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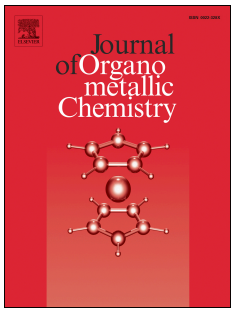

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Diels-Alder Route to Norbornane Derived Vicinal Phosphane/Borane Frustrated Lewis Pairs for the Metal-free Catalytic Hydrogenation of α, β-Unsaturated Ketones

*Christian Wölke, Constantin G. Daniliuc, Gerald Kehr, Gerhard Erker**

To the memory of Professor Pascual Royo, a great scientist and friend

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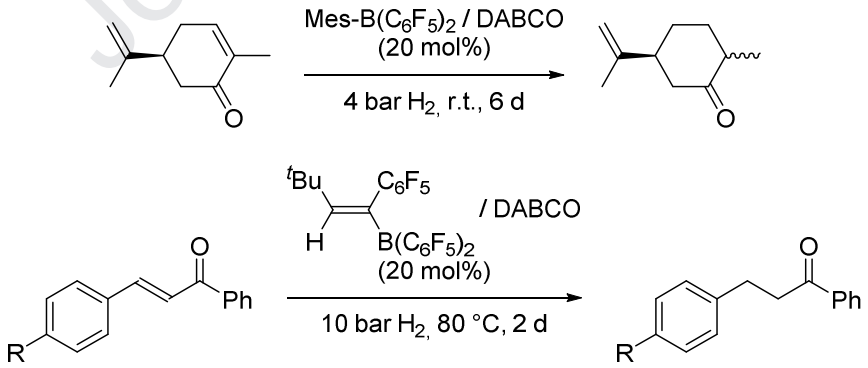
Keywords: Frustrated Lewis pairs, metal-free hydrogenation, α,β-unsaturated ketones, Diels-Alder reaction

Abstract

The [4+2]-cycloaddition reaction of the (dimesitylphosphino)cyclopentadienes **5a,b** with *N*-phenylmaleimide gave the norbornene derivative **9**. Its reduction with $LiAlH_4$ produced the *N*-phenylpyrrolidino-annulated system **10**. Treatment with Piers' borane gave the respective P/B FLP **12** as the major product, which cleaved dihydrogen under mild conditions to yield the phosphonium/hydrido borate product **14**. Reaction of the phosphino-norbornene **10** with two molar equiv. of Piers' borane [$HB(C_6F_5)_2$] followed by exposure to dihydrogen eventually gave the $HB(C_6F_5)_2$ adduct **15**. This served as a catalyst for the hydrogenation of a series of chalcone derivatives. The system requires a pre-activation period before becoming active for the conjugated enone hydrogenation.

1. Introduction

Frustrated Lewis Pairs (FLPs) are comprised of combinations of Lewis acids and bases that are effectively hindered from strong mutual adduct formation that would annihilate their specific chemical features. [1] This is mostly achieved by attachment of bulky substituents at the core atoms of the pair, although geometric factors in specific intramolecular situations have equally well been used, [2] as have electronic variations. [3] FLPs often show chemical features that had usually been associated typically with transition metal chemistry. The frequently observed heterolytic splitting reaction of dihydrogen is a prominent example. [4] It has been used in many cases as the basis for the development of metal-free catalytic hydrogenation processes. In the very beginning this was done with a very limited substrate scope; initially reducing bulky imines to the respective amines. [4,5,6] Polar electron-rich π-systems such as enamines or silyl enol ethers followed, [6] but by now an increasing variety of catalytic hydrogenation reactions of different types of organic substrates has been reported, including various heterocycles, unfunctionalized alkynes and even ketones. [7] At present there have only surprisingly few examples of FLP hydrogenation reactions of α,β-unsaturated carbonyl compounds been reported. Soós *et al.* had described the single example of the FLP catalyzed hydrogenation of the internal carbon-carbon double bond of (+)-carvone by a special catalyst [mesityl-$B(C_6F_5)_2$ / DABCO], [8] The slow reaction went to completion within 6 d at 4 bar H_2 with 20 mol% of the catalyst mixture.

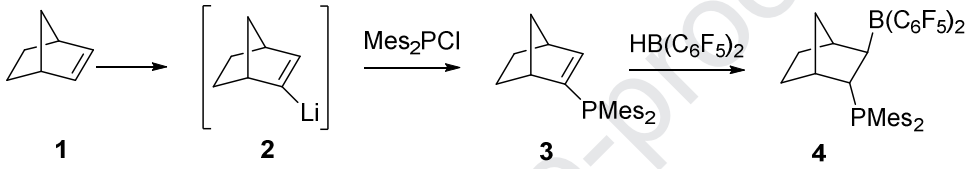


Scheme 1. FLP catalyzed enone hydrogenation reactions from the literature.

Our group had reported that a few aryl substituted conjugated ynones were hydrogenated at the FLP catalyst $^tBuCH{=}C(C_6F_5)B(C_6F_5)_2$ / DABCO under more forcing conditions (5 mol% cat.,

10 bar H_2, 80°C, 2 d) to give the respective enones. These could subsequently be further reduced under similar conditions to give the corresponding saturated ketone products (see Scheme 1). [9]

We had previously prepared a variety of intramolecular phosphane/borane frustrated Lewis pairs (P/B FLPs) by means of hydroboration reactions using Piers' borane [$HB(C_6F_5)_2$], [10] among them the vicinal non-interacting P/B FLP **4** at the norbornane framework (see Scheme 2). [2a] It was an active dihydrogen splitting reagent, but also showed a great variety of other typical FLP reactions, among them specific CO reduction chemistry and the formation of a persistent FLPNO nitroxide radical upon treatment with nitric oxide (NO). [11]



Scheme 2. The previously reported synthesis of the FLP **4**.

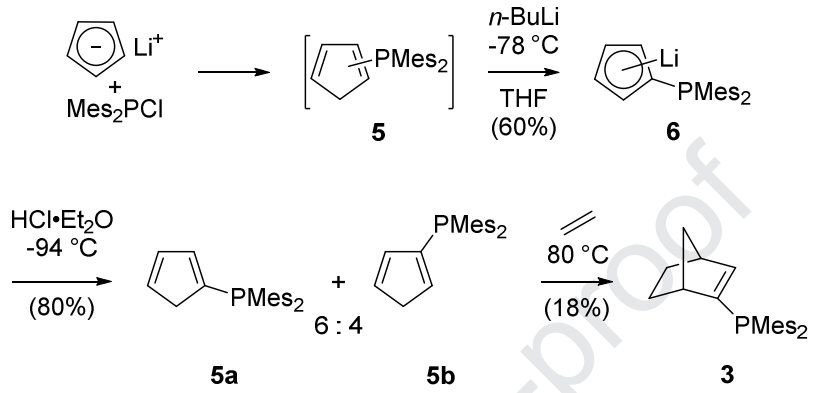
Compound **4** was synthesized by a procedure involving a norbornene metalation step [12] followed by phosphination and hydroboration. We have now tried to develop a different entry into such *trans*-2,3-P/B FLP systems at derivatized norbornane backbones by using Diels-Alder reactions starting from the dimesitylphosphino-cyclopentadienyl isomer precursors. This has eventually resulted in the development of a specific functionalized example of this norbornane derived P/B FLP type that showed very special catalytic features, namely it turned out to be an active catalyst for the hydrogenation of chalcone derivatives and related compounds under mild reaction conditions. This development will be outlined and discussed in this account.

2. Results and discussion

2.1 [4+2]Cycloaddition reactions with the (dimesitylphosphinyl)cyclopentadiene isomers

(Dimesitylphosphino)cyclopentadiene (**5**) was prepared in analogy to methods previously worked out by our group. [13] Cyclopentadienyllithium was reacted with Mes_2PCl in THF at -78 °C. As it turned out that the resulting product **5** could not easily be isolated pure from that

reaction mixture we decided to circumvent this problem by a pair of additional reaction steps, initiated by deprotonation of the P-substituted cyclopentadiene by treatment with *n*-BuLi (at -78 °C). This gave the respective P-functionalized lithium cyclopentadienide **6**, which was easily purified and which we isolated as a solid in 60% yield (see Scheme 3).



Scheme 3. Synthesis of the phosphanylnorbornene derivative **3**.

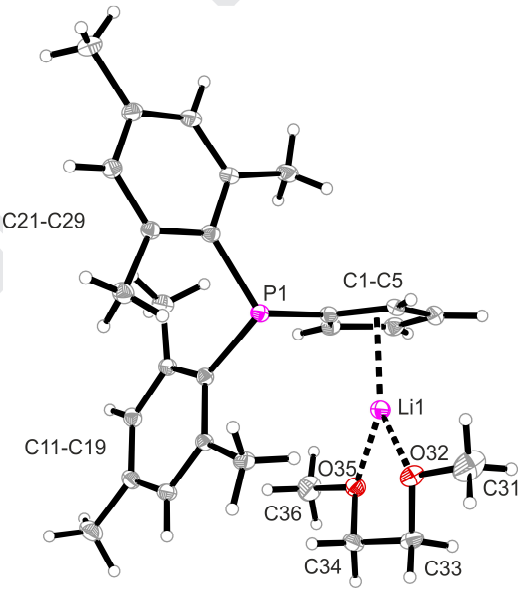


Figure 1. A view of the molecular structure of the lithium Mes_2P-Cp compound **6** (dme). Thermal ellipsoids are set at 15% probability. Selected bond lengths (Å) and angles (°): P1-C1 = 1.798(3), P1-C11 = 1.852(3), P1-C21 = 1.851(3), Li1-O32 = 1.971(5), Li1-O35 = 1.959(6), C1-P1-C11 = 101.6(2), C1-P1-C21 = 113.1(2), C21-P1-C11 = 104.8(2).

Compound **6** was characterized by NMR spectroscopy in THF-D_8 solution [^{31}P: δ -39.5; ^{7}Li: δ -6.7]. [14] Crystallization from 1,2-dimethoxyethane gave the **6**(dme) adduct that was characterized by X-ray diffraction. The X-ray crystal structure analysis shows the five-membered ring of the functionalized cyclopentadienide that features a rather uniform set of five carbon-lithium contacts (2.240(5) – 2.270(6) Å). Carbon atom C1 has the Mes_2P-substituent bonded to it. The coordination geometry at phosphorus is distorted trigonal-pyramidal ($\sum P1^{CCC}$ = 319.5°). The lithium atom has one dme molecule κO,O-bonded to it (see Figure 1).

The purified lithium Mes_2P-Cp compound **6** was then protonated by treatment with HCl in ether at -94 °C to give the reasonably pure Mes_2P-substituted cyclopentadienes **5a** and **5b** (6:4). They were characterized by NMR spectroscopy from the mixture [^{31}P: δ -36.7 (major), δ -36.9 (minor), see the Supporting Information for further details]. Low temperature crystallization from pentane gave single crystals of the major isomer **5a** that were suited for its characterization by X-ray diffraction. It shows the Mes_2P-substituent ($\sum P1^{CCC}$ = 319.9°) attached to the terminal carbon atom of the conjugated diene moiety at the five-membered carbocycle. The adjacent carbon atom C5 is saturated and bears the pair of hydrogen atoms (see Figure 2).

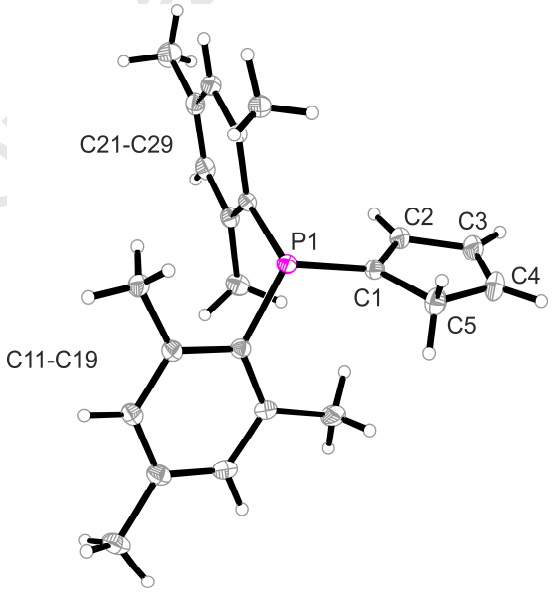
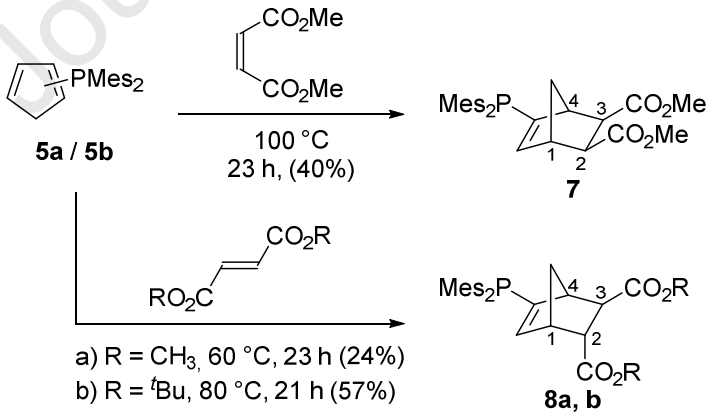


Figure 2. A projection of the molecular structure of the major C_5H_5-$PMes_2$ isomer **5a**. Thermal ellipsoids are set at 15% probability. Selected bond lengths (Å) and angles (°): P1-C1 = 1.803(3), P1-C11 = 1.845(3), P1-C21 = 1.849(3), C1-C2 = 1.346(4), C1-C5 = 1.484(4), C2-C3 = 1.463(4),

C3-C4 = 1.388(5), C4-C5 = 1.420(4), C1-P1-C11 = 110.9(2), C1-P1-C21 = 101.5(2), C11-P1-C21 = 107.5(2).

It was a natural choice to try reacting the **5a**/**5b** equilibrium mixture with ethylene in an attempt to improve the synthesis of the norbornenylphosphane **3** and, consequently, of the FLP **4**. The **5a**/**5b** mixture reacted with ethylene under forcing conditions (50 bar ethylene, 80 °C, 16 d in toluene) to eventually give the product **3** (see Scheme 3). However, we so far could only isolate it after workup, involving column chromatography, in a meager yield of 18% as a viscous oil. The isolated compound **3** contained a ca 12% unidentified impurity, as judged from the ^{31}P NMR spectrum (for further details see the Supporting Information).

Since the reaction of the **5a**/**5b** mixture with ethylene did not provide an improvement above our previous norbornene based FLP synthesis, we turned to investigating [4+2]-cycloaddition reactions with functionalized olefins. [15] In each case did we employ freshly prepared solutions of the **5a**/**5b** equilibrium mixture in toluene and we reacted it with a variety of typical "Diels-Alder dienophiles" having electron-withdrawing substituents attached at their olefinic C-C double bonds. Here we will briefly describe the outcome of reactions with fumarate and maleate esters, an analogous example with *trans*-1,4-diphenylbut-2-ene-1,4-dione is mentioned in the Supporting Information.



Scheme 4. Diels Alder reactions of compounds **5** with fumarate or maleate.

The reaction of the **5a**/**5b** mixture with dimethylmaleate required 23 h at 100 °C to go to completion on a preparative scale. The [4+2]cycloadduct **7** was isolated in 40% yield after

chromatography. The X-ray crystal structure analysis revealed the *exo,exo*-orientation of the pair of methylester substituents at carbon atoms C5 and C6 at the newly formed norbornene framework of **7** (see Figure 3). The bulky Mes_2P-substituent is attached at the olefinic norbornene carbon atom C2. Consequently, compound **7** shows the NMR resonances of an inequivalent pair of methylester groups in addition to the typical resonances of the Mes_2P-substituent [^{31}P: δ -38.1] and the characteristic NMR resonances of the norbornene core (see the Supporting Information for details).

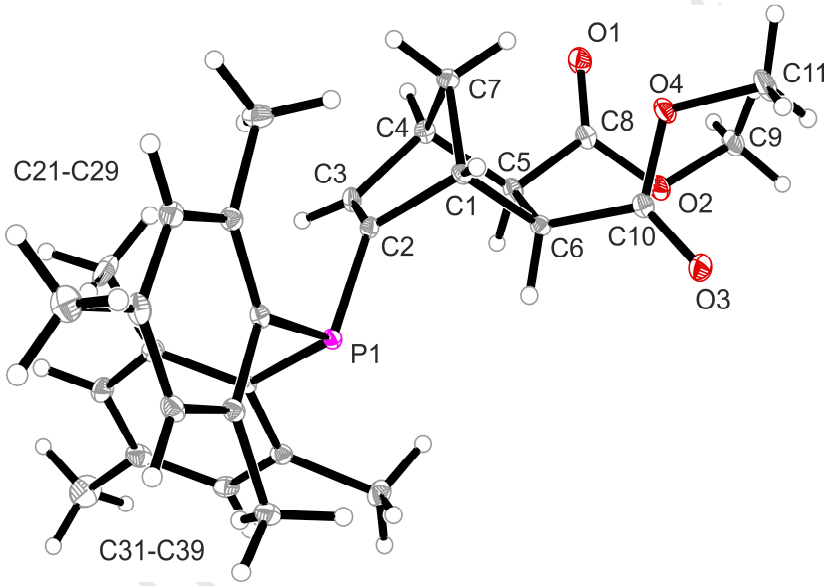


Figure 3. A view of the molecular structure of the [4+2]cycloaddition product **7** (with unsystematical atom numbering scheme). Thermal ellipsoids are set at 30% probability. Selected bond lengths (Å) and angles (°): P1-C2 = 1.798(2), P1-C21 = 1.838(2), P1-C31 = 1.844(2), C2-C3 = 1.342(2), C2-P1-C21 = 111.1(1), C2-P1-C31 = 101.9(1), C21-P1-C31 = 106.9(1), C2-C1-C6-C10 = -163.2(1), C3-C4-C5-C8 = 171.1(1); $\sum P1^{CCC}$ = 320.0.

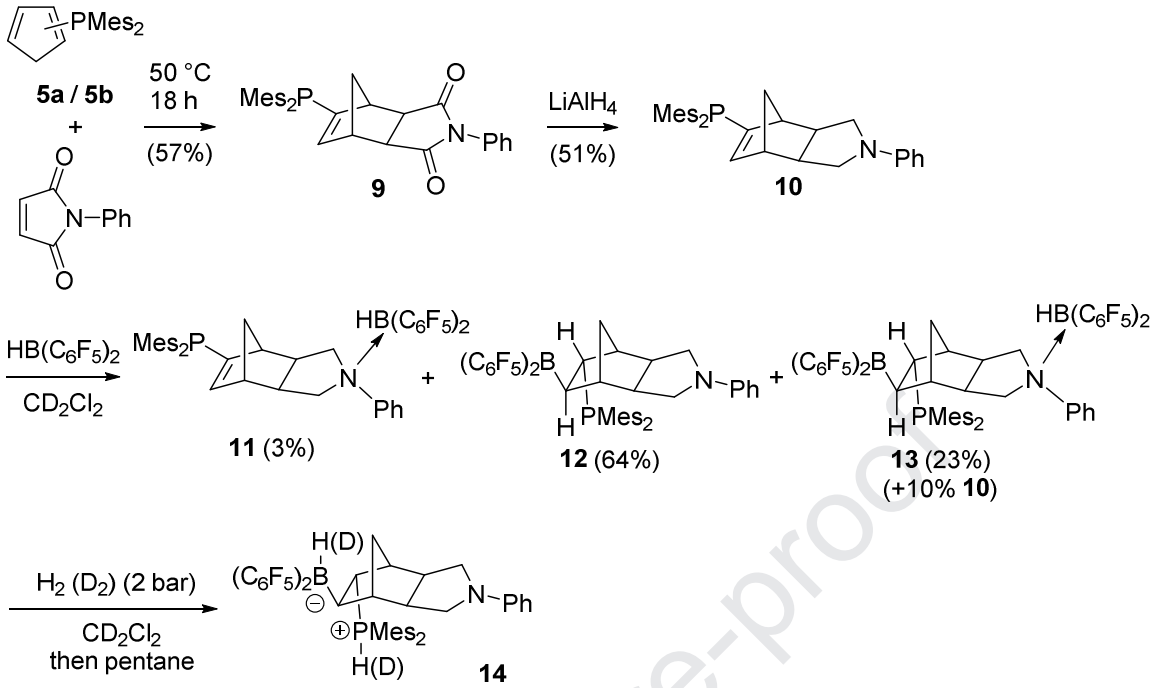
The reaction of **5a**/**5b** with dimethylfumarate was carried out at 60 °C (23 h). We isolated a single [4+2]cycloaddition diastereoisomer from the reaction in 24% yield. From both the detailed NMR study and the X-ray crystal structure analysis (for details including the depicted structure see the Supporting Information) it was identified as the *endo*-2,*exo*-3-diester derivative **8a**. The Mes_2P-substituent at carbon atom C5 gives rise to a ^{31}P NMR feature at δ -39.1.

The reaction of the **5a**/**5b** mixture with di-*tert*-butylfumarate took the analogous course. From the reaction (80 °C, 21 h) we isolated the product **8b**. in 57% yield as a single diastereoisomer. Its structure was secured by X-ray diffraction and a detailed NMR analysis (see the Supporting Information for details).

We tried to use the [4+2]cycloaddition products **7** and **8a,b** as precursors for the preparation of respective P/B FLPs by means of their reaction with Piers' borane, but in all these (and a few related cases that are stated in the Supporting Information) we could not observe clean product formation. Apparently, the ester functionalities proved to be not compatible with the attempted synthetic scheme. Even the bulky *tert*-butylesters were not sufficiently inert. Therefore, we had to search for another way of developing a successful [4+2]cycloaddition derived pathway to the anticipated new norbornane derived P/B FLP systems and we found that starting from the Diels-Alder reactions of the **5a**/**5b** equilibrium mixture of (dimesitylphosphino)cyclopentadiene isomers with *N*-phenylmaleimide.

*2.2 Norbornane based P/B FLP systems derived from the **5a**/**5b** Diels-Alder reaction with* N-*phenylmaleimide*

The reaction of the **5a**/**5b** mixture with *N*-phenylmaleimide [16] was carried out at 50 °C in toluene (18 h reaction time). Workup involving recrystallization from toluene/pentane at -30 °C gave the crystalline [4+2]cycloaddition product **9** in 54% yield. It was characterized by C,H,N-elemental analysis, by spectroscopy and by X-ray diffraction. The X-ray crystal structure analysis (see Figure 4) shows the newly formed norbornene core that has the bulky Mes_2P-substituent attached to one olefinic carbon atom ($\sum P1^{CCC}$ = 316.6°). The section originating from the maleimide building block has contributed the pair of sp^3-hybridized carbon atoms of the bicyclic framework; the imido functionality is found in the bis-*exo*-orientation. Its nitrogen atom N1 is planar-tricoordinate ($\sum N1^{CCC}$ = 360.0°). The plane of the attached phenyl substituent is rotated out of conjugation with the imido-π-system (angle between the C8-N1-C9 and the phenyl plane: 75°).



Scheme 5. Reaction scheme for the synthesis of the FLP derivatives **12 - 14.**

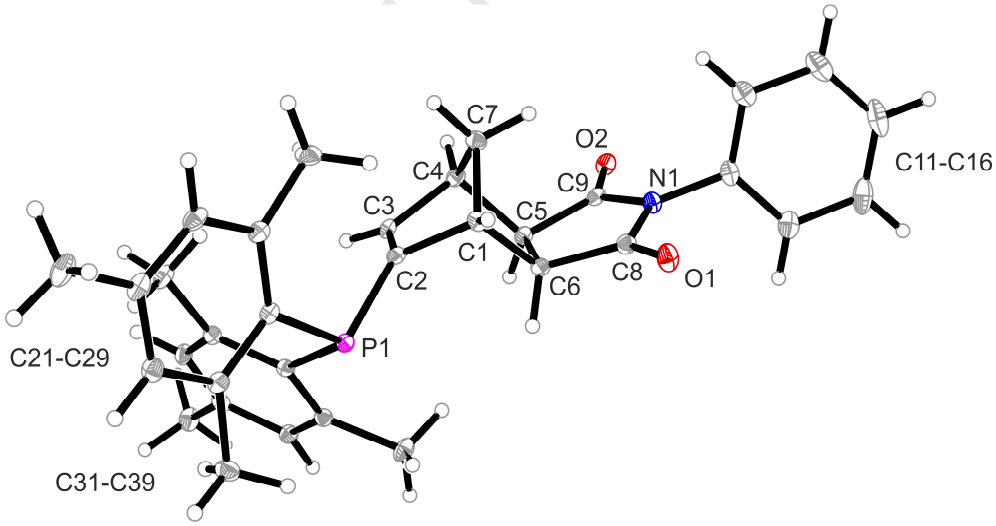


Figure 4. Molecular structure of the [4+2]cycloaddition product **9** of the **5a**/**5b** mixture with *N*-phenylmaleimide (with unsystematical atom numbering scheme). Thermal ellipsoids are set at 30% probability. Selected bond lengths (Å) and angles (°): P1-C2 = 1.815(2), P1-C21 = 1.855(2), P1-C31 = 1.848(2), C2-C3 = 1.340(2), N1-C11 = 1.435(2), C2-P1-C21 = 97.8(1), C2-P1-C31 = 111.6(1), C31-P1-C21 = 107.2(1), C2-C1-C6-C8 = 178.7(2), C3-C4-C5-C9 = -179.6(2), C9-N1-C11-C12 = -75.7(2).

Compound **9** is chiral. Consequently, its $^{1}H/^{13}C$ NMR spectra show the signals of pairs of diastereotopic mesityl substituents at phosphorus. We monitored the typical NMR features of the norbornene core [e.g. ^{1}H (6-H): δ 5.38]. The pair of *exo*-attached carbonyl groups showed up in the ^{13}C NMR spectrum of compound **9** at δ 175.9 and δ 175.3, respectively, and the ^{31}P NMR resonance was located at δ -38.3. Compound **9** was cleanly reduced to the norbornene annulated pyrrolidine derivative **10** by treatment with lithium aluminum hydride. [17] Product **10** was isolated in 51% yield. The X-ray crystal structure analysis showed the *exo*-annulated saturated five-membered heterocycle. Its nitrogen atom is close to planar-tricoordinate ($\sum N1^{CCC}$ = 355.2°) and it is in π-conjugation with the attached phenyl substituent (N1-C11: 1.377(4) Å, C8-N1-C11-C12 = 8.1(5)°). The coordination geometry at phosphorus is trigonal-pyramidal ($\sum P1^{CCC}$ = 317.6°, P1-C2 1.810(3) Å) (see Figure 5).

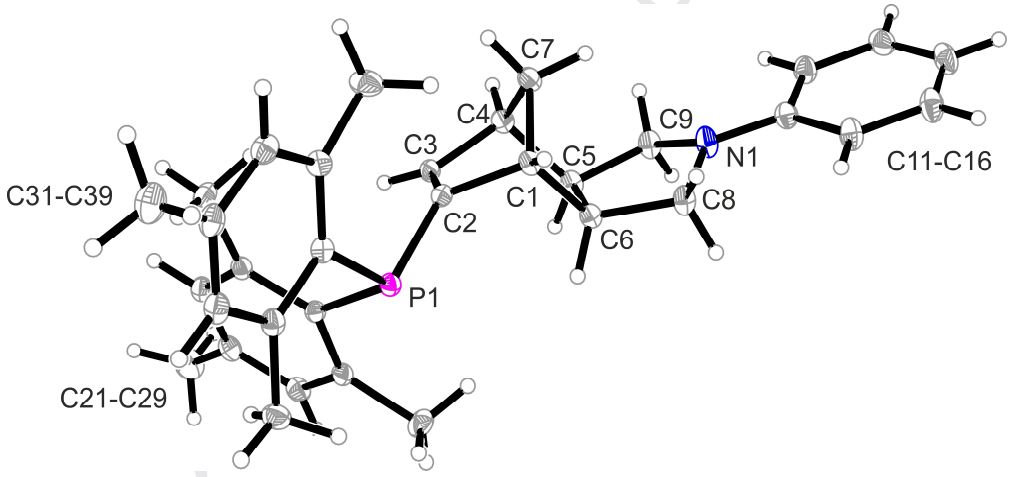


Figure 5. Molecular structure of compound **10 (**with unsystematical atom numbering scheme). Thermal ellipsoids are set at 15% probability. Selected bond lengths (Å) and angles (°): P1-C2 = 1.810(3), P1-C21 = 1.848(3), P1-C31 = 1.847(3), C2-C3 = 1.335(4), N1-C11 = 1.377(4), C2-P1-C21 = 98.8(2), C2-P1-C31 = 111.9(2), C31-P1-C21 = 107.00(2), C2-C1-C6-C8 = 174.8(2), C3-C4-C5-C9 = 179.1(2), C8-N1-C11-C12 = 8.1(5).

Compound **10** shows the NMR signals of the phenyl group at nitrogen. The pair of endocyclic N-CH_2-groups gives rise to four well-separated ^{1}H NMR features. The 7-H/H' protons show up as an AX system and we observe the olefinic 6-H NMR signal at δ 5.54. Compound **10** shows a ^{31}P NMR resonance at δ -37.1.

We next treated the pyrrolidino-norbornene derivative **10** with Piers' borane. The reaction was carried out in a **10** : $HB(C_6F_5)_2$ ratio of 1:1. The mixture was kept at 40 °C for 19 h in dichloromethane. The NMR analysis revealed the presence of a mixture of four components. The $HB(C_6F_5)_2$ hydroboration product **12** was the major component (64%) followed by its $HB(C_6F_5)_2$ amine adduct **13** (23%), and then there was the simple Lewis pair **11** as a very minor component (3%) plus unreacted starting material **10** (ca. 10%, as judged from the ^{31}P NMR spectrum of the mixture). The major product **12** shows a ^{31}P NMR resonance at δ -24.3 and a broad ^{11}B NMR signal at δ 75. Its ^{19}F NMR spectrum features a set of *o,m,p*-C_6F_5 fluorine signals with a large $\Delta\delta^{19}F_{m,p}$ chemical shift separation of 11 ppm which is typical for a Lewis acidic planar-tricoordinate R-$B(C_6F_5)_2$ situation. [18] The minor component **13** shows two sets of ^{19}F NMR signals as expected, one with a large $\Delta\delta^{19}F_{m,p}$ chemical shift separation (11.5 ppm, tricoordinate -$B(C_6F_5)_2$) and one with a small one [$\Delta\delta^{19}F_{m,p}$ = 6.5 ppm, N-coordinated $HB(C_6F_5)_2$]. The latter one shows a ^{11}B NMR resonance in the tetracoordinate boron range at δ -7.6 (for further details concerning the characterization of the compounds **12** and **13** see the Supporting Information).

Compound **12** turned out to be difficult to isolate pure. Since we wanted to use it for metal-free dihydrogen splitting purposes anyway, we decided to directly react it with dihydrogen from the mixture. For this purpose we pre-reacted the phosphane **10** with one molar equivalent of $HB(C_6F_5)_2$ (r.t., 20 h, in dichloromethane) and then exposed the resulting mixture of products to dihydrogen (2 bar H_2 pressure, r.t., 18 h). Layering with heptane (14 d) eventually gave the crystalline product **14** which we isolated in 64% yield (see Scheme 5).

Single crystals of **14** suited for the X-ray crystal structure analysis were obtained by slow solvent evaporation from a solution in dichloromethane. The molecular structure shows the pyrrolidine-annulated bicyclo[2.2.1]heptane framework. The norbornane carbon atom C2 bears the bulky -$P(H)Mes_2$ phosphonium moiety *endo*-attached; the -$B(H)(C_6F_5)_2$ borate type group is, consequently, found in the *exo*-position at carbon atom C3 (see Figure 6). Both the phosphorus atom P1 ($\sum P1^{CCC}$ = 344.1°) and the boron atom B1 ($\sum B1^{CCC}$ = 336.9°) show distorted pseudotetrahedral coordination geometries. We note that the amine nitrogen atom N1 shows a non-planar geometry ($\sum N1^{CCC}$ = 348.9°), as expected. The phenyl substituent is attached at N1 (C8-N1-C11-C16 = 19.0(6)°, the angle between the C8-N1-C9 and phenyl planes is ca. 30°).

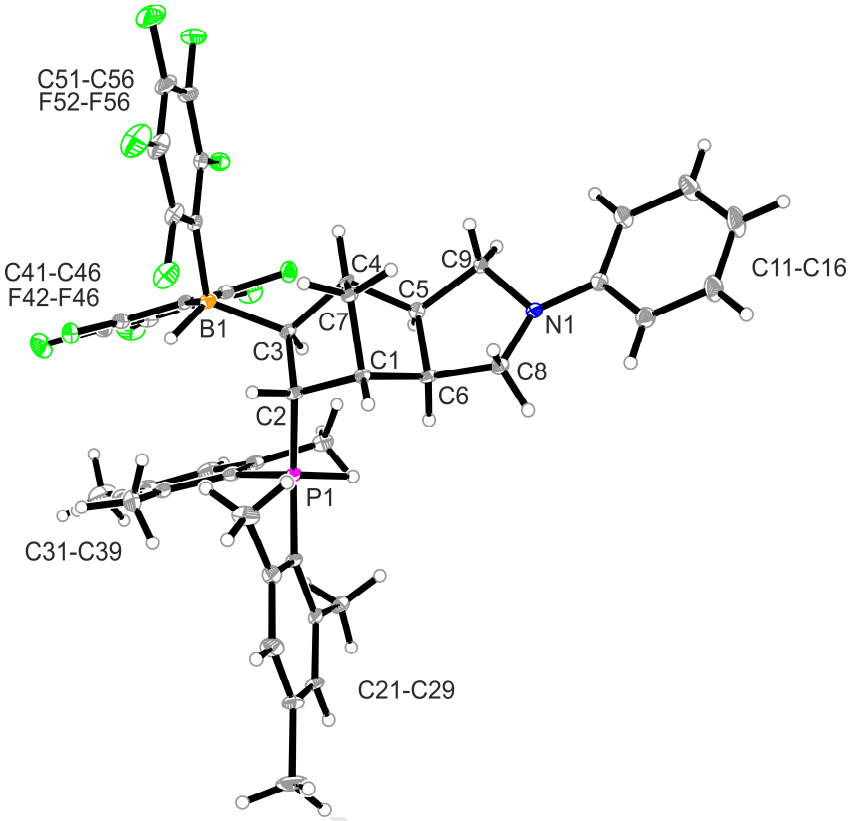
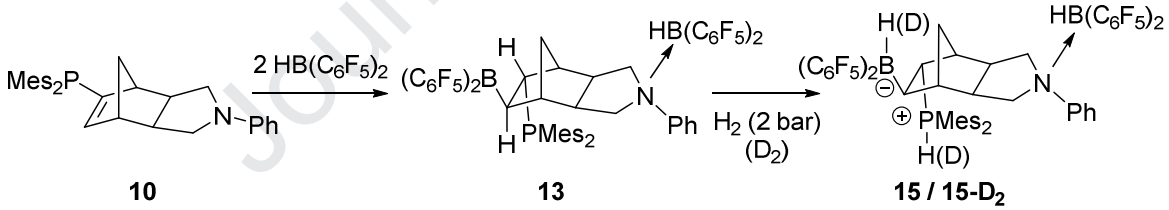


Figure 6. Molecular structure of the dihydrogen splitting product **14**. Thermal ellipsoids are set at 15% probability. Selected bond lengths (Å) and angles (°): P1-C2 = 1.808(4), P1-C21 = 1.815(4), P1-C31 = 1.806(4), B1-C3 = 1.664(6), B1-C41 = 1.653(6), B1-C51 = 1.645(6), C2-C3 = 1.571(5), N1-C11 = 1.386(6), C2-P1-C21 = 119.9(2), C31-P1-C2 = 113.6(2), C31-P1-C21 = 110.6(2), C41-B1-C3 = 113.0(3), C51-B1-C3 = 111.8(3), C51-B1-C41 = 112.1(3), C8-N1-C11-C16 = 19.0(6), C6-C1-C2-P1 = 57.1(4), B1-C3-C4-C5 = -159.5(3).

In solution (CD_2Cl_2) compound **14** shows the typical ^{1}H NMR phosphonium [P]-H resonance at δ 7.31with a large $^{1}J_{PH}$ = 468 Hz coupling constant [$^{3}J_{HH}$ = 7.5 Hz, ^{31}P NMR signal at δ -9.1]. [19] We did not observe the [^{11}B]-H signal in the ^{1}H NMR spectrum, but in the ^{11}B NMR spectrum compound **14** featured a doublet at δ -19.6 with a typical $^{1}J_{BH}$ = 76 Hz coupling constant. [20] In addition compound **14** shows the typical NMR resonances of the tricyclic framework and the substituents at nitrogen, phosphorus and boron (e.g. ^{19}F NMR: two separate sets of *o*,*p*,*m*-C_6F_5 signals of the pair of diastereotopic C_6F_5 groups on boron with typically small borate type chemical shift differences of $\Delta\delta^{19}F_{m,p}$ = 2.4 / 2.7 ppm; see the Supporting Information about further details of the spectroscopic characterization of compound **14**).

We have also exposed the $HB(C_6F_5)_2$ hydroboration mixture (see Scheme 5) to dideuterium under analogous conditions. Workup gave the corresponding zwitterionic D-phosphonium/deuterio-borate product **14-D_2**, which we isolated in 24% as a colorless solid. Its ^{2}H NMR spectrum showed the broad [P]-D doublet at δ 7.32 with a $^1J_{PD}$ coupling constant of 72 Hz and a broad unstructured [B]-D signal at δ 2.6 (the spectrum is depicted in the Supporting Information).

The reaction of the pyrrolidine-annulated dimesitylphosphino-norbornene **10** with two molar equivalents of Piers' borane $[HB(C_6F_5)_2]$ proceeded more selectively. In an experiment under direct NMR control without workup we obtained compound **13** as by far the major product. It shows a pair of ^{11}B NMR signals [δ 75 (broad, tricoordinate $(C_6F_5)_2$B-Nor; δ -7.6 (N-B(H)$(C_6F_5)_2$)] and a ^{31}P NMR feature at δ -25.9 (for further details see the Supporting Information). Compound **13** is rather sensitive and we could not isolate it in pure form. Therefore, we only generated it *in situ* on a preparative scale and exposed it directly to a dihydrogen atmosphere (2 bar, r.t.). After a few minutes reaction time at -80 °C colorless crystals of compound **15** began to form (see Scheme 6). The crystalline N-B(H)$(C_6F_5)_2$ / phosphonium / hydridoborate product was isolated in 59% yield. It was characterized by spectroscopy and by X-ray diffraction.



Scheme 6. Formation of the FLP derivatives **13** and **15.**

The X-ray crystal structure analysis of **15** shows the $HB(C_6F_5)_2$ equivalent that is attached at the pyrrolidine nitrogen atom N1. It is oriented toward the *exo*-face of the adjacent norbornane core framework. That has the -B(H)$(C_6F_5)_2$ unit bonded at the distal end at carbon atom C3 in the *exo*-position and the -P(H)Mes_2 unit at C2 in the *endo*-orientation (see Figure 7).

The ^{1}H NMR spectrum of the zwitterion **15** shows the typical $[P]^+$-H signal at δ 7.05 with the typical $^1J_{PH}$ = 477 Hz coupling constant (^{31}P: δ -6.9). The H-$[B]^-$ unit shows a doublet in the ^{11}B NMR spectrum at δ -19.8 with $^1J_{BH}$ = 81 Hz. The analogous reaction of the in situ generated

compound **13** with D_2 gave the respective product **15-D$_2$** (see the Supporting Information for details of the characterization of compounds **15** and **15-D$_2$**).

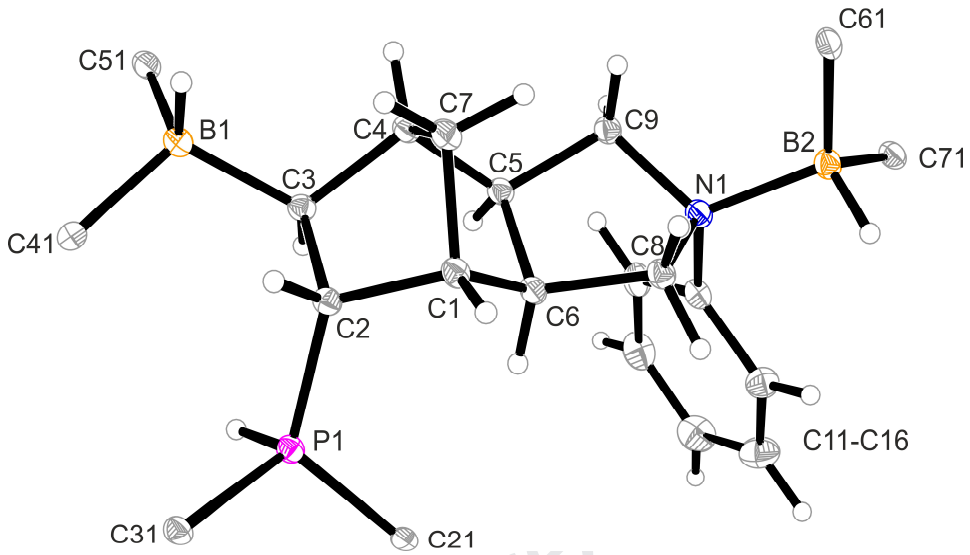
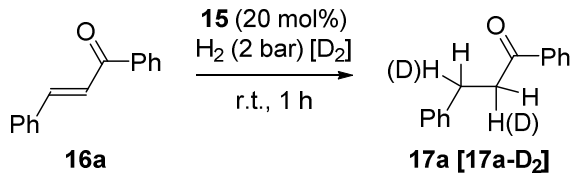


Figure 7. A view of the molecular structure of the phosphonium / hydridoborate compound **15.** Thermal ellipsoids are set at 15% probability. Only the *ipso*-carbon atoms of the C_6F_5 substituents on boron and the mesityl groups at phosphorus are shown for clarity. Selected bond lengths (Å) and angles (°): P1-C2 = 1.825(3), P1-C21 = 1.812(3), P1-C31 = 1.808(3), C3-B1 = 1.640(4), B1-C41 = 1.646(4), B1-C51 = 1.647(3), C2-C3 = 1.589(4), N1-B2 = 1.672(4), N1-C11 = 1.497(4), C21-P1-C2 = 118.7(2), C31-P1-C2 = 114.9(2), C31-P1-C21 = 112.1(2), C3-B1-C41 = 110.7(2), C3-B1-C51 = 114.6(2), C41-B1-C51 = 108.0(2), C6-C1-C2-P1 = -64.9(3), B1-C3-C4-C5 = 160.8(2).

2.3 Catalytic hydrogenation

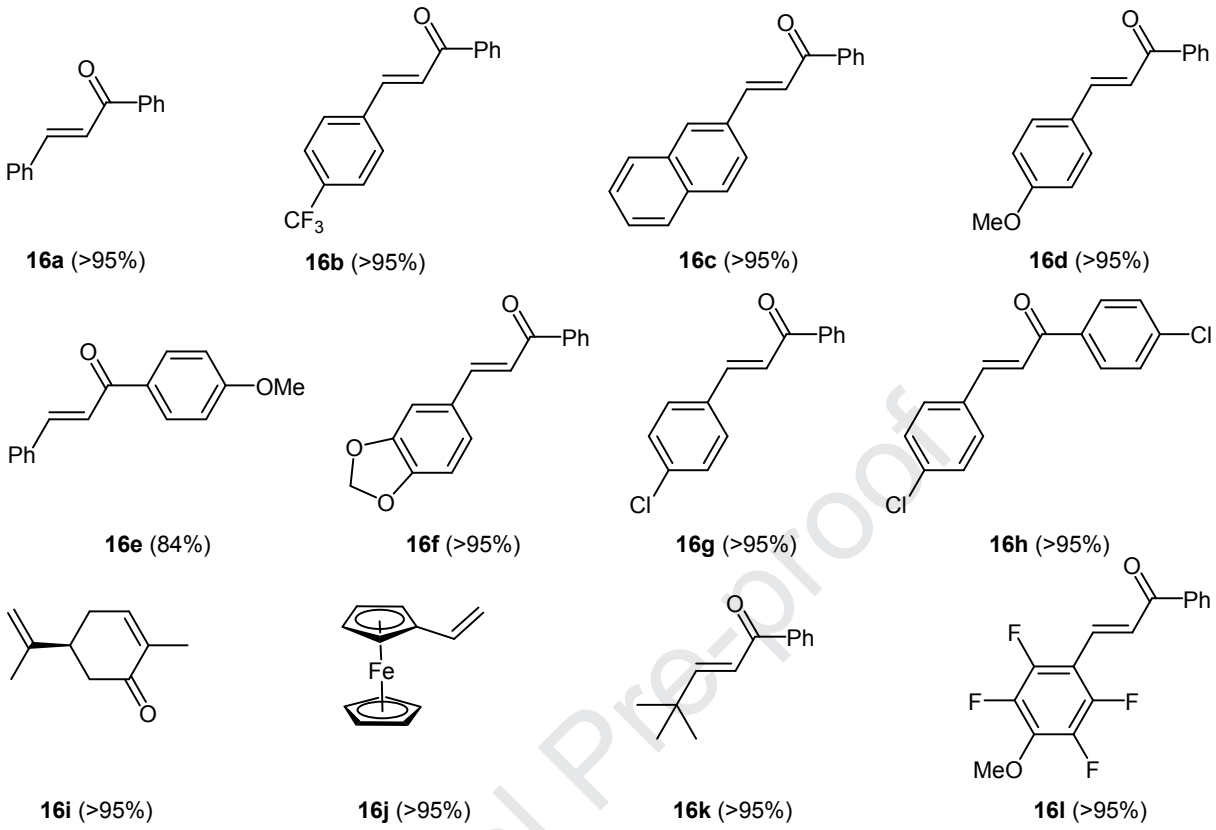
We tried to employ both the zwitterionic H_2 activation products **14** and **15** as catalysts for the hydrogenation of the typical "FLP-hydrogenation substrates" *N-tert*-butyl acetophenone imine and the enamine pyrrolidinocyclohexene. [5,6a] However, both were not hydrogenated under the typical conditions in the presence of 10 mol% of **14** or **15**. In contrast, the conjugated enone chalcone (**16a**) was hydrogenated to the respective saturated ketone **17a** at r.t. (2 bar, 1 h) with 10-20 mol% of the catalyst **15** (see Scheme 7, see the Supporting Information for details). The respective reaction with D_2 gave the product **17a-D$_2$**.



16a **17a [17a-D_2]**

Scheme 7. Catalytic hydrogenation of chalcone (**16a**) using catalyst **15**.

A close inspection of this reaction revealed that it exhibited an unexpected effect. We observed that adding an excess of chalcone (**16a**) to the pale yellow solution of compound **15** resulted in the formation of a deep red solution within a period of ca. 30 min. Application of dihydrogen then resulted in a hydrogenation reaction to give **17**. We also treated compound **14** with chalcone but found no color change. Addition of $HB(C_6F_5)_2$ resulted in the formation of a red solution; subsequent exposure to H_2 then resulted in hydrogenation and formation of **17**. We carried out a number of control experiments (see the Supporting Information for details) but could not elucidate the very nature of the actual hydrogenation catalyst in these systems. In these experiments we found that $B(C_6F_5)_3$ served as an activating co-catalyst in these enone hydrogenation reactions, even better than the $HB(C_6F_5)_2$ originally present. Therefore, we carried out the catalytic hydrogenations of a variety of enones with 20 mol% of the catalyst **15** combined with 5 mol% of the co-catalyst $B(C_6F_5)_3$ [r.t., 2 bar of dihydrogen]. In all cases a pre-activation period of the respective catalyst/co-catalyst/substrate mixture of 30 min in the absence of dihydrogen was allowed. The reactions were performed in C_6D_6 and the progress of the catalytic hydrogenations was directly followed by ^1H NMR spectroscopy. Most catalytic hydrogenation reactions of the substrates **16a-l** shown in Scheme 8 proceeded rather cleanly and they mostly gave a complete conversion to the respective hydrogenation products **17a-l** after some time (some with minor impurities), but the reaction rates varied markedly between substrates. This is shown in Table 1 which gives e.g. the times needed to achieve 50% conversion under these typical catalytic hydrogenation processes.



Scheme 8. Substrates employed in the hydrogenation reaction with the pre-activated FLP catalyst derived from **15**/$B(C_6F_5)_3$. Achieved conversions are given in parentheses as determined by ^{1}H-NMR spectroscopy.

The results listed in Table 1 show that the **15**/$B(C_6F_5)_3$ derived system is one of the few presently known metal-free FLP catalysts for the hydrogenation of these α,β-unsaturated ketone substrates. [8,9] The overall observations made are consistent with the assumption that hydride transfer from the active catalyst is probably the decisive step in these processes. Consequently, there are electronic features in addition to some steric constraints that become apparent from the data compiled in Table 1. Chalcone itself and chalcones that bear electron withdrawing substituents at their aryl groups are the most active substrates. Electron donating substituents at the aryl groups lead to reduced hydrogenation rates, as is the presence of the electron-donating, bulky ^{t}Bu-substituent at the C=C double bond. (+)-Carvone had been the first enone that was hydrogenated at an FLP catalyst, [8] it is also reduced at our system with moderate reaction rates.

Vinylferrocene is a reactive substrate that shows a surprisingly high reactivity under our conditions. [21]

Table 1. Reaction times necessary for achieving a) 50% and b) 80% product conversion for the catalytic hydrogenation reactions of the chalcones and related $Ar^1CH=CHCOAr^2$ substrates **16a-k** at the **15** (20 mol%) / $B(C_6F_5)_3$ (5 mol%) catalyst at r.t. (2 bar H_2, in C_6D_6 solution).[a]

	Ar^1	**Ar^2**	**t [min] 50%**	**t [min] 80%**	**complete[c] [min]**
16a	Ph	Ph	40	80	n. d.[d]
16g	ClC_6H_4	Ph	30	83[b]	180
16c	Napht	Ph	40	87[b]	115
16b	$F_3CC_6H_4$	Ph	47[b]	110	205
16h	ClC_6H_4	ClC_6H_4	30	145[b]	195
16f	$(CH_2O_2)C_6H_3$	Ph	190	304[b]	1210
16d	$H_3COC_6H_4$	Ph	195	270	370
16e	Ph	$H_3COC_6H_4$	1340	2920	n. d.
16k	^{t}Bu	Ph	1190	1675	2630
16j	Vinylferrocene		85[b]	155	215
16i	(+)-Carvone		210	766[b]	1200

a: After a catalyst pre-formation time of 30 min in the absence of H_2; conversion determined by ^{1}H NMR spectroscopy, b: interpolated, c: time after which complete conversion was confirmed, d: not determined

3. Conclusions

We had previously shown that the norbornane based compound **4** is a very active P/B frustrated Lewis pair. It undergoes interesting FLP reactions, among them some unusual reactions with carbon monoxide, and it is an active dihydrogen splitting reagent. Unfortunately, the system **4** is not convenient to synthesize, so we looked for an alternative. We actually could prepare the direct starting material for **4**, namely the phosphanyl norbornene **3** by the Diels-Alder route as planned, but only in a very low yield. After some search a solution seemed to be the use of the

easily available Diels-Alder adduct of the phosphanyl cyclopentadienes **2** with N-phenylphthalimide. Its subsequent conversion eventually resulted in the formation of the active FLP systems **12** and **13** and their dihydrogen splitting products **14** and **15**. Our study revealed that the reactivity of these systems was quite different from that of **4** and its dihydrogen splitting product.

We used the new systems for catalytic hydrogenation of chalcone derivatives. At the beginning of our study we found a puzzlingly poor reproducibility in our FLP induced hydrogenation reactions. Conversions seemed to vary substantially without apparent reason. This resulted in the observation of the appearance of some deeply colored as yet unknown species during the pre-generation phase of the actual hydrogenation catalyst in the presence of the respective enone substrate but in the absence of additional dihydrogen. For most systems a 30 min pre-reaction time was optimal; shorter or longer times resulted in less active catalysts. We tried hard but were not able to elucidate the very nature of the active catalyst systems so far, and also the specific role of the $B(C_6F_5)_3$ co-catalyst remained in the dark beyond speculation. We found that related boranes $[HB(C_6F_5)_2$ or $EtB(C_6F_5)_2$ [10b] could also serve as co-catalysts, but markedly less effectively. It should be noted that except (+)-carvone it is the mentioned family of chalcone derivatives and a few selected additional compounds that seem to play a specific role as substrates in the FLP reduction of conjugated enones to their saturated ketone derivatives. That was not *a priori* easy to interpret in view of an assumed general hydrido borate attack at the enone electrophile, but our observations of a possible participation of these enones in the actual generation of the active catalyst species might eventually direct us toward a future understanding of the actual catalyst composition in these processes and, consequently, in a design of general active FLP catalysts for the hydrogenation of α, β-unsaturated carbonyl compounds.

4. Experimental

4.1 General

All syntheses involving air- and moisture-sensitive compounds were carried out with standard Schlenk-type glassware or in a glove box under an atmosphere of argon. Solvents were dried and stored under argon. NMR scale gas reactions were carried out in J-Young NMR tubes. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian*

2100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (*TA Instruments*). $B(C_6F_5)_3$ was obtained from Boulder Scientific Co.

4.2 Syntheses

See the Supporting Information for spectroscopic data of the newly prepared compounds and the experimental details on compounds **3** and **8**.

*4.2.1 Synthesis of compound **6*** [13]

A solution of dimesitylchlorophosphane (3.126 g, 10.26 mmol) in THF (50 mL), was cooled to -78 °C and subsequently a solution of cyclopentadienyl lithium (0.739 g, 10.26 mmol) in THF (50 mL) was added dropwise over a period of 2 h. The resulting pale yellow solution was allowed to warm to room temperature and the solvent was removed in vacuo. After storage of the residue at -30 °C overnight, it was suspended in toluene (50 mL) and filtered through a plug of Celite. The obtained yellow solution was cooled to -78 °C and n-butyl lithium (1.6 M in hexanes, 6.5 mL, 10.4 mmol) was added dropwise. After stirring for 10 min at -78 °C the reaction mixture was allowed to warm to room temperature, leading to the precipitation of a yellow solid. The suspension was concentrated in vacuo to approximately 10 mL, pentane (50 mL) was added and the suspension cooled to -30 °C. After 6 d the yellow precipitate was collected on a glass frit, washed with pentane (3 x 10 mL) and dried in vacuo. Compound **6** (2.016 g, 5.92 mmol, 60%) was obtained as a pale yellow solid. Anal. Calc. for $C_{23}H_{26}LiP$: C, 81.16; H, 7.70. Found: C, 80.76; H, 7.63

*4.2.2 Synthesis of compound **5***.

A solution of compound **6** (0.657 g, 1.93 mmol) in THF (20 mL) was cooled to -94 °C and HCl (2 M in Et_2O, 1.0 mL, 2.0 mmol) was added in one portion. After stirring for 5 min at -94 °C the reaction mixture was allowed to warm to room temperature and the solvent was removed *in vacuo*. The residue was then re-suspended and dried again in pentane (20 mL) and then dichloromethane (20 mL), respectively. After suspending in pentane (20 mL) it was filtered through a plug of Celite and the solvent removed *in vacuo*. Compound **5** (0.520 g, 1.55 mmol, 80%) was obtained as a yellow powder, which contained 13% (^{31}P-NMR) of a side product. Anal. Calc. for $C_{23}H_{27}P$: C, 82.60; H, 8.14. Found: C, 82.24; H, 8.20.

*4.2.3 Synthesis of compound **7**.*

Compound **5** (0.3004 g, 0.90 mmol) was dissolved in toluene (5 mL) and dimethyl maleate (0.155 g, 1.08 mmol) was added. After heating to 100 °C for 23 h the solvent was removed *in vacuo* and a brown oily residue was obtained. NMR-analysis of the crude product suggested full conversion. The crude product was purified by column chromatography (silica; 30 x 2.5 cm, *n*-pentane : ethylacetate = 5 : 1) and compound **7** (0.173 g, 0.36 mmol, 40%; R_f = 0.79) was obtained as a colorless solid. Anal. Calc. for $C_{29}H_{35}O_4P$: C, 72.78; H, 7.37. Found: C, 72.70; H, 7.11.

*4.2.4 Synthesis of compound **9**.*

N-phenylmaleimide (0.1033 g, 0.60 mmol) was added to a solution of compound **5** (0.1998 g, 0.60 mmol) in toluene (2 mL) and the yellow solution kept at 50 °C for 18 h. After removal of the solvent *in vacuo* the residue was re-dissolved in dichloromethane (2 mL) and pentane (5 mL) and the solvent removed again. The resulting yellow solid was dissolved in toluene, pentane was added and the solution cooled to -30 °C overnight. The formed colorless crystals were separated from the solution, washed with pentane and dried. Compound **9** (0.166 g, 0.33 mmol, 54%) was obtained as a colorless crystalline solid. Elemental analysis: Calc. for $C_{33}H_{34}NO_2P$: C, 78.08; H, 6.75; N, 2.76. Found: C, 77.86; H, 6.61; N, 2.83.

*4.2.5 Synthesis of compound **10**.*

Lithium aluminum hydride (0.243 g, 6.4 mmol) was added to compound **9** (0.325 g, 0.64 mmol) in THF (5 mL) and the grey suspension stirred at room temperature overnight. After addition of water (3 mL) the solvent was removed *in vacuo* and the residue suspended in dichloromethane (20 mL). The solid was filtered off and the solvent of the supernatant solution was removed *in vacuo*. NMR-analysis of the brown residue suggested formation of a side product. Additional lithium aluminum hydride (0.093 g, 2.5 mmol) was added and suspended in THF (10 mL). After heating to 60 °C for 25 h water (1 mL) was added and all volatiles removed *in vacuo*. The residue was then suspended in dichloromethane (50 mL) and dried over sodium sulfate. After filtration and removal of the solvent, compound **10** (0.159 g, 0.33 mmol, 51%) was obtained as a pale yellow solid. Anal. Calc. for $C_{33}H_{38}NP$: C, 82.64; H, 7.99; N, 2.92. Found: C, 81.56; H, 8.24; N, 2.81.

4.2.6 In situ *generation of compound **13**.*

Compound **10** (0.0240 g, 0.05 mmol) was dissolved in CD_2Cl_2 (~0.7 mL) and the solution added to $HB(C_6F_5)_2$ (0.0346 g, 0.10 mmol) which gave a bright yellow solution. Compound **13** was characterized by NMR spectroscopy (see the Supporting Information).

*4.2.7 Synthesis of compound **14**.*

In a J-Young NMR tube compound **10** (0.048 g, 0.10 mmol) and $HB(C_6F_5)_2$ (0.0346 g, 0.10 mmol) were dissolved in CD_2Cl_2 (0.7 mL) and the yellow solution kept at room temperature for 20 h. After NMR measurements, the solution was cooled to -78 °C and the atmosphere removed. Dihydrogen (2 bar) was applied and the sample warmed to room temperature, leading to a slow fading of the yellow color. The sample was shaken at room temperature for 18 h and then layered with approximately the same volume of *n*-heptane. After 14 d the colorless, microcrystalline solid was collected by filtration and washed with *n*-pentane. Compound **14** (0.053 g, 0.064 mmol, 64%) was obtained as a colorless solid. Anal. Calc. for $C_{45}H_{41}BF_{10}NP$: C, 65.31; H, 4.99; N, 1.69. Found: C, 62.90; H, 4.57; N, 1.64.

*4.2.8 Synthesis of compound **15**.*

Compound **10** (0.0480 g, 0.10 mmol) and $HB(C_6F_5)_2$ (0.0692 g, 0.20 mmol) were dissolved in CD_2Cl_2 (~0.7 mL) and the yellow solution cooled to -80 °C. After removal of the atmosphere, dihydrogen (2 bar) was applied. After several minutes colorless crystals formed, which were suitable for X-ray crystal structure analysis. The crystals were collected and washed with pentane. Compound **15** (0.070 g, 0.060 mmol, 59%) was obtained as colorless crystals.

4.3 Catalytic hydrogenation

General procedure: In a J-Young NMR tube substrate (0.10 mmol), catalyst precursor **15** (23.5 mg, 0.02 mmol) and $B(C_6F_5)_3$ (2.6 mg, 0.005 mmol) were dissolved in C_6D_6 (0.7 mL). After 30 min the atmosphere was removed, dihydrogen (2 bar) applied and the reaction monitored by ^{1}H-NMR spectroscopy. Conversion was determined from the ^{1}H-NMR spectra. (see the Supporting Information for control experiments and spectroscopic data of hydrogenation products **17a-l**)

Acknowledgement

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Supporting Information

Contains experimental data and details about the characterization of the compounds by spectroscopy and X-ray crystal structure analysis.

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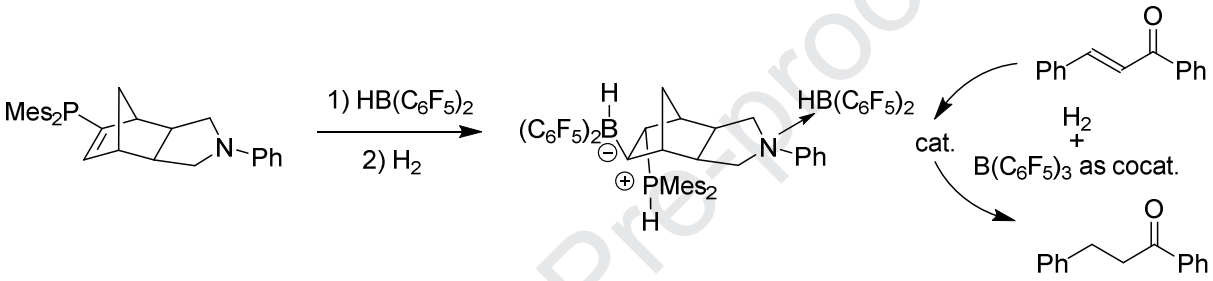
TOC



The [4+2]-cycloaddition reaction of the (dimesitylphosphino)cyclopentadienes **5a,b** with *N*-phenylmaleimide gave the norbornene derivative **9**. Its reduction with $LiAlH_4$ produced the *N*-phenylpyrrolidino-annulated system **10**. Treatment with Piers' borane gave the respective P/B FLP **12** as the major product, which cleaved dihydrogen under mild conditions to yield the phosphonium/hydrido borate product **14**. Reaction of the phosphino-norbornene **10** with two molar equiv. of Piers' borane [$HB(C_6F_5)_2$] followed by exposure to dihydrogen eventually gave the $HB(C_6F_5)_2$ adduct **15**. This served as a catalyst for the hydrogenation of a series of chalcone derivatives. The system requires a pre-activation period before becoming active for the conjugated enone hydrogenation.