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and 2-substituted phosphacyclohexadienyls (where the substituent is connected to an adjacent carbon atom) is observed. Consequently, the molecular structures of the complexes display the C₅ and the CpP coordination mode, respectively (Figure 1).

Results and discussion

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 (Figure 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 (Figure 2b).⁸

³¹P(¹H) NMR monitoring ([D₅]THF, Figure 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 endo-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) or a decomposition product. The ³¹P(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, exo-3 and endo-3 at 50 °C for several days (³¹P(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 [D₅]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, exo-3 and endo-3 as pure compounds by protonation 1 with HCl(OEt₂).

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 Figure 3). The 2-hydrophosphacyclohexadienyl...
complexes **endo-3** and **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 **endo-3** and **exo-3** are close in energy, while **2** was calculated to be +7.0 kcal mol\(^{-1}\) less stable than **endo-3** (Figure 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 **endo-3** and **exo-3** in a 65:35 ratio (NMR integration). The formation of **2** as an intermediate was not observed by \(^{31}\)P\{1H\} NMR in this case, which indicates that the reaction proceeds via a different mechanism. Purification by column chromatography gave NMR-spectroscopically pure **exo-3** and **endo-3** after crystallization.

**Exo-3** was isolated as orange rods in 25% yield, whereas pure **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, Me\(_3\)SiCl, and Ph\(_2\)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 2-substituted phosphacyclohexadienyl complex **7** was obtained as bright orange crystals by a similar reaction with one equiv. of chlorocatecholborane (Scheme 2d). Compound **7** is moderately soluble in n-pentane and n-hexane, but dissolves well in more polar solvents such as diethyl ether, toluene and THF. \(^{31}\)P\{1H\} NMR monitoring ([D\(_8\)]THF, see ESI, Figure S23) at \(-100^\circ\mathrm{C}\) revealed a signal at \(-26\,\mathrm{ppm}\), which we tentatively assign to the intermediate \([\text{Cp}^*\text{Fe}(1\text{-BCat-PC}_{\text{5}}\text{Ph})_2]\) (**7-P**, Scheme 3) containing a direct P−B bond. The signal is broad, therefore the \(^{31}\)P\(^{10/11}\)B coupling constant cannot be precisely determined, but the characteristic 1:1:1:1 quartet structure is clearly visible. The resonance of intermediate **7-P** decreased upon warming and completely disappeared at \(-40^\circ\mathrm{C}\). The signal of **7** simultaneously appeared above \(-60^\circ\mathrm{C}\).
The observation of this mixture shows that other processes than

\[
\text{[K(18)crown-6)(thf)]} 
\]

byroration may also occur, explaining the modest isolated yield (26%).

An analogous reaction with Ph₃SnCl in THF produced the P–Sn functionalized complex 8 (Scheme 2e), but the reaction was unselective. According to \(^{31}\text{P}^{(1)}\text{H}\) 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. Diphosphine \([\text{Cp}^{*}\text{Fe}(\text{PC₆H₄})₂] \)

and hexaphenyldistannane were identified as decomposition products by \(^{31}\text{P}^{(1)}\text{H}\) and \(^{119}\text{Sn}^{(1)}\text{H}\) NMR, suggesting decomposition by a radical pathway.

Crystallographic characterization of \textit{exo}-3, \textit{endo}-3, and 4 – 7

Single-crystal X-ray structure determinations of \textit{exo}-3, \textit{endo}-3 and 4 – 7 (Figure 4 and Table 1) revealed \(\eta^3\)-Cp* and \(\eta^3\)-phos-
phacyclohexadienyl ligands. As a consequence, the phosphacyclohexadienyl units are not planar. The P atom points away from

gated compared to that in unsymmetrically-substituted diphosphanes such as 9-diphenylphosphanyl-9-phosphabicyclo-

clohexadienyl units are not planar. The P atom points away from

Table 1 Selected Bond Lengths (Å) and Angles (°) of the Structures of Compounds endo-3, exo-3 and 4 – 7.

<table>
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<th>endo-3</th>
<th>exo-3</th>
<th>4</th>
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<th>6</th>
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<td>123.6(2)</td>
<td>95.50(9)</td>
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</tbody>
</table>

a) Cp* = centroid of the cyclopentadienyl ring

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

[Cr(Fe(CO)3(C6H5)2)]2 (39.7°) previously reported by us (Figure 2c, vide supra). The corresponding fold angle for 6 (27.2°)

is over 10° shorter and similar to that of [Cr(Fe(1-NMe2PC6H5)]2 (28.1°, vide supra). In endo-3, exo-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 corre-

sponding 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 phosphinine-type complexes, which show η4-coordination through a Cp-unit. To the best of our knowledge, the sole example comprising the same structural motif is endo-F (Figure 2b, vide supra). The C–C distances of the η5-coordinated Cs and Cp-units endo-3, exo-3 and 4 – 7 (Table 1) are in between typical single and double bond distances. Similar bond lengths were observed for the η5-coordinated phosphinine ring in complex G. 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. The P–C bond lengths in 4 – 6 are typical for single bonds and similar to those in B and H (Figure 2, vide supra). The P–C 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, whereas the P1–C5 (1.792(2)–1.785(2) Å) bonds are shorter and close to those found in the η6-coordinated ring in G. While the P1–Si bond length (2.270(2) Å) of 5 is typical for a P–Si single bond, the P1–P2 bond (2.3062(7) Å) of 6 is elon-

[3.3.1]nonane (2.229(1) Å). An analogous observation was made by Gudat et al for P-phosphinylazaphospholes, e.g. 2-diphenylphosphanyl-1,3-dimesityldiazaphosphole, which displays a similarly elongated P–P bond (2.334(1) Å). 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 Mathes and co-workers synthesized related phosphine borates, e.g. Li[2-B2Et2PC6H4]2 by reaction of 2-bromophosphinines with two equiv. LiBHEt2. These anionic molecules contain a tetrahedral boron atom in the 2-position; they can be converted into 2-ethylated phosphinines by reaction with iodine. Braunischweig et al. prepared a series of (dimethoxyborylmethyl)dimethylphosphinane complexes where a P–C(OMe)2 unit of coordinates to chromium or iron via the P atom. An example is the compound [(FeH2(CO)3(SiPh3)2B(OMe)2]7. Different from these η5-coordinated complexes, the phosphacyclohexadienyl ligand of 7 acts as a η6-ligand to iron through the planar Cp-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 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 1H, 13C(1H) and 31P(1H) NMR data of endo-3, exo-3 and 4 – 7 recorded in [D6]THF. The 31P NMR signals of exo-3 (~160.7 ppm, 2JPN not detected) and endo-3 (~136.3 ppm,
(−126.7 ppm) as enyl moiety, gives rise to a similar high-field shift of the 1-substituted species bands at 260, 290sh, 360sh and 460sh nm. The UV/vis spectra of 2-H-substituted complexes 4−6 showed a weak shoulder at 450 nm; three stronger bands are characteristic of the phosphinine ring (ppm). The signal at 12.8 ppm is assigned to the PPh3 and phosphine units as their Cp*-substituted equivalents. Notably, the simple change of the configuration of a carbon atom in the phosphinine ring causes an upfield shift of the 31P NMR doublet of endo-3 by almost 25 ppm with respect to endo-3. The aliphatic hydrogen atom of the phosphinine ring resonate 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(η3-C5H5)].

The spectra of 1-substituted compunds 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 λmax = 550−580 nm and λmax = 480−580 nm, respectively. Similar spectra were observed for other complexes of this type (type H, Figure 2c). Previous TD-DFT calculations indicated that these bands predominantly arise from excitations from filled metal-centered MOs into the ligand-based unoccupied MOs (MLCT).

### 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(OEt2)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, Me₃SiCl, Ph₂PhCl and Ph₃SnCl, 1-substituted complexes 4−6 and 8 were obtained. Thus, HCl(OEt2)2, isopropyl chloride and chlorocatecholborane result in products substituted at the 2-carbon atom, whereas MeI, Me₃SiCl, Ph₂PhCl and Ph₃SnCl provides 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 1H and 13C 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[18]crown-6][CH3][CH2+PC6H5]2]1 was prepared according to literature procedures. HCl(EtO) solution, methyl iodide, triethylsilane chloride, chloroacetaldehyde and chlorobenzephene were purchased from Sigma-Aldrich and TCI and were used as received.

[Cp*Fe(2-endo-H-PC6H5)] (endo-3) and [Cp*Fe(2-exo-H-PC6H5)] (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 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’(n-hexane/toluene, 5/1) = 0.42), slightly overlapping with endo-3, which followed immediately (R’(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, λmax / nm, εmax / L·mol−1·cm−1): 220sh (37000), 260 (29600), 320sh (9300), 450 (670). 1H NMR (400.13 MHz, 300 K, [D8]THF); δ = 1.36 (s, 15H, C6(CH3)), 2.76 (dd, JHP = 15.2 Hz, JHH = 8.1 Hz, IH, C5-H of TPP), 2.98 (dd, JHP = 2.4 Hz, JHH = 8.1 Hz, IH, C1-H of TPP), 6.77 − 6.81 (m, 3H, C4,6,8-H of C6-Ph), 6.90 − 6.94 (m, 2H, C5,5-H of C6-Ph), 7.16 (t, JHH = 7.2 Hz, 1H, C4-H of C6-Ph), 7.20 − 7.24 (m, 3H, C5,5-H of C6-Ph overlapping with C5-H of TPP), 7.31 (t, JHH = 7.3 Hz, 1H, C6-H of C6-Ph), 7.37 − 7.42 (m, 2H, C5,5-H of C6-Ph), 7.80 (d, 2H, C6,6-H of C6-Ph), 7.93 (d, JHH = 7.8 Hz, 2H, C6,6-H of C6-Ph). 13C NMR (100.16 MHz, 300 K, [D8]THF): δ = 10.0 (d, JCP = 3.4 Hz, C6(CH3)), 26.3 (s, C5-H of TPP), 34.7 (d, JCP = 23.2 Hz, C1-H of TPP), 87.9 (s, C6(CH3)), 88.8 (d, JCP = 7.9 Hz, C4-H of TPP), 91.8 (s, C6 of TPP), 95.2 (d, JCP = 69.9 Hz, C5-H of TPP), 125.2 (s, C4,6,8-H of C6-Ph), 126.2 (d, JCP = 5.3 Hz, C5-H of C6-Ph), 127.1 (d, JCP = 1.1 Hz, C1-H of C6-Ph), 127.7 (s, C4,6,8-H of C6-Ph), 127.5 (s, C4,6,8-H of C6-Ph), 127.9 (s, C5,5-H of C6-Ph), 128.6 (d, JCP = 1.0 Hz, C5,5-H of C6-Ph), 129.0 (s, C5,5-H of C6-Ph), 141.8 (s, C5,5-H of C6-Ph), 143.8 (d, JCP = 17.8 Hz, C1-H of C6-Ph), 144.7 (d, JCP = 1.8 Hz, C4-H of C6-Ph). 13P NMR (161.98 MHz, 300 K, [D8]THF); δ = −136.3 (s). 31P NMR (161.98 MHz, 300 K, [D8]THF); δ = −136.3 (d, 2JHP = 15.3 Hz). Elemental analysis calcd. for C33H33FeP (Mw = 516.45 g·mol−1) C 76.75, H 6.44; found C 76.11, H 6.55.

**exo-3.** M.p. 177 °C. UV/vis: (n-hexane, λmax / nm, εmax / L·mol−1·cm−1): 230sh (72000), 275 (59000), 325sh (17000), 450 (1100). 1H NMR (400.13 MHz, 300 K, [D8]THF); δ = 1.50 (s, 15H, C6(CH3)), 1.66 (s br, 1H, C5-H of TPP), 2.44 (s br, 1H, C1-H of TPP), 7.13 − 7.40 (overlapping m, 12H, Ar-H of C6-Ph + C5-H of TPP + C5,5-H of C6-Ph), 7.86 (d, JHH = 7.9 Hz, 2H, C5,5-H of C6-Ph), 7.90 (d, JHH = 7.9 Hz, 2H, C5,5-H of C6-Ph). 13C(1H) NMR (100.61 MHz, 300 K, [D8]THF); δ = 9.9 (d, JCP = 2.8 Hz, C6(CH3)), 21.4 (d, JCP = 5.1 Hz, C6-H of TPP), 31.7 (d, JCP = 19.7 Hz, C5-H of TPP), 86.9 (d, JCP = 7.3 Hz, C5-H of TPP), 88.1 (s, C6(CH3)), 92.3 (d, JCP = 1.8 Hz, C1-H of TPP), 97.7 (d, JCP = 67.5 Hz, C5-H of TPP), 125.9, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 128.9, 129.0 (C5,5,5,5-H of C6-Ph), 143.9 (s, C1-H of TPP), 145.9 (d, JCP = 12.9 Hz, C5-H of TPP). 31P NMR (161.98 MHz, 300 K, [D8]THF); δ = −160.7 (s). 31P NMR (161.98 MHz, 300 K, [D8]THF); δ = −160.7 (s). Elemental analysis calcd. for C33H33FeP (Mw = 516.45 g·mol−1) C 76.75, H 6.44; found C 77.15, H 6.50.
A solution of trimethylsilylethyl chloroformate (0.9 mL, c = 0.152 mol·L⁻¹) was added to a dark orange solution of 1 (132 mg, 0.137 mmol) in THF (7 mL) and stirred at room temperature for 16 h. The resulting dark green brown mixture was dried in vacuo, and the residue was extracted with n-pentane (16 x 0.5 mL). The fractions were combined and dried in vacuo. 18-crown-6 was sublimed at 60°C and < 1.0 · 10⁻³ mbar. The remaining residue was dissolved in n-hexane (8 mL). The greenish black solution was filtered and concentrated to 5 mL. 5 was isolated as dark green to black crystals after storage at -30°C for three days. Yield: 48 mg (59%). M.p. 213°C. UV/vis: (n-hexane, λmax / nm, εmax / L·mol⁻¹·cm⁻¹): 250 (36300), 300 (26000), 500 (2300), 580 (2100).¹³C NMR (400.13 MHz, 300 K, [D₆]THF): δ = -38.8 (d, JCP = 3.8 Hz, 2H, C₃-H of C₃-PPh), 123.5 (s, JCP = 3.2 Hz, 4H, C₂-H of C₂-PPh), 120.2 (d, JCP = 19.4 Hz, C₁-H of C₁-PPh).\(^{31}P^31^H NMR (161.98 MHz, 300 K, [D₆]THF): δ = 12.8 (d, JCP = 293 Hz, P₆), 38.8 (d, JCP = 293 Hz, P₅), 34.9 (d, JCP = 24.5 Hz, C₁ of C₁-PPh). \(^{31}P^31^H NMR (161.98 MHz, 300 K, [D₆]THF): δ = 12.8 (d, JCP = 293 Hz, P₆), 38.8 (d, JCP = 293 Hz, P₅), 34.9 (d, JCP = 24.5 Hz, C₁ of C₁-PPh). Elemental analysis calcd. for C₃₆H₄₃FePSi₂ (Mw = 700.62 g·mol⁻¹): C 77.14, H 6.04; found C 77.55, H 6.36.

A solution of chloroacetophenone (150 mg, 0.156 mmol) in THF (10 mL) at −35°C was stirred and heated to room temperature overnight. All volatiles were removed in vacuo and the dark orange-green residue was washed with n-hexane (5 x 1 mL) and extracted with diethyl ether (10 x 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, εmax / L·mol⁻¹·cm⁻¹): 260 (15000), 290 (10000), 360 (1700), 460 (300).¹¹H NMR (400.13 MHz, 300 K, [D₆]THF): δ = 1.34 (s, 15H, C₃(CH₃)₃), 3.51 (s, 1H, C₁-H of C₁-PPh), 6.68 - 6.72 (m, 1H, C₂-H of C₂-PPh), 6.89 - 6.91 (m, 2H, C₃-H of C₃-PPh), 6.03 - 6.05 (overlapping m, 3H, C₄-H of C₄-PPh overlapping with C₅-H of C₅-PPh), 7.07 - 7.11 (m, 2H, C₆-H of catecholboryle), 7.17 - 7.21 (m, 1H, C₇-H of C₇-PPh), 7.23 - 7.26 (m, 2H, C₈-H of C₈-PPh), 7.28 - 7.30 (m, 2H, C₉-H of catecholboryle), 7.32 - 7.36 (m, 1H, C₁₀-H of C₁₀-PPh), 7.44 - 7.48 (m, 2H, C₁₁-H of C₁₁-PPh), 7.85 (d, JHH = 7.9 Hz, 2H, C₁₂-H of C₁₂-PPh), 8.04 (d, JHH = 7.9 Hz, 2H, C₁₃-H of C₁₃-PPh).\(^{13}C^1H NMR (100.61 MHz, 300 K, [D₆]THF): δ = 7.89 (s, CH₃(CH₃)₃), 41.00 (dd, JCP = 12.5 Hz, JCP = 10.6 Hz, C₁₀-H of C₅-PPh), 80.90 (dd, JCP = 12.6 Hz, JCP = 10.5 Hz, C₁₂-H of C₁₀-PPh), 89.18 (s, CH₃(CH₃)₃), 93.50 (s, JCP = 2.2 Hz, C₁₀ of C₁₀-PPh), 112.00 (d, JCP = 3.3 Hz, C₁₀-H of C₁₀-PPh), 127.30 (s, C₁₂-H of C₁₂-PPh), 124.40 (d, JCP = 3.3 Hz, C₁₀-H of C₁₀-PPh). \(^{31}P^31^H NMR (161.98 MHz, 300 K, [D₆]THF): δ = 35.1 (s, JCP = 293 Hz, C₁₁), 38.5 (s, JCP = 293 Hz, C₁₂), 34.9 (d, JCP = 24.5 Hz, C₁ of C₁-PPh). All P₁₁-P₁₂ peaks were observed at the edge of the NMR spectrum.\(^{11}B^1H NMR (128.38 MHz, 300 K, [D₆]THF): δ = 34.3 (s, br).\(^{11}B
NMR (128.38 MHz, 300 K, [D₆]THF): δ = 34.3 (s br). ³¹P ¹H) NMR (161.98 MHz, 300 K, [D₆]THF): δ = −126.7 (s). ³¹P ¹H) NMR (161.98 MHz, 300 K, [D₆]THF): δ = −126.7 (s br). Elemental analysis calcd. for C₉₆H₈₇FeO₂P (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 (endo-3 and 5) and an Agilent Technologies SuperNova (endo-3, 4, and 6 – 8) with Cu Ka radiation (λ = 1.5418 Å). Semi-empirical multi-scan absorption corrections were applied and analytical ones were applied to the data. The structures were solved with SHELXT and least-square refinements on F² were carried out with SHELXL.

CCDC 1448678–1448684 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculations

The calculations on 2, endo-3 and exo-3 were performed using the ORCA program package (version 3.0.2). The BP86 density functional and the Ahlrichs def2-TZVP basis set were employed for all atoms. The RI approximation was used. 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. The nature of the stationary points was verified by numerical frequency analysis.

Acknowledgements

Funding by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Notes and references

Electrophilic attack of π-coordinated 2,4,6-triphenylphosphinine afforded a range of novel complexes with substituted η⁵-phosphacyclohexadienyl ligands.