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P/B Ketene Adduct Formation from Acyl Chlorides at a Vicinal Phosphane/Borane Frustrated Lewis Pair

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Abstract: The intramolecular frustrated phosphane/borane Lewis pair $Mes_2PCH_2CH_2B(C_6F_5)_2$ (**3**) reacts with acetyl chloride to give a 1:1 mixture of the FLP-ketene adduct, **6a**, and the FLP-HCl addition product, **7**. Similarly, the acyl chlorides phenylacetyl chloride and isobutyryl chloride react with **3** to give the respective substituted FLP ketene adducts, **6b** and **6c**, with HCl elimination. A series of aroyl chlorides reacts with **3** by formation of the respective aroyl-phosphonium/chloroborate zwitterions, **11a–d**. The hetero-aromatic furoyl chloride reacts with **3** in a more complicated, but mechanistically probably closely related pathway, to form the 2:1 reaction product, **14**. Most of the products were characterized by X-ray diffraction.

Keywords: acyl chloride · boranes · frustrated Lewis pair · ketene · phosphanes

1 Introduction

Ketenes are very reactive organic carbonyl compounds.[1] Therefore, some of their syntheses have required rather extreme conditions. The parent ketene $H_2C{=}C{=}O$, a poisonous gas, can be obtained, e.g., by thermolytic cleavage (500 °C) of acetic anhydride.[2] A common way of generating the parent ketene is methane elimination from acetone in a flow system at very high temperatures (see Scheme 1).[3] Substituted ketenes can be obtained by a variety of methods, among them the dehydrohalogenation of suitably substituted acyl halides.[4]

We have now found that stable ketene adducts are readily formed upon treatment of suitable acyl chlorides with the vicinal intramolecular P/B frustrated Lewis pair (FLP) $Mes_2PCH_2CH_2B(C_6F_5)_2$ (**3**,[5] see Scheme 2).[6,7] In this reaction, the P/B FLP serves two functions: it acts as a favourable trapping agent of the HCl formed (and probably facilitates its abstraction kinetically), and at the same time, the FLP framework supports the formation of the ketene moiety to give a stable P/B FLP ketene addition product. In fact, this adduct formation is so favourable that it makes the described ketene-forming reaction strictly stoichiometric under the applied conditions. In this paper, we shall describe the formation and characterization of the parent $H_2C{=}C{=}O$/P/B FLP adduct, and in addition, those of a pair of substituted analogues. We will also present some experimental evidence that might provide a mechanistic rationalization of the observed reaction pathways.

$$CH_3COCH_3 \xrightarrow[-CH_4]{\Delta\Delta} H_2C{=}C{=}O$$

$$R'_2HCCOCl \xrightarrow[-HCl]{R_3N} R'_2C{=}C{=}O$$

Scheme 1. Ketene generating reactions.

2 Results and Discussion

2.1 Ketene Adduct Formation

For this study, we generated the ethylene-bridged frustrated phosphane/borane Lewis pair, **3**, *in situ* by hydroboration of dimesitylvinylphosphane (**1**)[5] with Piers' borane $[HB(C_6F_5)_2]$ (**2**).[8] The reaction was complete within ca. 10 min at r.t. in dichloromethane. Acetylchloride (**4a**) (0.5 molar equivalents) was then added to the

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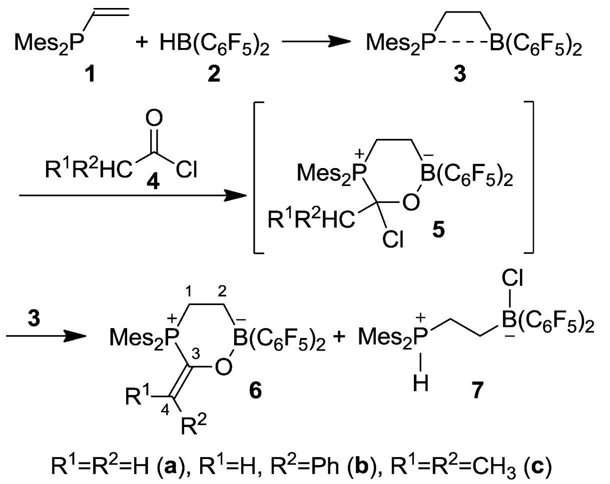


Scheme 2. FLP-ketene adduct formation.

pale yellow solution, which turned colorless immediately (see Scheme 2). Compound **6a** was isolated by column chromatography and crystallization. It was identified as the formal addition product of the parent ketene $H_2C=C=O$ to the FLP **3** by an X-ray crystal structure analysis, by elemental analysis (C, H) and by multinuclear NMR spectroscopy (see Tables 1 and 2).

Table 1. Selected structural parameters of the FLP ketene adducts **6a–c**.[a]

Compound	6a	6b	6c
C3–C4	1.329(3)	1.344(3)	1.341(3)
C3–O1	1.334(3)	1.342(2)	1.357(3)
C3–P1	1.828(2)	1.826(2)	1.826(2)
O1–B1	1.512(3)	1.517(3)	1.518(3)
B1–C2	1.624(3)	1.610(3)	1.616(3)
C1–C2	1.540(3)	1.540(3)	1.533(3)
C1–P1	1.811(2)	1.814(2)	1.834(2)
O1–C3–P1	119.2(2)	119.1(2)	111.3(2)
O1–C3–C4	122.2(2)	123.6(2)	121.3(2)
P1–C3–C4	118.6(2)	117.3(2)	127.2(2)
P1–C3–O1–B1	−20.4(3)	25.7(3)	47.2(3)
P1–C1–C2–B1	70.2(2)	−71.1(2)	46.5(2)

[a] Bond lengths in Å; angles in degrees.

In the crystal, compound **6a** features a non-planar six-membered heterocyclic framework in a close-to-half-chair conformation.[9] The P and B heteroatoms are arranged in 1,4-position. The ring carbon atom C3 is part of the exocyclic C=C double bond of the incorporated ketene moiety. The C3–C4 bond is in the C=C double bond length range; the adjacent C3–O1 bond is long; it is consistent with a C–O single bond (see Figure 1 and Table 1).

In solution, compound **6a** shows the typical NMR signals of the phosphonium and borate units inside the ring. The homotopic pair of C_6F_5 groups at boron shows a small $^{19}F_{m,p}$ chemical shift difference of 4.1 ppm, which is typical of a four-coordinated boron coordination situation.[10] The exocyclic $=CH_2$ functional group shows the characteristic $^1H/^{13}C$ NMR features (see Table 2) and we have monitored the signals of the bridging $–CH_2–CH_2–$ unit derived from the P/B FLP backbone of the six-membered heterocyclic framework.

Table 2. Selected NMR data of the FLP ketene adducts **6a–c**.[a]

Compound	6a	6b	6c
$\delta^1H(PCH_2)$	2.99	2.98	2.71
$\delta^1H(BCH_2)$	1.40	1.48	1.54
$\delta^1H(R^2)$	5.35	–	–
$^3J(P,H)$	38.9	–	–
$\delta^1H(R^1)$	4.73	5.83	–
$^3J(P,H)$	11.0	12.8	–
$\delta^{13}C(C1)$	27.4	26.6	28.8
$^1J(P,C)$	46.1	47.2	53.3
$\delta^{13}C(C2)$	15.2	15.0	15.7
$\delta^{13}C(C3)$	148.4	140.3	132.1
$^1J(P,C)$	70.1	74.5	86.4
$\delta^{13}C(C4)$	110.9	123.2	136.5
$^2J(P,C)$	36.8	35.5	33.3
$\delta^{31}P$	4.2	6.6	0.8
$\delta^{11}B$	0.0	−0.3	−0.2

[a] Chemical shifts in ppm (δ-scale); *J* in Hz; NMR spectra in CD_2Cl_2, 299 K.

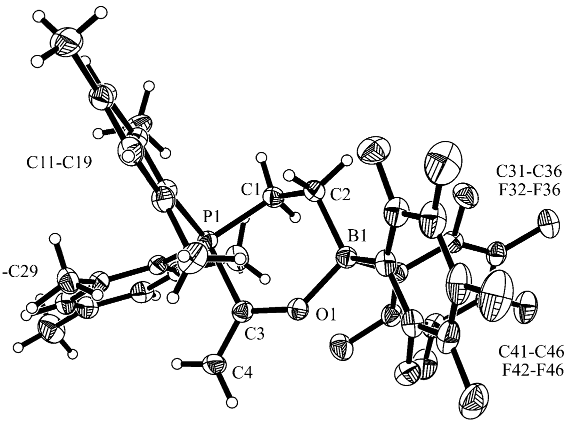


Figure 1. Molecular structure of the FLP ketene addition product **6a** (thermal ellipsoids are shown with 30 % probability).

We reacted the *in situ*-generated P/B FLP, **3**, in a similar way with phenylacetyl chloride (**4b**). The reaction consumed 0.5 molar equivalents of the acid chloride to give a mixture of the products **6b** and **7**. The HCl addition product, **7**, to the FLP, **3**, was separated from the ketene addition product by chromatography and the product **6b** was isolated in ca. 46 % (out of a possible 50 %) yield. The solid material contained ca. 0.5 equivalents of dichloromethane. Monitoring of the reaction by NMR revealed the formation of two P/B containing compounds in a ca. 1 : 1 ratio (for details, see the supporting information); namely, compound **7**, the known HCl adduct to the FLP **3**,[11] and the FLP ketene addition product **6b** (see Scheme 2).

The X-ray crystal structure analysis showed the typical six-membered heterocyclic structure (see Figure 2 and Table 1). It has the =CHPh group connected to the ring carbon atom C3. In the crystal, we have found the *E*-isomer of the tri-substituted exocyclic carbon-carbon double bond.

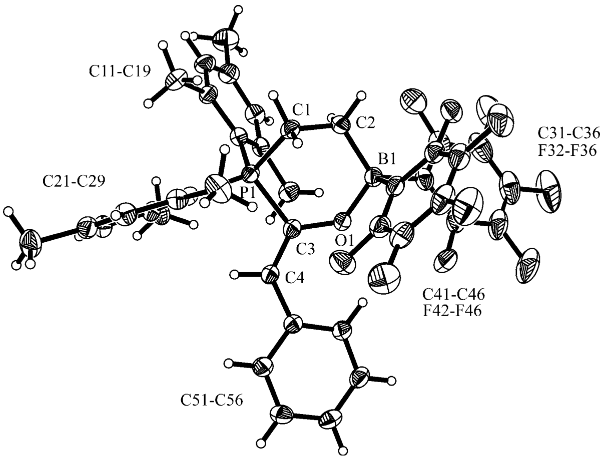


Figure 2. A view of the molecular structure of compound **6b** (thermal ellipsoids are shown with 30 % probability).

In solution, we have observed only a single isomer of compound **6b** by NMR spectroscopy. It shows a ^{1}H NMR doublet of the olefinic *Z*–4–H proton, with a $^{3}J_{PH}$ coupling constant of 12.8 Hz. This is typical of a *cis*-arrangement (cf. compound **6a** showed the $=CH_2$ ^{1}H NMR signals with $^{3}J_{PH}$ coupling constants of 11.0 Hz (vicinal-*cis*) and 38.9 Hz (vicinal-*trans*), respectively). For additional data, see Table 2 and the supporting information.

We have also reacted the P/B FLP, **3**, with isobutyric acid chloride (**4c**). Even in this slightly more hindered case, α-deprotonation by a second equivalent of the FLP, **3**, marks the favoured reaction path, and we isolated the dimethylketene adduct, **6c**, in 43 % yield, after chromatography. Figure 3 shows a view of the molecular structure of compound **6c** in the crystal. Structural data and conformational features are similar to those of its congeners, **6a** and **6b** (see Table 1), only that the system bears the $=CMe_2$ group attached at ring carbon atom C3. The product **6c** was also characterized by NMR spectroscopy (see Table 2 and the supporting information for details).

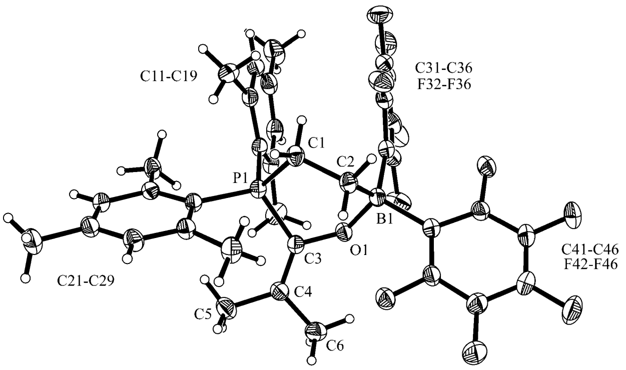
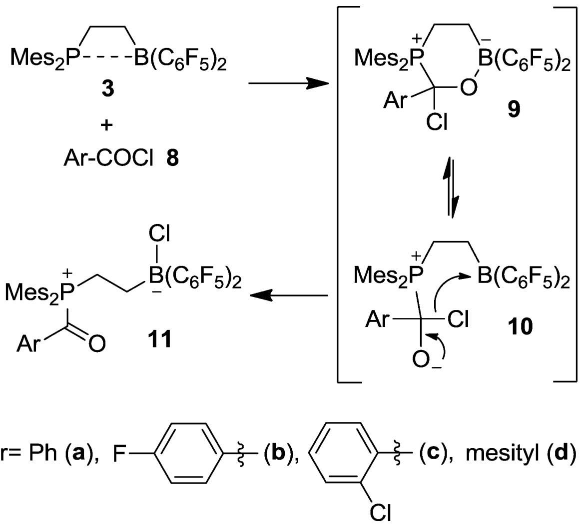


Figure 3. Molecular structure of compound **6c** (thermal ellipsoids are shown with 30 % probability).

2.2 FLP Reactions of Aroyl Chlorides

We have not observed any intermediate on the way to the FLP ketene adducts, **6**. Therefore, we have tried to learn about related reaction products derived from the P/B FLP, **3**, and acyl chlorides, without abstractable α-hydrogen atoms. In the cases studied, this resulted mostly in the formation of stable acyl phosphonium/chloroborate products (see Scheme 3). Only in one case (see below), did we observe the formation of a different, rather unusual product.



Scheme 3. Generation of stable acyl phosphonium/chloroborate compounds, **11a–d**.

The reaction of the *in situ*-generated P/B FLP, **3**, with benzoyl chloride (**8a**) (1.2 molar equivalents) was carried out in pentane at r.t. Soon after the aroyl chloride addition, the product, **11a**, precipitated as a colorless solid. It was isolated in 82 % yield. It shows a reasonably strong carbonyl band in the IR spectrum at 1676 cm^{-1} and a ^{13}C NMR carbonyl carbon resonance at typical δ 196.2 ppm, with a $^{1}J_{PC}$ coupling constant of 35.3 Hz. Single crystals, suitable for the X-ray crystal structure analysis, were grown from dichloromethane. It confirmed the formation of the $Mes_2P–COPh$ moiety, connected by means of the $–CH_2–CH_2–$ bridge with the $BCl(C_6F_5)_2$ unit (for details see Table 3 and Figure 4).

Table 3. Structural data of the compounds **11a–c**.[a]

Compound	11a	11b	11c
P1–C3	1.985(4)	1.961(7)	1.907(3)
C3–O1	1.224(4)	1.220(7)	1.199(3)
C3–C31	1.449(6)	1.448(9)	1.502(4)[b]
P1–C1	1.819(3)	1.816(6)	1.812(3)
C1–C2	1.538(5)	1.541(8)	1.537(4)
C2–B1	1.624(5)	1.627(9)	1.613(4)
B1–Cl1	1.938(4)	1.923(7)	1.915(3)
$\Sigma C3^{POC}$	359.8	359.6	359.9
C1–P1–C3	99.9(2)	99.7(3)	105.6(1)
C2–B1–Cl1	105.9(2)	105.9(4)	107.5(2)
C1–P1–C3–O1	−11.6(4)	−17.5(6)	−134.4(3)
P1–C1–C2–B1	−179.7(3)	−175.4(4)	−166.6(2)

[a] Bond lengths in Å; angles in degrees. [b] C3–C51.

Table 4. Selected NMR data of the compounds **11a–d**.[a]

Compound	11a	11b	11c	11d
Ar	Ph	p-F-C_6H_4	o-Cl-C_6H_4	mesityl
$\delta^1H(PCH_2)$	3.34	3.13	2.98	2.97
$\delta^1H(BCH_2)$	1.58	1.29	1.37	1.32
$\delta^{13}C(C1)$	29.7	29.4	27.9	27.3
$^1J(P,C)$	28.9	33.0	29.5	25.6
$\delta^{13}C(C2)$	22.3	21.9	21.2	21.4
$\delta^{13}C(C3)$	196.2	194.5	194.2	198.3
$^1J(P,C)$	35.3	38.1	41.1	23.7
$\delta^{31}P$	23.6	22.6	27.2	29.9
$\delta^{11}B$	−2.3	−2.5	−2.6	−2.6
$\Delta\delta^{19}F_{m,p}$	4.2	4.2	4.1	4.1

[a] Chemical shifts in ppm (δ-scale); J in Hz; NMR spectra in C_6D_6 (**11a**) or CD_2Cl_2 (**11b–d**), 299 K.

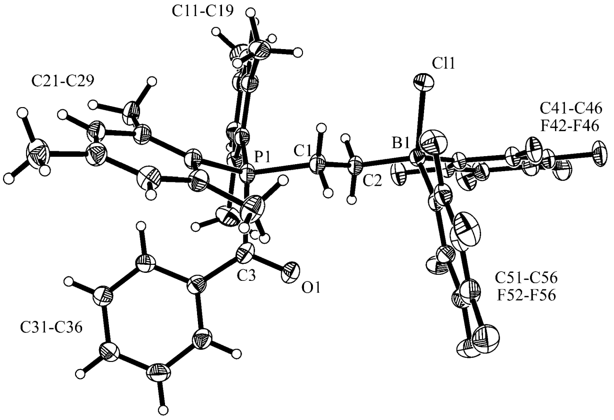


Figure 4. A projection of the molecular structure of compound **11a** (thermal ellipsoids are shown with 30% probability).

We observed the analogous reaction type upon treatment of the P/B FLP, **3**, with the substituted aroyl chlorides, **8b–d**, and isolated the respective zwitterionic aroyl phosphonium/chloroborate products, **11b–d**, all in around 80% yield. They showed similar spectroscopic parameters (see Table 4). The compounds **11b** and **11c** were also characterized by X-ray diffraction (see Table 3). Their structures are depicted in the supporting information.

Again, we could not spectroscopically detect any intermediate on the way to the products **11**. Scheme 3 provides a tentative mechanistic rationale for the formation of these products, involving the carbonyl addition products, **9** and **10**, as potential reactive intermediates. The chloride transfer is formulated in that scheme as taking place intramolecularly, although that is by no means proven.

We have also treated the FLP, **3**, with furoyl chloride (**8e**). This gave a different product, although its formation seems to follow a similar overall reaction pattern and is, therefore, relatively closely related. The reaction between **3** and furoyl chloride (**8e**) was performed at r.t. in pentane and it required only 0.5 molar equivalents of the acid chloride to go to completion. The product precipitated from the solution and it was isolated in 58% yield after crystallization from dichloromethane/pentane.

The X-ray crystal structure analysis (see Figure 5) confirmed that two molar equivalents of **3** had reacted with this acyl chloride to yield a single 2 : 1 reaction product. It shows the central furan-derived heterocycle with a distal carbon-carbon double bond (C5–C6 1.323(5) Å). Both of the α-positions at the five-membered ring have substituents attached. Carbon atom C4 has become part of the exocyclic C=C bond (C3–C4 1.355(4) Å) that was formed by addition of one P/B FLP unit to the carbonyl group of the furoyl chloride starting material. The chloride was removed by the borane Lewis acid of the second FLP equivalent, whose nucleophilic phosphane end then became attached at the furan α-carbon atom C7 (P2–C7 1.860(3) Å).

Consequently, compound **14** shows two ^{31}P NMR resonances in solution (δ 26.3 ppm, −0.9 ppm (233K)). It has only a single broad ^{11}B NMR signal in the typical borate range (δ −1.6 ppm), but shows the ^{19}F NMR signals of two pairs of diastereotopic C_6F_5 substituents at boron.

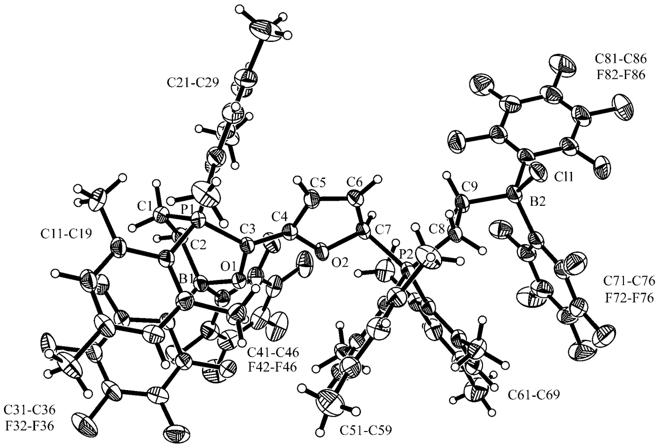
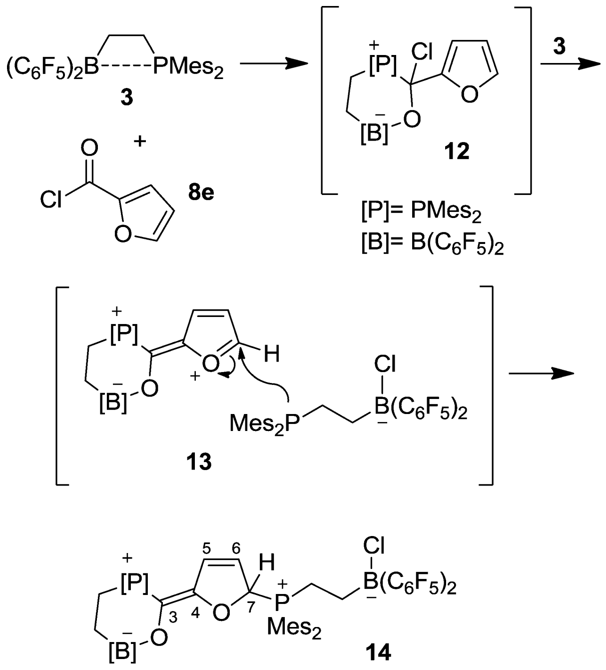


Figure 5. A projection of the molecular structure of product **14** (thermal ellipsoids are shown with 30% probability).

The olefinic ^{1}H NMR resonances (5–H, 6–H) of the central furan-derived heterocycle occur at δ 6.52 and 5.37 ppm, respectively, and we have located the ^{13}C NMR signals of the former furoyl halide reagent in the product, **14**, at δ 85.2 (C7), 126.1, 126.0 (C5,6), 119.3 (C3), and δ 157.4 ppm (C4). The C7 ^{13}C NMR resonance shows coupling to phosphorus ($^1J_{PC}=55.7$ Hz), as does the C3 signal ($^1J_{PC}=94.3$ Hz).[12]

We assume a possible pathway of the formation of the observed product, **14**, as it is tentatively sketched in Scheme 4. Compound **8e** possibly reacts by carbonyl addition with the P/B FLP, **3**. The resulting adduct, **12**, in this case, does not undergo stabilization by intramolecular chloride transfer, but rather seems to react intermolecularly to potentially give the salt, **13**. Subsequent nucleophilic phosphane attack at the available α-position of the activated furyl system would then directly lead to the observed product, **14** (see Scheme 4).



Scheme 4. Treatment of FLP **3** with furoyl chloride (**8e**).

3 Conclusion

We had previously shown that the P/B FLP, **3**, reacts readily with Br_2 or with $SOCl_2$ to give the respective halogenophosphonium/halogenoborate zwitterions $Mes_2P(X)CH_2CH_2B(X)(C_6F_5)_2$.[11,13] With HCl, the system **3** forms the respective phosphonium/chloroborate zwitterion, **7**.[11] Now we have shown that the FLP **3** reacts readily with a variety of acyl chlorides. The non-enolizable benzoyl chlorides, **8a–d**, form the corresponding aroyl phosphonium/chloroborate zwitterions, **11**. The hetero-aromatic furoyl chloride (**8e**) evades this pathway, probably because the reaction proceeds *via* a reactive intermediate that contains an activated furan-derived moiety which is prone to stabilizing phosphane attack. This slightly more complicated pathway is not possible for the simple benzoyl chloride-derived substrates. Only in the case of the furoyl substrate, the addition reaction prevails leading to the obtained rather unusual product **14**.

We assume that a principally related sequence is followed in the case of the reaction of the P/B FLP, **3**, with the aliphatic acyl chlorides, **4a–c**. However, in these cases, the presence of an abstractable proton in the α-position to the carbonyl functionality opens a dehydrohalogenation pathway, and consequently, the reaction of the alleged intermediate with an additional equivalent of the bifunctional P/B FLP, **3**, results in HCl elimination, with formation of the FLP·HCl adduct, **7**, and the formal ketene adducts (**6a–c**) to the FLP **3**. We shall see if we can chemically utilize these readily formed FLP adducts of the cumulated unsaturated ketones.

4 Experimental Section

4.1 Materials

Bis(pentafluorophenyl)borane,[5] dimesitylvinyl phosphane[3] and the P/B FLP, **3**,[3] were prepared according to modified literature procedures.

4.2 Preparation of Compound 6a

A mixture of dimesitylvinylphosphane (**1**) (70.0 mg, 0.24 mmol) and bis(pentafluorophenyl)borane (**2**) (81.7 mg, 0.24 mmol, 1.0 eq.) was dissolved in dichloromethane (3 mL) and stirred for 10 minutes to give a yellow solution. Addition of acetyl chloride (**4a**) (8.4 μL, 0.12 mmol, 0.5 eq.) immediately gave a colorless reaction solution. Compound **6a** was separated from the HCl addition product **7** *via* column chromatography (SiO_2, dichloromethane, $R_f=0.88$) and was isolated as a colorless powder. Crystals suitable for the X-ray single crystal structure analysis were obtained by slow concentration of a dichloromethane solution of compound **6a** at room temperature. m.p.: 208 °C. Anal. calc. $C_{34}H_{28}BF_{10}OP$: C 59.67, H 4.12; found: C 59.63, H 3.93.

4.3 Preparation of 11a

A mixture of dimesitylvinylphosphane (**1**) (50.0 mg, 0.17 mmol) and bis(pentafluorophenyl)borane (**2**) (58.4 mg, 0.17 mmol, 1.0 eq.) was dissolved in *n*-pentane (5 mL) and stirred for 15 minutes to give a yellow solution. Upon addition of benzoyl chloride (**8a**) (23.5 μL, 0.20 mmol, 1.2 eq.) a colorless solid started to precipitate which was separated from the reaction solution via decantation, washed with *n*-pentane (2×2 mL) and dried *in vacuo*. Crystals suitable for the X-ray single crystal structure analysis were obtained by slow concentration of a dichloromethane solution of compound **11a** at −30 °C. d.p.: 174 °C. Anal calc. $C_{39}H_{31}BClF_{10}OP$: C 59.83, H 3.99; found: C 59.72, H 3.73.

4.4 Preparation of 14

A mixture of dimesitylvinylphosphane (**1**) (80.0 mg, 0.27 mmol) and bis(pentafluorophenyl)borane (**2**) (93.4 mg, 0.27 mmol, 1.0 eq.) was dissolved in *n*-pentane (3 mL) and stirred for 20 minutes to give a yellow solution. Upon addition of furoyl chloride (**8e**) (13.5 µL, 0.14 mmol, 0.5 eq.) a light yellow solid started to precipitate. The precipitation was separated from the reaction solution via decantation. Then it was crystallized from dichloromethane (2 mL)/*n*-pentane (5 mL) at −30 °C to give colorless crystals, which were collected and dried *in vacuo*. Crystals suitable for the X-ray single crystal structure analysis were obtained from a toluene solution of compound **14** which was layered with *n*-pentane and stored at −30 °C. m.p.: 170 °C. Anal. calc. $C_{69}H_{55}B_2ClF_{20}O_2P_2$: C 58.56, H 3.92; found: C 59.06, H 3.92.

For further details, and the preparation of the compounds **6b**, **6c** and **11b–d**, see the supporting information. The CCDC deposition numbers are 1029273-1029279.

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References

[1] a) Z. Zhang, Y. Zhang, J. Wang, *ACS Catal.* **2011**, *1*, 1621–1630; b) D. H. Paull, A. Weatherwax, T. Lectka, *Tetrahedron* **2009**, *65*, 6771–6803; c) T. T. Tidwell, *Eur. J. Org. Chem.* **2006**, 563–576; d) T. T. Tidwell, *Ketenes*, 2nd Ed., Wiley-Interscience, Hoboken, NJ, **2006**.

[2] G. J. Fisher, A. F. MacLean, A. W. Schnizer, *J. Org. Chem.* **1953**, *18*, 1055–1057.

[3] a) S. Andreades, H. D. Carlson, *Org. Synth.* **1965**, *45*, 50–54; b) J. W. Williams, C. D. Hurd, *J. Org. Chem.* **1940**, *5*, 122–125.

[4] a) G. A. Olah, A.-H. Wu, O. Farooq, *Synthesis* **1989**, 566–567; b) H. Staudinger, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1619–1623; c) H. Staudinger, *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 1735–1739; d) See also: S. G. Nelson, Z. Wan, T. J. Peelen, K. L. Spencer, *Tetrahedron Lett.* **1999**, *40*, 6535–6539.

[5] P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme, D. W. Stephan, *Chem. Commun.* **2007**, 5072–5074.

[6] G. Kehr, S. Schwendemann, G. Erker, *Top. Curr. Chem.* **2013**, *332*, 45–83.

[7] FLP Reviews: a) *Frustrated Lewis Pairs I: Uncovering and Understanding,* (Eds.: G. Erker, D. W. Stephan), Top. Curr. Chem. *332*, Springer Verlag, Berlin, Heidelberg, **2013**; b) *Frustrated Lewis Pairs II: Expanding the Scope,* (Eds.: G. Erker, D. W. Stephan), Top. Curr. Chem. *334*, Springer Verlag, Berlin, Heidelberg, **2013**; c) D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50–81; d) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76.

[8] a) W. E. Piers, D. J. Parks, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492–5503; b) D. J. Parks, R. E. von H. Spence, W. E. Piers, *Angew. Chem.* **1995**, *107*, 895–897; c) D. J. Parks, R. E. von H. Spence, W. E. Piers, *Angew. Chem. Int. Ed.* **1995**, *34*, 809–811.

[9] See for a comparison: a) M. Sajid, A. Klose, B. Birkmann, L. Liang, B. Schirmer, T. Wiegand, H. Eckert, A. J. Lough, R. Fröhlich, C. G. Daniliuc, S. Grimme, D. W. Stephan, G. Kehr, G. Erker, *Chem. Sci.* **2013**, *4*, 213–219; b) C. M. Mömming, G. Kehr, B. Wibbeling, R. Fröhlich, G. Erker, *Dalton Trans.* **2010**, *39*, 7556–7564; c) C. M. Mömming, S. Frömel, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *J. Am. Chem. Soc.* **2009**, *131*, 12280–12289; d) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem.* **2009**, *121*, 6770–6773; e) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2009**, *48*, 6643–6646.

[10] a) T Beringhelli, D. Donghi, D. Maggioni, G. D'Alfonso, *Coord. Chem. Rev.* **2008**, *252*, 2292–2313; b) W. E. Piers, *Adv. Organomet. Chem.* **2005**, *52*, 1–76.

[11] S. Frömel, R. Fröhlich, C. G. Daniliuc, G. Kehr, G. Erker, *Eur. J. Inorg. Chem.* **2012**, 3774–3779.

[12] *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*, (Eds.: L. D. Quin, J. G. Verkade), Wiley-VCH, Weinheim **1994**.

[13] See also: O. Ekkert, C. B. Caputo, C. Pranckevicius, C. G. Daniliuc, G. Kehr, G. Erker, D. W. Stephan, *Chem. Eur. J.* **2014**, *20*, 11287–11290.

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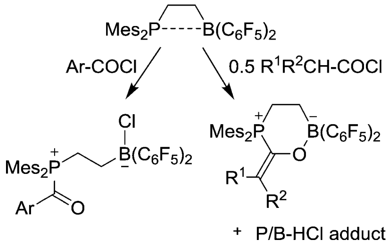

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P/B Ketene Adduct Formation from Acyl Chlorides at a Vicinal Phosphane/Borane Frustrated Lewis Pair