Reaction of a 2,4,6-triphenylphosphininem ferrate anion with electrophiles: a new route to phosphacyclohexadienyl complexes†

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A novel, versatile route to phosphorus- and carbon-substituted \( \eta^5 \)-phosphacyclohexadienyl complexes was developed. Reaction of the anionic 2,4,6-triphenylphosphininem iron complex \([\text{K}([18] \text{crown-6}) \ \text{[thf]}_2][\text{Cp*Fe(PC_5\text{Ph}_3\text{H}_2)]}\) (1) with selected main group element electrophiles afforded the new complexes \([\text{Cp*Fe}(2-\ \text{endo}-\ \text{H}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (endo-3), \([\text{Cp*Fe}(2-\ \text{exo}-\ \text{H}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (exo-3), \([\text{Cp*Fe}(1-\ \text{Me}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (4), \([\text{Cp*Fe}(1-\ \text{Me}_2\text{Si}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (5), \([\text{Cp*Fe}(1-\ \text{PPh}_2-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (6) and \([\text{Cp*Fe}(2-\text{BCat}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (7). BCat = 2-benzo[d][1,3,2]dioxaborol-2-yl. Initial attack of the electrophile at phosphorus was observed, leading to a P-substituted phosphinine ligand. A subsequent rearrangement occurred in some cases, resulting in C-substituted phosphinine complexes endo-3, exo-3 and 7. The new complexes were characterized by \(^1\text{H}, \ ^{31}\text{P}(\ ^1\text{H})\), and \(^{13}\text{C}(\ ^1\text{H})\) NMR spectroscopy, UV-vis spectroscopy and elemental analysis; their molecular structures were determined by X-ray crystallography.

Introduction

Phosphacyclohexadienyls are six-membered heterocycles, which can be distinguished from the related purely carbon-containing cyclohexadienyls by their ambidentate donor properties and versatile coordination behaviour (Fig. 1).† The donation of six \( \pi \)-electrons through an \( \eta^5 \)-coordinated anionic carbocyclic backbone of the phosphacyclohexadienyl ligand (C\( _3 \) mode) is the most common motif. Additionally, the phosphorus atom may also become part of the coordinated \( \pi \)-system (C\( _4 \)P unit and CPC\( _3 \) mode, Fig. 1).§

While \( \eta^5 \)-coordination is the most frequent coordination mode, \( \eta^3 \)-coordination can be found less often. The two electron donation of the P lone pair may be induced by additional chelating donor moieties such as pyridyl and phosphasulfide in the periphery of 1-substituted phosphacyclohexadienyl complexes. Rare \( \eta^4 \)-coordination was found in Pd\( ^{11} \) and Pt\( ^{11} \) complexes, while a bridging \( \eta^3 \)-\( \eta^1 \)-mode was observed for dinuclear Ni and Zr complexes.

Phosphacyclohexadienyls thus are versatile ligands that bind to a range of transition metals and have successfully been applied in homogeneous catalysis, e.g. catalytic olefin polymerization and hydroformylation. Nevertheless, preparative methods are limited to merely three routes (Fig. 2). The conventional method (exemplified in Fig. 2a) is based on the initial synthesis of phosphacyclohexadienyl anions by reacting a phosphinine with an organometallic nucleophile and subsequent salt metathesis. This method was first established by Märkl in 1974. Nief and Fischer developed the reduction of the phosphinine oxide complex \( \text{C} \) with HSiCl\(_3\) as a more specialized approach (Fig. 2b) to the synthesis of hydrophosphacyclohexadienyl complexes. The P–H functionalized complex \( \text{D} \) was formed as the kinetic product with an excess of HSiCl\(_3\) at room temperature. The thermodynamically more stable carbon-protonated isomer \( \text{exo-F} \) was obtained by reflux.

![Fig. 1](image-url) Overview of the versatile coordination modes of the ambi dentate 1-substituted, 2-substituted and 3-substituted phosphacyclohexadienyl complexes; \( M \) = transition metal; \( R \) = organic residue; further substituents on the phosphinine rings are omitted for clarity.

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†Electronic supplementary information (ESI) available: \(^1\text{H}, \ ^{13}\text{C}(\ ^1\text{H}), \ ^{31}\text{P}(\ ^1\text{H})\) and UV-vis spectra of complexes endo-3, exo-3 and \( \eta^5 \)-\( \eta^5 \)-system (C\( _4 \)P unit and CPC\( _3 \) mode, Fig. 1).§

‡ CCDC 1448684. For ESI and crystallographic data of \([\text{Cp*Fe}(2-\ \text{endo}-\ \text{H}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (endo-3), \([\text{Cp*Fe}(2-\ \text{exo}-\ \text{H}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (exo-3), \([\text{Cp*Fe}(1-\ \text{Me}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (4), \([\text{Cp*Fe}(1-\ \text{Me}_2\text{Si}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (5), \([\text{Cp*Fe}(1-\ \text{PPh}_2-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (6) and \([\text{Cp*Fe}(2-\text{BCat}-\text{PC}_5\text{Ph}_3\text{H}_2)]\) (7). BCat = 2-benzo[d][1,3,2]dioxaborol-2-yl. Initial attack of the electrophile at phosphorus was observed, leading to a P-substituted phosphinine ligand. A subsequent rearrangement occurred in some cases, resulting in C-substituted phosphinine complexes endo-3, exo-3 and 7. The new complexes were characterized by \(^1\text{H}, \ ^{31}\text{P}(\ ^1\text{H})\), and \(^{13}\text{C}(\ ^1\text{H})\) NMR spectroscopy, UV-vis spectroscopy and elemental analysis; their molecular structures were determined by X-ray crystallography.

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Synthesis of novel phosphacyclohexadienyl complexes

We recently reported that the 1-hydrophosphacyclohexadienyl complex 2 can be synthesized by reacting the cationic phosphinine complex G with one equivalent LiBHET3 (Fig. 2c). Assuming that the protonation of the anionic complex 1 might give the same product, 1 was treated with one equivalent of HCl-(OEt2) in THF. The reaction affords a mixture of compounds, including 2 and the new compounds endo-3 and exo-3. The latter are isomers of 2 and display 2-hydrophosphacyclohexadienyl ligands. In the case of endo-3, the hydrogen atom in the 2-position of the phosphinine is attached to the metal-coordinated face, causing the phenyl substituent to point to the bottom. The diastereomer exo-3 formally results from protonation of the phosphinine ring at the remote face to the iron center. Isomers 2, endo-3 and exo-3 are analogous to D, endo-F and exo-F previously prepared by Nief and Fisher via a completely different route (Fig. 2b).8

$^{31}$P{1H} NMR monitoring ([D$_8$]THF, Fig. 3) revealed the signal of 2 (−80 ppm) at −80 °C. Two additional signals at 10 ppm and −64 ppm arise from unknown intermediates, which disappear at higher temperature. The signal of the starting material 1 (−49 ppm) continuously decreased on slow warming to 0 °C, whereas the signal of 2 increased. The signals of the 2-H-substituted species exo-3 (−162 ppm) and endo-3 (−137 ppm) were observed in low intensity at −30 °C; their intensity increased significantly at 0 °C, whereas the signal of 2 decreased. An additional signal corresponding to an unidentified species became apparent at −14 ppm at −40 °C. This signal could plausibly arise from a by-product similar to complex E (−20.4 ppm)8 or a decomposition product. The $^{31}$P{1H} NMR spectrum of the reaction mixture recorded at room temperature displays the signals of 2, exo-3, endo-3 as well as a few weak singlets of further unidentified species. The signal intensities did not change further after one day. Stirring the raw product mixtures of 2, endo-3 and exo-3 at 50 °C for several days ($^{31}$P{1H} NMR monitoring) also did not lead to a further change of the integral ratios.

Even though 2 appears to be formed selectively at low temperature, we were not able to isolate it as a pure material from reactions performed at −40 °C. However, 2 slowly converts to exo-3 upon treatment with HCl(OEt2) (10 mol%) at room temperature in [D$_8$]THF. This indicates the rearrangement to be acid-catalysed. Attempts to optimise the reaction gave poorly reproducible product mixtures. Thus, it appears difficult to
access 2, \(\text{exo-3}\) and \(\text{endo-3}\) as pure compounds by protonating 1 with \(\text{HCl(OEt}_2\))

The results of the monitoring experiment indicate that the 1-hydrophosphacyclohexadienyl complex 2 is formed as the main kinetic product along with two unidentified species (marked with an asterisk in Fig. 3). The 2-hydrophosphacyclohexadienyl complexes \(\text{endo-3}\) and \(\text{exo-3}\) appear to be thermodynamic products that form at higher temperatures. Indeed, gas-phase DFT calculations performed at the BP86/def2-TZVP level (see the Experimental section for details) indicate that \(\text{endo-3}\) and \(\text{exo-3}\) are close in energy, while 2 was calculated to be +7.0 kcal mol\(^{-1}\) less stable than \(\text{endo-3}\) (Fig. 3, see the Experimental section for details).

Gratifyingly, the reaction of 1 with one equiv. isopropyl chloride in THF at room temperature (Scheme 1) proceeded cleanly, reproducibly affording a mixture of \(\text{endo-3}\) and \(\text{exo-3}\) in a 65:35 ratio (NMR integration). The formation of 2 as an intermediate was not observed by \(^{31}\text{P}\{\text{H}\}\) NMR in this case, which indicates that the reaction proceeds via a different mechanism. Purification by column chromatography gave NMR-spectroscopically pure \(\text{exo-3}\) and \(\text{endo-3}\) after crystallization.

\(\text{exo-3}\) was isolated as orange rods in 25% yield, whereas pure \(\text{endo-3}\) crystallized as orange plates in 41% yield. Both compounds are air-sensitive and dissolve well in \(n\)-hexane, diethyl ether, toluene and THF.

Complexes 4–6 are accessible in a similar fashion in moderate yields by reacting 1 with one equiv. of MeI, \(\text{Me}_3\text{SiCl}\), and \(\text{Ph}_2\text{PCl}\) (Scheme 2a–c). The compounds are deeply coloured crystalline solids that dissolve well in polar and apolar solvents such as \(n\)-pentane, \(n\)-hexane, diethyl ether, toluene and THF.

‡ The synthesis of 6 needs to be performed at \(-95^\circ\text{C}\) by slow addition of \(\text{Ph}_2\text{PCl}\) to a solution of complex 1. In this case, 6 was isolated in 38% yield. Addition of \(\text{Ph}_2\text{PCl}\) at room temperature led to an almost quantitative formation of tetraphenylidiphosphane and the dimeric complex \([\text{Cp}^*\text{Fe}]_2[\mu-\{\text{PC}_3\text{Ph}_3\text{H}_2\}]_2\).
An analogous reaction with Ph₃SnCl in THF produced the P–Sn functionalized complex 8 (Scheme 2e), but the reaction was unselective. According to ³¹P¹[H] NMR integration complex 8 is only present in a low amount (26% of the total P content) in the reaction mixture after stirring for 17 h at room temperature. Several attempts to isolate it as a pure compound were not successful due to its low stability. Diphenosmine \([\text{Cp}^*\text{Fe}(1-\text{BCat-PC}_5\text{Ph}_3\text{H}_2)]\) and hexaphenyl-distannane were identified as decomposition products by ³¹P¹[H] and ¹¹²Sn¹[H] NMR, suggesting decomposition by a radical pathway.

**Crystallographic characterization of exo-3, endo-3, and 4–7**

Single-crystal X-ray structure determinations of exo-3, endo-3 and 4–7 (Fig. 4 and Table 1) revealed \(\eta^5\)-Cp* and \(\eta^5\)-phosphacyclohexadienyl ligands. As a consequence, the phosphacyclohexadienyl units are not planar. The P atom points away from iron in complexes 4–6, and the heterocycle is folded along the C1–C5 axis. The dihedral angles between the carbocyclic mean plane and the plane defined by C1/P1/C5 (39.4° for 4, 37.0° for 5) are close to the values in the related complexes 2 (38.2°) and \([\text{Cp}^*\text{Fe}(1-\text{Cp*–PC}_5\text{Ph}_3\text{H}_2)]\) (39.7°) previously reported by us (Fig. 2c, vide supra).⁷ The corresponding fold angle for 6 (27.2°) is over 10° shorter and similar to that of \([\text{Cp}^*\text{Fe}(1-\text{NMMe}_2\text{–PC}_5\text{Ph}_3\text{H}_2)]\) (28.1°, vide supra).⁷

In exo-3, endo-3 and 7 the C1 atom adjacent to phosphorus is bent away from the iron center; consequently the six-membered phosphinine ring is folded along the P1–C2 axis. The corresponding plane to plane angles are larger than in 4–6 (60.6° for endo-3, 63.4° for exo-3 and 59.7° for 7). Complexes endo-3, exo-3 and 7 are rare phosphine-type complexes, which show \(\eta^5\)-coordination through a C₆P-unit. To the best of our knowledge, the sole example comprising the same structural motif is endo-F (Fig. 2b, vide supra).⁸

The C–C distances of the \(\eta^5\)-coordinated C₅ and C₆P-units exo-3, endo-3 and 4–7 (Table 1) are in between typical single and double bond distances.⁹ Similar bond lengths were observed for the \(\eta^6\)-coordinated phosphine ring in complex G.⁷ In addition, it is noteworthy that the C1–C2 distances of endo-3 (1.521(2) Å), exo-3 (1.540(3) Å) and 7 (1.526(2) Å) correspond to the value for a normal single bond.⁹ The C–P bond lengths in 4–6 are typical for single bonds and similar to those in B and H (Fig. 2, vide supra).⁴,⁷ The C–P bond lengths are distinct in endo-3, exo-3 and 7: the P1–C1 distances (1.891(2)–1.851(2) Å) are in the typical range for P–C single bonds,⁹ whereas the P1–C5 (1.792(2)–1.785(2) Å) bonds are shorter and close to those found in the \(\eta^5\)-coordinated ring in G.⁷

While the P1–Si1 bond length (2.270(2) Å) of 5 is typical for a P–Si single bond,¹⁰ the P1–P2 bond (2.306(2) Å) of 6 is elongated compared to that in unsymmetrically-distributed diphosphanes such as 9-diphenylphosphanyl-9- phosphabicyclo[3.3.1]nonane (2.229(1) Å).¹¹ An analogous observation was made by Gudat et al. for P-phosphanyl-diazaphospholes, e.g. 2-diphenylphosphanyl-1,3-dimesityldiazaphospholene, which displays a similarly elongated P–P bond (2.334(1) Å).¹²

In 7, the B1–C1 distance (1.563(2) Å) is in the range of normal boron–carbon single bonds (1.597 Å). The boron...
centre comprises a trigonal planar environment (angular sum = 360°). It seems noteworthy that Mathey and co-workers synthesized related phosphinine borates, e.g. Li[2-BET₃PC₅H₄] by reaction of 2-bromophosphinines with two equiv. LiBHEt₃. These anionic molecules contain a tetrahedral boron atom in the 2-position; they can be converted into 2-ethylated phosphinines by reaction with iodine. Braunschweig et al. prepared a series of (dimethoxyborylmethyl)dimethylphosphane complexes where a P–C–B(OMe)₂ unit coordinates to chromium or iron via the P atom. An example is the compound [FeH(CO)₃(SiPh₃)(Me₂PC₆B(OMe)₂)]. Different from these σ-coordinated complexes, the phosphacyclohexadienyl ligand of 7 acts as a π-ligand to iron through the planar C₅P-unit. Thus, the phosphorus lone pair remains uncoordinated and should be able to act as a Lewis base. The trivalent boron center might function as a Lewis acid in related complexes.
Table 2 Characteristic $^1$H, $^{13}$C($^1$H) and $^{31}$P($^1$H) NMR data of complexes endo-3, exo-3 and 4–7; atom labelling according to Fig. 3

| Complex | $^3$P{1H} NMR | $^1$H NMR | $^3$C{1H} NMR | $^3$F{1H} (Hz) |
|---------|--------------|------------|---------------|----------------|
| endo-3  | −136.3 (s)   | 1.36 (s)   | 2.98 (dd), 7.20–7.24 (m)$^a$ | 2.4            |
| exo-3   | −160.7 (s)   | 1.30 (s)   | 2.44 (s), 7.13–7.40 (m)$^b$ | n.d.           |
| 4       | −57.4 (s)    | 1.02 (s)   | 6.07 (d)      | 2.6            |
| 5       | −77.7 (s)    | 1.02 (s)   | 6.21 (d)      | 2.5            |
| 6       | −38.8 (d)    | 0.98 (s)   | 6.02 (d)      | 2.9            |
| 7       | −126.7 (s)   | 1.34 (s)   | 3.51 (s), 6.03–6.05 (m)$^c$ | n.d.           |

$^a$ Overlapping with meta-H of C5-Ph. $^b$ Overlapping with Ar-H of C1-Ph and meta/para-H of C3-Ph/C5-Ph. $^c$ Overlapping with ortho-H of C1-Ph. n.d. = not detected.

with less strongly electron-donating substituents at boron, enabling the formation of a new frustrated Lewis pair type system.

NMR and UV-Vis spectroscopic characterization

Table 2 summarizes $^1$H, $^{13}$C($^1$H) and $^{31}$P($^1$H) NMR data of endo-3, exo-3 and 4–7 recorded in [D$_8$]THF. The $^{31}$P NMR signals of exo-3 (~160.7 ppm, $J_{PH}$ not detected) and endo-3 (~136.3 ppm, $J_{PH}$ = 15.2 Hz) are slightly downfield shifted in comparison with those of the cyclopentadienyl analogues exo-$^1$F (~173.0 ppm) and endo-$^1$F (~150.1 ppm) synthesised by Nief and Fischer,$^7$ which otherwise feature similar $^1$H and $^{13}$C NMR shifts of the phosphacyclohexadienyl units as their Cp*-substituted equivalents. Notably, the simple change of the configuration of a carbon atom of the phosphinine ring causes an upfield shift of the $^{31}$P NMR doublet of exo-3 by almost 25 ppm with respect to endo-3. The aliphatic hydrogen atom of the phosphacyclohexadienyl ring resonates at 2.76 ppm for endo-3 and at 1.66 ppm for exo-3. The spectrum of exo-3 thus displays a pronounced upfield shift for the exo-hydrogen atom comparable to that observed for the related cyclohexadienyl complex [CpFe(n$_2$C$_6$H$_4$)].$^{25}$

The spectra of 1-substituted 4–6 overall resemble those of related complexes of type H (Fig. 2c).$^7$ Characteristic $^1$H NMR features of 4 and 5 are the doublets at ~0.13 ppm ($J_{HH}$ = 5.5 Hz) for the methyl group of 4 and the Me$_3$Si group of 5 (~0.41 ppm, $J_{HH}$ = 3.4 Hz). The $^{31}$P($^1$H) NMR signal of the trimethylsilyl-substituted complex 5 is upfield shifted by 20.3 ppm compared to the methyl-substituted analogue 4. Two $^{31}$P($^1$H) NMR doublets are observed for 6 at 12.8 and −38.8 ppm with a large $J_{PP}$ coupling constant (293 Hz) in the typical range for a covalent P–P single bond.$^{26}$ The signal at 12.8 ppm is assigned to the PPh$_2$ group, because it splits into a doublet of quintets in the $^{31}$P NMR spectrum ($J_{HH}$ = 6.5 Hz).

Complex 7, which features a 2-substituted phosphacyclohexadienyl moiety, gives rise to a similar high-field $^{31}$P($^1$H) NMR singlet (~126.7 ppm) as endo-3 (~136.3 ppm); the $^1$H NMR data (Table 2) are also similar in agreement with the similar structures.$^8$

The UV/vis spectra of endo-3–7 were recorded in n-hexane. The spectra of 2-H-substituted endo-3 and exo-3 are similar and display a weak shoulder at 450 nm; three stronger bands are found in the UV range (endo-3 220, 260 and 320 nm; exo-3 230, 275 and 325 nm). The spectrum of the structurally related complex 7 is analogous, showing slightly bathochromically shifted bands at 260, 290sh, 360sh and 460sh nm. The UV/vis spectra of the 1-substituted species 4–6 are distinct from those of the aforementioned complexes and feature two visible absorptions each with moderate intensities in the ranges $\lambda_{max}$ = 550–580 nm and $\lambda_{max}$ = 480–580 nm, respectively. Similar spectra were observed for other complexes of this type (type H, Fig. 2c).$^7$ Previous TD-DFT calculations indicated that these bands predominantly arise from excitations from filled metal-centered MOs into the ligand-based unoccupied MOs (MLCT).$^7$

Conclusions

The reaction of the anionic phosphinine complex 1 with diverse electrophiles represents a novel and straightforward synthetic pathway to phosphacyclohexadienyl iron complexes. Protonation of 1 using HCl(OEt)$_2$ initially affords the 1-substituted complex 2 at low temperature, which appears to undergo an acid catalyzed rearrangement and converts to a mixture of isomers, including the 2-H-substituted compounds endo-3 and exo-3. The latter complexes were conveniently isolated in good yields from the reaction of 1 with isopropyl chloride. An analogous 2-substituted complex 7 formed in the reaction with chlorocatecholborane. Similar to the hydrophosphinine complexes, an initial formation of a phosphorus-substituted complex followed by a subsequent 1,2-shift of the substituent was observed. Using MeI, Me$_3$SiCl, Ph$_2$PhCl and Ph$_3$SnCl, 1-substituted complexes 4–6 and 7 were obtained. Thus, HCl(OEt)$_2$, iso-propyl chloride and chlorocatecholborane result in products substituted at the 2-carbon atom, whereas MeI, Me$_3$SiCl, Ph$_3$SnCl and Ph$_2$PhCl provide phosphorus-substituted products.

An extensive family of related compounds could become accessible via this route. In addition, the reactivity and possible catalytic activity of the new complexes presented here needs to be examined, where the unusually long P–P bond in 6 and the FLP type motif in 7 will be of particular interest. Investigations in these directions are underway in our laboratory.
Experimental

General considerations

All experiments were performed under an atmosphere of dry argon, by using standard Schlenk and glovebox techniques. Solvents were purified, dried, and degassed with an MBraun SPS800 solvent purification system. NMR spectra were recorded on Bruker Avance 300 and Avance 400 spectrometers at 300 K and internally referenced to residual solvent resonances. The assignment of the $^1$H and $^{13}$C NMR signals was confirmed by two-dimensional (COSY, HSQC, and HMBC) experiments. Melting points were measured on samples in sealed capillaries on a Stuart SMP10 melting point apparatus. UV/vis spectra were recorded on a Varian Cary 50 spectrometer. Elemental analyses were determined by the analytical department of Regensburg University. The starting material [K[18crown-6](thf)]$_2$[Cp*Fe(η⁵-Pc$_3$H$_2$)] (1) was prepared according to literature procedures. HCl(EtO) solution, methyl iodide, trimethylsilyl chloride, chlorocatecholborane and chlorodiphenylphosphine were purchased from Sigma-Aldrich and TCI and were used as received.

$[\text{Cp'Fe(2endo-HPC$_5$H$_3$)}]$ (endo-3) and $[\text{Cp'Fe(2exo-HPC$_5$H$_3$)}]$ (exo-3). A solution of isopropyl chloride in THF (1.0 mL, c = 0.108 mol L$^{-1}$) was added to a dark orange solution of 1 (104 mg, 0.108 mmol) in THF (5 mL). The solution was stirred at room temperature for 24 hours. The resulting dark orange brown mixture was subjected to column chromatography (silica gel, 22 × 1 cm, n-hexane/toluene gradient, 100/1 to 5/1). Two bright orange bands were obtained: exo-3 was eluted first (R$_f$(n-hexane/toluene, 5/1) = 0.42), slightly overlapping with endo-3, which followed immediately (R$_f$(n-hexane/toluene, 5/1) = 0.32). Removal of the solvent gave exo-3 and endo-3 as pure bright orange solids. Yield of exo-3: 14 mg (25%), yield of endo-3: 23 mg (41%), total including mixed fractions: 45 mg (80%). X-ray quality crystals formed upon storage of concentrated n-hexane solutions at room temperature for three days. Variable elemental analyses were obtained for exo-3 and endo-3. Traces of silica gel can be removed by taking up the product in n-hexane, filtration and removal of the solvent.

endo-3.

M.p. 196 °C. UV/vis: (n-hexane, $\lambda_{max}$nm$^{-1}$, $\epsilon_{max}$/L mol$^{-1}$ cm$^{-1}$): 230sh (72 000), 275 (59 000), 325sh (17 000), 450sh (11 000). $^1$H NMR (400.13 MHz, 300 K, [D$_8$]THF): $\delta$ = 1.36 (s, 15H, C$_5$(CH$_3$)$_3$), 1.66 (s br, 1H, C$_2$-H of TPP), 2.44 (s br, 1H, C$_3$-H of TPP), 7.13–7.40 (overlapping m, 12H, Ar-H of C$_3$-Ph + C$_5$-H of TPP + C$_{14,15,16}$-H of C$_6$-Ph + C$_{14,15}$-H of C$_5$-Ph). 13C{1H} NMR (100.61 MHz, 300 K, [D$_8$]THF): $\delta$ = 10.9 (d, $^3$J$_{CP}$ = 3.4 Hz, C$_2$(CH$_3$)$_3$), 26.3 (s, C$_3$-H of TPP), 34.7 (d, $^3$J$_{CP}$ = 23.2 Hz, C$_2$ of TPP), 87.9 (s, C$_6$(CH$_3$)$_3$), 88.8 (d, $^3$J$_{CP}$ = 7.9 Hz, C$_5$-H of TPP), 91.8 (s, C$_4$ of TPP), 95.2 (d, $^3$J$_{CP}$ = 69.9 Hz, C$_6$ of TPP), 125.2 (s, C$_4$-H of C$_3$-Ph), 126.3 (d, $^3$J$_{CP}$ = 3.5 Hz, C$_2$-H of C$_2$-Ph), 127.1 (d, $^3$J$_{CP}$ = 1.1 Hz, C$_4$-H of C$_6$-Ph), 127.7 (s, C$_4$-H of C$_3$-Ph), 127.5 (s, C$_{14,15}$-H of C$_5$-Ph), 127.9 (s, C$_{14,15}$-H of C$_5$-Ph), 128.1 (s, C$_{14,15,16}$-H of C$_6$-Ph), 128.6 (d, $^3$J$_{CP}$ = 1.0 Hz, C$_5$-H of C$_6$-Ph), 129.0 (s, C$_{14,15,16}$-H of C$_5$-Ph), 141.8 (s, C$_4$-H of C$_3$-Ph), 143.8 (d, $^3$J$_{CP}$ = 17.8 Hz, C$_5$-H of C$_6$-Ph), 147.1 (d, $^3$J$_{CP}$ = 1.8 Hz, C$_2$-H of C$_5$-Ph), 31P{1H} NMR (161.98 MHz, 300 K, [D$_8$]THF): $\delta$ = 136.3 (s). 31P NMR (161.98 MHz, 300 K, [D$_8$]THF): $\delta$ = 136.3 (d, $^3$J$_{PH}$ = 15.3 Hz).

A solution of methyl iodide in THF (1 mL, c = 0.106 mol L$^{-1}$) was added to a dark orange solution of 1 (102 mg, 0.106 mmol) in THF (5 mL) at room temperature. The reaction mixture turned burgundy red immediately, and was stirred for four hours at room temperature. After removing the solvent in vacuo, the remaining dark red residue was extracted with n-hexane (10 × 1 mL). The burgundy red extracts were com-
bined and the solution was concentrated to 5 mL. Dark red crystals of 4 formed during storage at −30 °C for three days. Yield: 23 mg (41%). M.p. 239 °C. UV/vis: (n-hexane, λmax nm−1, εmax L mol−1 cm−1): 3805 (3150), 480 (1440), 550 (1000). 1H NMR (400.13 MHz, 300 K, [D8]THF): δ = −0.13 (d, δJHH = 5.5 Hz, 3H, P–CH3), 1.02 (s, 15H, C5(CH3)3), 6.07 (d, δJHP = 2.6 Hz, 2H, C2,6–H of TTP), 7.12 (t, δJHH = 7.3 Hz, 2H, C4–H of C2,6–Ph), 7.27–7.31 (m, 4H, C2,6–H of C5,6–Ph), 7.46 (t, δJHH = 7.3 Hz, 1H, C1–H of C–Ph), 7.54–7.58 (m, 2H, C5,6–H of C1,3–Ph), 8.11–8.13 (m, 4H, C2,6–H of C2,6–Ph), 8.32 (d, δJHH = 7.7 Hz, 2H, C2,6–H of C–Ph). 13C{1H} NMR (100.61 MHz, 300 K, [D8]THF): δ = −8.9 (s, C5(CH3)3), 18.2 (d, δJCP = 39.0 Hz, P–CH3), 41.1 (d, δJCP = 1.1 Hz, C2,6–H of TTP), 79.1 (d, δJCP = 7.3 Hz, C2,6–H of TTP), 85.3 (s, C5(CH3)3), 95.9 (d, δJCP = 2.4 Hz, C2,6–H of TTP), 124.7 (d, δJCP = 2.8 Hz, C5–H of C2,6–Ph), 128.1 (C1–H of C4–Ph overlapping with C2,6–H of C–Ph), 128.7 (s, C2,6–H of C2,6–Ph), 128.8 (d, δJCP = 19.5 Hz, C2,6–H of C–Ph), 129.4 (s, C2,6–H of C–Ph), 141.6 (s, C–Ph), 145.5 (d, δJCP = 25.2 Hz, C4–H of C2,6–Ph). 31P{1H} NMR (161.98 MHz, 300 K, [D8]THF): δ = −57.4 (3P). 31P NMR (161.98 MHz, 300 K, [D8]THF): δ = −57.4 (s, br). Elemental analysis calculated for C34H44FeP3 (Mw = 588.63 g mol−1) C 73.46, H 7.02; found C 73.81, H 6.97.

A solution of chlorodiphenylphosphine (35 mg, 0.159 mmol) in THF (5 mL) at −95 °C was added dropwise to a dark orange solution of 4 (150 mg, 0.156 mmol) in THF (10 mL) at −95 °C. The reaction mixture turned deep red to violet and was slowly warmed to room temperature. The solvent was removed in vacuo after stirring at room temperature for 16 h. The remaining residue was extracted with n-pentane (8 × 1 mL). The extracted fractions were combined and concentrated to 4 mL. 6 was isolated as dark violet crystals after storage at −30 °C for three days. Yield: 48 mg (38%). M.p. 192 °C. UV/vis: (n-hexane, λmax nm−1, εmax L mol−1 cm−1): 240s (42 000), 295 (30 800), 483 (2400), 550 (1900). 1H NMR (400.13 MHz, 300 K, [D8]THF): δ = 0.98 (s, 15H, C5(CH3)3), 6.02 (d, , δJHH = 2.9 Hz, 2H, C1–H of TTP), 6.84–6.93 (m, 6H, C4,5,6–H of PPh3), 6.96–7.00 (m, 4H, C2,6–H of PPh3), 7.10 (t, δJHH = 7.2 Hz, 2H, C1–H of C2,6–Ph), 7.21–7.25 (m, 4H, C1–H of C4–Ph), 7.47 (t, δJHH = 7.2 Hz, 1H, C4–H of C2,6–Ph), 7.52–7.56 (m, 2H, C3,5–H of C–Ph), 7.99–8.02 (m, 4H, C2,6–H of C2,6–Ph), 8.13 (d, δJHH = 7.8 Hz, 2H, C2,6–H of C1,3–Ph). 13C{1H} NMR (100.61 MHz, 300 K, [D8]THF): δ = 8.79 (s, C5(CH3)3), 41.0 (dd, δJCP = 12.5 Hz, δJCP = 10.6 Hz, C2,6–H of C4–Ph), 80.9 (dd, δJCP = 12.6 Hz, δJCP = 10.5 Hz, C1–H of C–Ph), 85.8 (s, C5(CH3)3), 97.3 (d, δJCP = 2.2 Hz, C1–H of C–Ph), 125.0 (d, δJCP = 3.3 Hz, C4–H of C2,6–Ph), 127.4 (s, C3,5–H of C–Ph), 128.0 (d, δJCP = 6.0 Hz, C3,5–H of PPh3), 128.1 (s, C1–H of C–Ph), 128.4 (s, C2,6–H of C–Ph), 128.6 (s, C2,6–H of C4–Ph), 129.1 (s, C3,5,6–H of C–Ph), 129.2 (d, δJCP = 18.1 Hz, C1–H of C2,6–Ph), 134.7 (dd, δJCP = 17.2 Hz, δJCP = 4.1 Hz, C1–H of C–Ph), 138.7 (dd, δJCP = 25.5 Hz, δJCP = 6.9 Hz, C1–H of PPh3), 141.0 (s, C–Ph), 144.9 (d, δJCP = 24.5 Hz, C4–H of C4–Ph), 31P{1H} NMR (161.98 MHz, 300 K, [D8]THF): δ = 12.8 (3P). 31P NMR (161.98 MHz, 300 K, [D8]THF): δ = 12.8 (s, δJCP = 293 Hz, δJCP = 293 Hz, P of TPP). 31P NMR (161.98 MHz, 300 K, [D8]THF): δ = 12.8 (quint, δJCP = 293 Hz, δJCP = 293 Hz, δJCP = 6.5 Hz, PPh3), −38.8 (d, δJCP = 293 Hz, P of TPP). Elemental analysis calculated for C34H44FeP3 (Mw = 700.62 g mol−1) C 77.14, H 6.04; found C 77.55, H 6.36.

[CP*Fe(2-BCat-PC3Ph2H3)] (7).
A solution of chlorocatecholborane (24 mg, 0.155 mmol) in THF (5 mL) was added to a dark orange solution of 1 (150 mg, 0.156 mmol) in THF (10 mL) at −35 °C. The mixture was stirred and warmed to room temperature overnight. All volatiles were removed in vacuo and the dark orange-green residue was washed with n-hexane (5 × 1 mL) and extracted with diethyl ether (10 × 0.5 mL). The deep orange diethyl ether fractions were combined and the major impurities including [18]crown-6 were crystallized by storage at room temperature for five days. The deep orange mother liquor was decanted and concentrated to 3 mL. Deep orange crystals of 7 formed during storage at room temperature for two days. Yield: 25 mg (25%).

M.p. 196 °C (decomposition to a dark green solid). UV/vis: (n-hexane, λmax nm−1, εmax L−1 mol−1 cm−1): 260 (15 000), 290(sh) (10 000), 360(sh) (1700), 460(sh) (300). 1H NMR (400.13 MHz, 300 K, [D8]THF): δ = 1.34 (s, 15H, C6(CH3)5), 3.51 (s, 1H, C3–H of TPP), 6.68–6.72 (m, 1H, C4–H of C2–Ph), 6.89–6.91 (m, 2H, C7.5–H of C2–Ph), 6.03–6.05 (overlapping m, 3H, C2,6–H of C2–Ph overlapping with C5–H of TPP), 7.07–7.11 (m, 2H, C3,5–H of catecholboryle), 7.17–7.21 (m, 1H, C4–H of C6–Ph), 7.23–7.26 (m, 2H, C7.5–H of C6–Ph), 7.28–7.30 (m, 2H, C4,14–H of catecholboryle), 7.32–7.36 (m, 1H, C3–H of C2–Ph), 7.44–7.48 (m, 2H, C7,5–H of C2–Ph), 7.85 (d, δHH = 7.9 Hz, 2H, C6n–H of C6–Ph), 8.04 (d, δCP = 7.2 Hz, 2H, C6n–H of C6–Ph). 13C{1H} NMR (100.61 MHz, 300 K, [D8]THF): δ = 3.2 Hz, C7(CH3)5), 26.1 (s, C3–H of TPP), 88.4 (s, C6(CH3)5), 88.6 (d, JCP = 7.3 Hz, C3–H of TPP), 90.9 (s, C7–H of C2–Ph), 95.2 (d, JCP = 74.5 Hz, C6–H of TPP), 112.9 (s, C4–H of catecholboryle), 123.3 (s, C2,6–H of C2–Ph), 124.3 (s, C3–H of C2–Ph), 127.3 (s, C2,6–H of C2–Ph overlapping with C4–Ph), 127.4 (d, JCP = 4.6 Hz, C2,6–H of C2–Ph), 127.6 (s, C7–H of C2–Ph), 127.7 (s, C4,5–H of C2–Ph), 127.9 (d, JCP = 15.0 Hz, C2,6–H of C2–Ph), 128.7 (s, C4,5–H of C6–Ph), 129.2 (s, C4,5–H of C4–Ph), 1416.5 (s, C1 of C4–Ph), 1435 (d, JCP = 18.0 Hz, C4 of C2–Ph), 147.8 (s, C1 of C2–Ph), 149.5 (s, C1,6 of catecholboryle), the signal for C2 of TPP was not observed. 11B{1H} NMR (128.38 MHz, 300 K, [D8]THF): δ = 34.3 (s br). 11B NMR (128.38 MHz, 300 K, [D8]THF): δ = 34.3 (s br). 19F NMR (161.98 MHz, 300 K, [D8]THF): δ = −126.7 (s). 31P NMR (161.98 MHz, 300 K, [D8]THF): δ = −126.7 (s br). Elemental analysis calculated for C29H18BF2O2P (Mw = 634.34 g mol−1) C 73.84, H 5.72; found C 73.45, H 5.73.

X-Ray crystallography

Crystals of endo-3, exo-3, 4, 5, and 8 suitable for X-ray diffraction were obtained from n-hexane. Crystals of 6 were obtained from diethyl ether. X-ray quality crystals of 7 were obtained from concentrated diethyl ether solutions of the crude reaction mixture resulting in crystallization along with half a molecule of [18]crown-6. The single crystal X-ray diffraction data were recorded on an Agilent Technologies Gemini Ultra R diffractometer (exo-3 and 5) and an Agilent Technologies SuperNova (endo-3, 4, and 6–8) with Cu Kα radiation (λ = 1.54184 Å). Semiempirical multi- scan absorption corrections27 and analytical ones28 were applied to the data. The structures were solved with SHELX29 and least-square refinements on F2 were carried out with SHELXL.30

CCDC 1448678–1448684 contain the supplementary crystallographic data for this paper.

DFT calculations

The calculations on 2, endo-3 and exo-3 were performed using the ORCA program package (version 3.0.2).31 The BP86 density functional and the Ahlrichs def2-TZVP basis set were employed for all atoms.12–36 The RI approximation was used.17,36 The Ahlrichs Coulomb fitting basis for the TZVP basis for all atoms (TZVJ) and the atom-pair-wise dispersion correction to the DFT energy with Becke-Johnson damping (d3bj) were applied.39,40 The nature of the stationary points was verified by numerical frequency analysis.

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Notes and references

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