


Figure 1. Ligand effect on the Pt-catalyzed cyclization of 2-ethynyl-1,1′-binaphthalene **9** into pentahelicene **10**. a) Conditions for L = Ph_3P, $(PhO)_3P$, and $(C_6F_5)_3P$: **9** (0.05 M), $PtCl_2$ (5 mol%), and ligand (5 mol%), dichloroethane, 80 °C; b) Conditions for precatalysts **6a**, **6f**, and **6g**: **9** (0.05 M), **6a**, **6f**, or **6g** (5 mol%), $AgBF_4$ (5 mol%), dichloroethane, 80 °C.

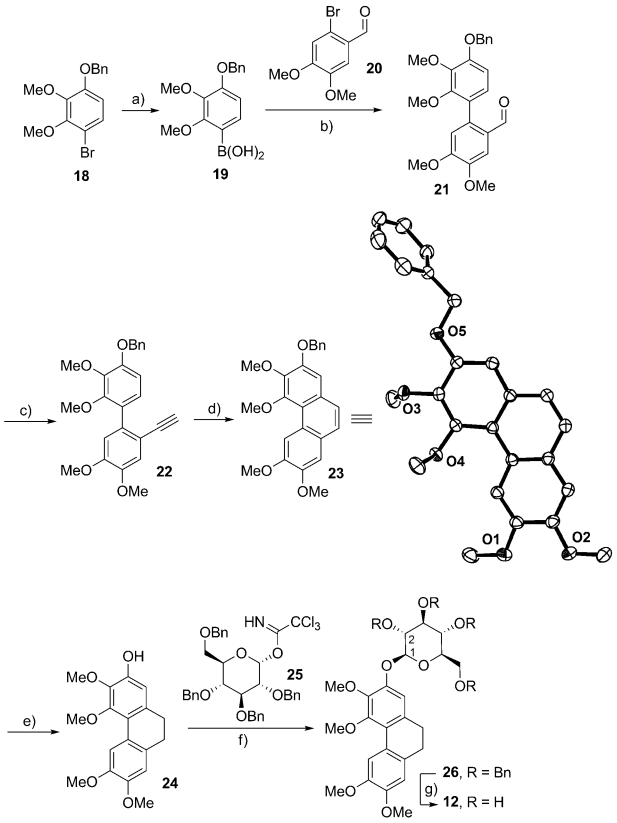
152.0 and 148.0 ppm in the synthetic and natural chrysotoxene, respectively (for details, see the Supporting Information).

Epimedoicarisoside A is also an interesting synthetic target that serves as testament of the utility of our catalysts towards the preparation of phenanthrenes. Moreover, several studies have revealed its cytotoxic effect on primary osteoblasts as well as its potential application in the treatment of cardiovascular and cerebrovascular diseases, such as myocardial infection or cerebral thrombosis.[17] Our synthesis (Scheme 7) commenced with the preparation of 4-bromo-2,3-dimethoxy-1-benzyloxybenzene **18** from pyrogallol following a reported procedure.[18] This compound could be efficiently transformed into the necessary boronic acid **19** after treatment with *n*BuLi, quenching with trimethylborate, and subsequent acidic hydrolysis. The second coupling partner, 6-bromoveratraldehyde **20**, was obtained in only one step from commercially available veratraldehyde following a reported bromination procedure.[19] Not unexpectedly, the Suzuki coupling between **19** and **20** provided the biaryl derivative **21**; however, excellent yields were only obtained when the reaction was carried out in a microwave oven at 120 °C. Subsequent transformation of the aldehyde moiety into the corresponding terminal alkyne **22** by the Ohira–Bestmann reaction set the stage for the key platinum-catalyzed 6-*endo*-dig cycloisomerization to the desired phenanthrene **23** by employing **6g** as precatalyst. This transformation took place with excellent yield, and furthermore, the structure of **23** could be unambiguously confirmed by single-crystal X-ray analysis. At this stage, simultaneous hydrogenation of the double bond at positions 9,10 of the phenanthrene skeleton and deprotection of the benzyl group could be effected, giving access to the dihydrophenanthrene skeleton of epimedoicarisoside A.

With **24** in hand, only the installation of the β-D-glucopyranoside moiety was necessary to achieve our objective. To this end the required monosacaride **25** was prepared following known procedures and condensed with **24**.[20] After some optimization process, we found that the use of two equivalents of **25** and a stoichiometric amount of $BF_3{\cdot}OEt_2$ were the optimal conditions for this glycosidation step affording **26** in excellent yield. Finally, deprotection of all of the benzyl groups from the sugar fragment by hydrogenation over Pd on activated charcoal allowed us to elaborate **26** into epimedoicarisoside A (**12**). Comparison of the ^1H and ^{13}C NMR shifts of the synthetic sample with the reported data for the natural product closely matched. Furthermore, the observed coupling constant $^3J_{H1,H2} = 7.4$ Hz in the sugar moiety of **12** is characteristic for an



Scheme 6. Synthesis of chrysotoxene **11** and X-ray structures of **17** and **11**.[6] Hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability. Reagents and conditions (product yields in parentheses): a) $Pd(OAc)_2$ 0.05 mol%, Ph_3P 0.05 mol%, DMF/H_2O, 60 °C., 12 h, (68%); b) Ohira–Bestmann reagent (3 equiv), K_2CO_3 (4 equiv), MeOH, 48 h, RT, **16** (52%), **17** (22%); c) **6g** (5 mol%), $AgSbF_6$ (5 mol%), CH_2Cl_2 80 °C., 10 min.



Scheme 7. Synthesis of epimedoicarisoside A and X-ray structures of **23**. Hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability. Reagents and conditions (product yields in parentheses): a) *n*BuLi, −78 °C, $B(OMe)_3$, H^+, (59%); b) **21** (1 equiv) $[Pd(PPh_3)_4]$ (2 mol%), microwave oven, 120 °C, 25 min (98%); c) Ohira–Bestmann reagent, (3 equiv), K_2CO_3, MeOH, RT, 48 h (83%); d) **6g** (5 mol%), $Cl(CH_2)_2Cl$, 80 °C, 3 h, (92%); e) H_2 (30 bar), Pd/C (20%), MeOH, RT, 48 h, (82%); f) **25** (2 equiv), BF_3·OEt (1 equiv), CH_2Cl_2, −20 °C, 2 h, (93%); g) H_2 (1 bar), Pd/C (10%), MeOH: EtOAc (2:1), 24 h, RT, (75%).

axial relationship between these two protons, confirming that no epimerization at this site has taken place during the glycosidation.

Conclusions

This study provides a new approach for the design of very strong π-acceptor ligands through the incorporation of a cationic cyclopropenium substituent into an already polyfluorinated phosphine. The outstanding ability of these ligands to enhance the natural π-acid properties of Pt^{II} has been first demonstrated on the 6-*endo*-dig cyclization of 2-ethynyl-1,1′-binaphtalene **9** into pentahelicene **10** and subsequently applied to the synthesis of two natural products, chrysotoxene and epimedoicarisoside A, which both contain a phenanthrene derivative in their structures. Moreover, considering the very general mode of action of ligands **1a–g**, which relies on a simple reinforcement of the metal-to-ligand back-donation, and the multitude of transformations that may benefit from the use of strong accepting ligands, we believe that our approach has a vast potential in the development of metal catalysis.

Experimental Section

All of the experimental details can be found in the Supporting Information, which includes the characterization of all new compounds, their NMR spectra, and X-ray analysis. The synthesis of **1g** is shown here as a representative example.

Compound **1g**: A solution of bis[3,5-bis(trifluoromethyl)phenyl]-phosphine (1 g, 2.18 mmol) in dry THF (15 mL) was cooled to −78 °C, and then *n*BuLi (1.6 M in hexane, 1.6 mL, 2.18 mmol) was added and the resulting mixture was stirred for 2 h at this temperature. After this, chlorocyclopropenium salt **2** (782 mg, 2.18 mmol) was added and the mixture allowed to warm up slowly to RT and further stirred at 60 °C for 2 days. After cooling to RT, the solvents were evaporated, the residue suspended in CH_2Cl_2 (20 mL), and washed with saturated aq. $NaBF_4$ solution (3×15 mL). Once dried over Na_2SO_4, the organic phase was concentrated and the residue purified by column chromatography (CH_2Cl_2/acetone: 9/1), affording the title compound as a pale yellow solid (653 mg, 38%). ^1H NMR (400 MHz, $CDCl_3$); $\delta = 1.11$ (d, $J = 6.8$ Hz, 12H), 1.41 (d, $J = 6.8$ Hz, 12H), 3.48 (sept, $J = 6.8$ Hz, 2H), 4.16 (sept, $J = 6.8$ Hz, 2H), 7.93 (s, 2H), 7.95 (s, 2H), 8.02 ppm (2H). ^{31}P NMR (162 MHz, $CDCl_3$) $\delta = -26.9$ ppm. ^{19}F NMR (282 MHz, CD_2Cl_2) $\delta = -151.5$, −151.5, −63.1 ppm. ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 20.8$, 20.8, 21.2, 52.8,

54.6, 99.4 (d, $J=61.4$ Hz), 122.7 (q, 273.3 Hz), 124.8–125.1 (m), 133.3 (dq, $J=34.3$, 7.1 Hz), 133.6–134.1 (m), 134.3 (d, $J=15.4$ Hz), 140.0 ppm. HRMS calcd. for $C_{31}H_{34}N_2F_{12}P^+$: 693.226254; found 693.226826. IR $\tilde{\nu}=681$, 704, 845, 899, 1057, 1095, 1122, 1180, 1278, 1353, 1459, 1567, 1867, 2981 cm^{-1}.

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Keywords: cations · cycloisomerization · homogeneous catalysis · phosphines · platinum

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