 Geminal bis-borane formation by borane Lewis acid induced cyclopropyl rearrangement and its frustrated Lewis pair reaction with carbon dioxide†

Yun-Lin Liu, Gerald Kehr, Constantin G. Daniliuc and Gerhard Erker*

Cyclopropylacetylene reacts with two molar equivalents of Piers’ borane \([HB(C_6F_5)_2]\) under mild conditions by an addition/rearrangement sequence with cyclopropyl ring opening to give a mixture of two \(\alpha\)-B(C_6F_5)_2 substituted tetrahydroboroles. This compound forms an active frustrated Lewis pair with \(\text{PBu}_3\) that heterolytically splits dihydrogen and adds carbon dioxide as a geminal chelate bis-boryl component. The respective reactions of the two-fold HB(C_6F_5)_2 addition to Ph-CH_2CH_2C≡CH were studied as a geminal Lewis acid reference. Most of the products were characterized by X-ray diffraction.

Results and discussion

The Ph-CH_2CH_2C≡CH/2HB(C_6F_5)_2 system

Terminal acetylenes undergo regioselective 1,2-hydroboration with the HB(C_6F_5)_2 reagent to yield the respective substituted vinyl boranes. When the reaction is carried out in a 1 : 2 molar ratio of alkyne and \([B]H\) borane, the respective saturated geminal bis-borane is obtained in many cases under kinetic control. This typical reaction path was also observed when we treated the alkyne 5a with HB(C_6F_5)_2 in a 1 : 2 ratio in toluene solution at r.t. (1 hour reaction time). Workup gave the product 6a, which we isolated as a white solid with a 76% yield. The compound was characterized by C,H-elemental analysis and by spectroscopy, and we carried out some characteristic reactions.

Compound 6a shows a single \(^{11}\text{B}\) NMR resonance at \(\delta = 72.1\ \text{ppm}\), which is typical for Lewist acid planar tricoordinate \(R\)-B(C_6F_5)_2 situations. Consequently, we observed the three \(^{19}\text{F}\) NMR signals of the symmetry-equivalent C_6F_5 groups at boron. They show a typical large meta/para fluorine NMR chemical shift difference \((\Delta\delta \text{^19}F_{\text{meta}} = 13.7\ \text{ppm})\). The mixture of compound 6a with the bulky phosphine \(\text{PBu}_3\) (1 : 1)

Introduction

Bis-boranes featuring pairs of strongly Lewis acidic B(C_6F_5)_2 groups should be ideally matching templates for binding of CO2 under frustrated Lewis pair (FLP) conditions. Although such geminal bis-boranes are principally readily available from terminal alkynes by sequential hydroboration reactions with two molar equivalents of HB(C_6F_5)_2, as it has been shown by Piers et al., surprisingly little is known about this CO2-trapping reaction. Stephan et al. had used Siebert’s unsaturated geminal BCl_2 compound 1 (ref. 3) and the corresponding B(C_6F_5)_2 analogue 2, which was derived from 1 by treatment with Zn(C_6F_5)_2, for FLP/CO2 scavenging, but the vast majority of FLP/CO2 chemistry used non-chelate Lewis acidic binding motifs.

We have now investigated the ‘Bu_3P/CO2 trapping reaction using a pair of geminal C_6F_5 containing bis-boranes. Both were obtained by the treatment of the respective terminal acetylene starting materials with two molar equivalents of Piers’ borane [HB(C_6F_5)_2]. While we observed the expected normal behaviour upon reacting the alkyne Ph-CH_2CH_2C≡CH (5a) with the hydroboration reagent, we observed a rather complex rearrangement behaviour that took place upon the treatment of cyclopropylacetylene (5b) with the HB(C_6F_5)_2 borane. The characterization of the resulting special rearrangement product, its formation and its FLP reaction with CO2 in the presence of a tert-phosphine will be presented and discussed in this account.

† Electronic supplementary information (ESI) available: Experimental and analytical details are given. CCDC 1487584. For ESI and crystallographic data in CIF or other electronic formats see DOI: 10.1039/c6sc03468c
represents a reactive frustrated Lewis pair that is able to heterolytically split dihydrogen under mild conditions (r.t., 2.0 bar of H₂, overnight in pentane). The product precipitated from the reaction mixture and was isolated as a white solid with an 87% yield. Compound 7 was characterized by X-ray diffraction (single crystals were obtained from pentane/dichloromethane at −35 °C by the diffusion method).

Compound 7 shows a fully extended all anti-periplanar C₁ chain featuring the phenyl substituent at one end and the geminal pair of boryl groups at the other. The C₁–B₁/B₂ bonds are almost of the same length and the pair of boron atoms is bridged by the hydride (see Fig. 1). In the crystal there is an independent HPBu₃⁺ cation. In solution, compound 7 shows the¹H NMR signal at gauche (Scheme 2).

We then treated the bis(boryl)alkane/phosphine FLP [6a/PBu₃] with carbon dioxide. Exposure of the 6a/PBu₃ mixture in pentane at r.t. to CO₂ (2.0 bar) quickly (in 2 hours) resulted in the formation of a white precipitate of compound 8, which was isolated with an 81% yield. Compound 8 is sensitive in solution (CD₂Cl₂) and decomposes above 0 °C. Single crystals of the FLP/CO₂ adduct 8 suitable for characterization by X-ray diffraction were obtained from pentane/dichloromethane at −35 °C by the diffusion method (see Fig. 2). In the crystal, compound 8 shows a gauche/anti-periplanar conformation of the Ph–CH₂CH₂CH₂–CH-chain. The geminal pair of B(C₆F₅)₂ substituents at carbon atom C₁ has taken up the CO₂ molecule in a rather symmetric way by forming two boron–oxygen bonds of almost the same length, and also the C₅–O₁/O₂ bonds are almost equal in length, indicating a fully delocalized structure for this moiety of compound 8. The resulting six-membered heterocycle features an almost coplanar arrangement of the BOCOB unit with only the carbon atom C₅ being localized markedly outside of this plane. The bulky P'Bu₃ group is found attached at the central carbon atom C₅ of this heterocyclic subunit of the overall molecular zwitterionic FLP/CO₂ addition product 8.

In solution we observe the¹³C NMR resonance of the scavenged CO₂ molecule at δ = 172.7 ppm with a ḟJPC coupling constant of 92.6 Hz. Compound 8 shows a typical phosphonium ³¹P NMR signal at δ = 60.3 ppm, and a single broad¹⁹F NMR resonance at δ = 10.8 ppm. The C₆F₅ groups at the pair of boron atoms are pairwise diastereotopic, giving rise to two equal intensity pairs of o,p,m ¹⁹F NMR features, with a rather small chemical shift difference Δδ₃¹Fmp around 5.5 ppm, as is typical for borate type structures based on the B(C₆F₅)₃ subunit.

**The cyclopropylacetylene/2HB(C₆F₅)₃ system: rearrangement to tetrahydroborole derivatives**

We next reacted cyclopropylacetylene (5b) with two molar equivalents of Piers’ borane [HB(C₆F₅)₂] (toluene, r.t., 1 hour). In
this case, we did not obtain the simple cyclopropyl-\(\text{CH}_2\text{CH}[\text{C}_6\text{F}_5\text{F}_2]\), \(\text{C}_2\text{H}_2\text{F}_2\) product (6b), but found that a rearrangement had occurred. In situ NMR spectroscopy revealed the formation of a ca. 7 : 1 mixture of the \(\alpha\)-boryl-tetrahydroborole products cis-9 and trans-9. We isolated the compound cis-9 in an almost pure condition (96 : 4) after workup as a pale yellow solid with a 67% yield (see Scheme 3).

Compound cis-9 was characterized by X-ray diffraction using single crystals that were grown from a pentane solution of the compound at \(-35^\circ\text{C}\) (see Fig. 3, left). The X-ray crystal structure analysis has shown that a five-membered saturated tetrahydroborole framework had been formed in the reaction, bearing a \(\text{B}[\text{C}_6\text{F}_5\text{F}_2]\) substituent at the \(\alpha\)-position C1, a methyl substituent at C3 and a \(\text{C}_6\text{F}_5\text{F}_2\) substituent at C4. The pair of substituents in cis-9 at carbon atoms C1 and C4 are cis-oriented; both are in a trans-arrangement with the methyl substituent at carbon atom C3. The plane of the \(\text{C}_6\text{F}_5\text{F}_2\) group at C4 is oriented markedly away from the mean heterocyclic core [dihedral angle \(\theta\) B1–C4–C21–C21 – 119.6(1)°], whereas the \(\text{C}_6\text{F}_5\text{F}_2\) group at the adjacent boron atom B1 is rotated slightly in the opposite direction [\(\theta\) C1–B1–C11–C12 49.0(7)°, C4–B1–C11–C12 – 136.2(5)°]. Both of the boron atoms B1 and B2 show trigonal planar coordination geometries (\(\sum B_1^{\text{trig}} 359.8^\circ, \sum B_2^{\text{trig}} 359.9^\circ\)), which should render these both as strongly Lewis acidic centres. Consequently, we have monitored a pair of \(^{11}\text{B}\) NMR features for compound cis-9 in solution (d\(_8\)-benzene) in the typical range of Lewis acidic \(\text{B}[\text{C}_6\text{F}_5\text{F}_2]\)R signals (\(\delta = 78.0\) ppm, 67.6 ppm) and a similar appearance of the \(^{19}\text{F}\) NMR spectrum was observed for the \(\text{B}[\text{C}_6\text{F}_5\text{F}_2]/\text{B}[\text{C}_6\text{F}_5\text{F}_2]\) units [\(\Delta\delta^{19}\text{F}_{\text{m}}\delta = 13.9\) ppm, 16.0 ppm] (for details, see the ESI†).

We tried to find a mechanistic rationale for the formation of the boryl tetrahydroborole product 9 in the reaction of cyclopropylacetylene (5b) with two \(\text{HB}[\text{C}_6\text{F}_5\text{F}_2]\) equivalents. It is known that cyclopropanes are often readily opened to the respective olefin isomers upon exposure to boron Lewis acids.\(^{10}\) Therefore, we briefly checked whether the opened isomer of 5b, 2-methyl-1-butene-3-yne, might be involved in this reaction. However, this was not the case. Its reaction with two equivalents of \(\text{HB}[\text{C}_6\text{F}_5\text{F}_2]\) took a different course (for details, see the ESI†).

Therefore, we assumed a reaction pathway as outlined in Scheme 4. It is known that 5b undergoes a single hydroboration with Piers’ borane to give 10, so we assume it to be the initial intermediate.\(^{11}\) With a second \(\text{HB}[\text{C}_6\text{F}_5\text{F}_2]\) equivalent this can then undergo the subsequent hydroboration reaction to give the geminal bis-boryl substituted compound 6b. In the in situ NMR experiment we observed an intermediate which is likely 6b (for details, see the ESI†). This is not stable under our typical reaction conditions but undergoes Lewis acid induced cyclopropyl ring opening, potentially leading to 11 which is subsequently stabilized by a sequence of hydride/C\(_6\)F\(_5\) 1,2-shifts to result in the observed product 9. We must stress that we so far have no information about the alleged intermediates on the way and we cannot convincingly explain, let alone predict, the preferred stereochemical outcome, aside from the assumption that the formation of the observed cis-9 product is following a pathway of least steric hindrance on the way (Scheme 5).

The geminal bis-boryl compound contains a pair of Lewis acidic boron atoms and, consequently, it may serve as a chelate boron Lewis acid component in FLP chemistry. The isolated cis-9 in conjunction with the phosphorus Lewis base P\(_3\)Bu\(_3\) served as an active dihydrogen splitting reagent. Thus, treatment of a 1 : 1 mixture of cis-9 and P\(_3\)Bu\(_3\) with dihydrogen (2.0 bar) in pentane solution overnight produced the dihydrogen splitting product cis-12 as a precipitate. The salt cis-12 was isolated as a white solid with a 71% yield. We obtained single crystals of compound cis-12 from pentane/dichloromethane by a diffusion method which were suitable for characterization by X-ray

Scheme 3 Formation of the tetrahydroborole derivative 9 (with unsystematical atom numbering scheme as used in Fig. 3).

Scheme 4 Rearrangement reaction leading to 9.
The bulk isolated product cis-12 (in CD$_3$Cl$_2$) contained ca. 15–20% contamination of the isomer trans-12 since we had started from a not completely pure starting material (for details, see the ESI† the characterization of the independently synthesized isomer trans-12 will be described below). Compound cis-12 shows a pair of $^{11}$B NMR signals in the typical borate chemical shift range ($\delta = -14.5$ ppm, $-19.7$ ppm). It shows a $^{31}$P NMR phosphonium doublet at $\delta = 60.6$ ppm with $^{1}J_{PH} \approx 428$ Hz. We also exposed the cis-9/PBu$_3$ FLP (again contaminated with a small amount of trans-9) to carbon dioxide (2.0 bar, r.t., overnight) in pentane solution. Under the typical conditions, the zwitterionic FLP/CO$_2$ addition product precipitated and was recovered by filtration to give cis-13 as a white solid with a 73% yield. The NMR analysis (in THF-d$_8$) again showed the presence of a second isomer (trans-13, see below, ca. 3%).

Single crystals of cis-13 suitable for X-ray crystal structure analysis were obtained from pentane/dichloromethane at $-35$ °C by the diffusion method (see Fig. 5). The compound contains a central heterocyclic six-membered ring that was formed by double chelate coordination of the geminal bis-boryl acceptor with the oxygen atoms of the phosphate activated carbon dioxide molecule. The structure of this subunit is largely delocalized with similar bond lengths in the B1–O1/B2–O2 pair as well as the C6–O1/O2 pair of carbon–oxygen bonds. Carbon atom C6 has the PBu$_3$ group attached to it. This chelate heterocycle is interlocked with the five-membered tetrahydroborole framework, which has the boron atom B1 incorporated in it. This section of the molecule shows the same characteristic stereochemical features as we had found for its precursor cis-9. The hydrogen atoms at C1/C4 and the methyl substituent at carbon atom C3 are all in a cis-arrangement on this five-membered ring.

The boryl tetrahydroborole system 9 contains three independent carbon chirality centres. Therefore, there is the possibility of forming four diastereosomers. So far our rearrangement reaction was rather stereoselective and produced the major product cis-9 with the relative stereo-sel ectivity r-1, t-3, c-4 plus a small amount of a minor isomer which probably represents one of the other three diastereoisomers, but whose relative stereochemistry we did not know. We have now prepared and characterized the isomer “trans-9” (of relative r-1, c-3, t-4 stereochemistry) by a selective isomerization process at the saturated central heterocyclic framework.

For that purpose, we treated the substituted tetrahydroborole product cis-9 [r-1, t-3, c-4] with a catalytic amount (20 mol%) of the persistent nitroxide radical TEMPO (pentane, r.t., 4 days). This reaction apparently proceeded with reversible H-atom abstraction at the activated C1 position of the heterocycle and we isolated the trans-9 epimer [r-1, c-3, t-4] as a colourless solid with a 74% yield. This compound was characterized by C,H-elemental analysis, by NMR spectroscopy ($^{11}$B; $\delta = 79.6$ ppm, 72.9 ppm, for details see the ESI†) and by X-ray diffraction. Single crystals suitable for the X-ray crystal structure analysis of compound trans-9 were obtained from a pentane/dichloromethane mixture at $-35$ °C (see Fig. 3, right). It shows the typical five-membered tetrahydroborole framework with the B(C$_6$F$_5$)$_2$ and C$_6$F$_5$ substituents at carbon atoms C1 and C4 now in a trans relationship. The methyl group at C3 has remained trans oriented to the C$_6$F$_5$ group at C4.

Compound trans-9 also formed an active frustrated Lewis pair with PBu$_3$. The system heterolytically cleaved dihydrogen at near to ambient conditions (pentane, r.t., 2.0 bar H$_2$, overnight), and we isolated the hydridoborate/phosphonium salt with a 62% yield. It shows typical $^{11}$B NMR signals at $\delta = -13.3$ ppm and $-17.1$ ppm and a $^{31}$P NMR feature at $\delta = 60.7$ ppm ($^{1}J_{PH} \approx 428$ Hz). Compound trans-12 was characterized by X-ray diffraction (single crystals were obtained from pentane/dichloromethane at r.t. by the diffusion method). The X-ray crystal structure analysis (see Fig. 6) showed the presence of the hydride bridged pair of boron atoms inside the anion and...
the separate HP\textsuperscript{3}Bu\textsuperscript{+} cation. The framework of compound trans-12 features the expected trans-orientation of the B(H)(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}/C\textsubscript{6}F\textsubscript{5} pair of substituents at the ring carbon atoms C1/C4 and the vicinal trans-orientation of the C3–CH\textsubscript{3} group with the C4–C\textsubscript{6}F\textsubscript{5} substituent. The system has consequently conserved the relative stereochemistry of the starting material trans-9. Compound trans-12 shows a relative stereochemistry of r-1, c-3, t-4 (see Scheme 6 and Fig. 6).

Compound trans-9 also reacts with carbon dioxide in the presence of P\textsubscript{3}Bu\textsubscript{3}. Exposing a mixture of trans-9 and tris(tert-butyl)phosphine in pentane solution overnight at r.t. to a CO\textsubscript{2} atmosphere gave the FLP/CO\textsubscript{2} adduct trans-13 as a white precipitate with a 76% yield. The compound turned out to be sparingly soluble in many solvents. However it could be isolated the independent synthesis of trans-13 is described below; thermal ellipsoids are shown with a 30% probability level; hydrogen atoms of the P\textsubscript{3}Bu\textsubscript{3} group and the C\textsubscript{6}F\textsubscript{5} substituents at boron atoms B1, B2, and at carbon atom C4 are omitted for clarity: for details see the ESI; † selected bond lengths (Å) and angles (degrees): P1–C6 1.905(2), B1–O1 1.675(2), B2–O2 1.636(2), O2–C6 1.258(2), O1–C6–O2 128.0(2), B2–C1–B1 110.9(2)] and trans-13 [right, the independent synthesis of trans-13 is described below; thermal ellipsoids are shown with a 30% probability level; hydrogen atoms of the P\textsubscript{3}Bu\textsubscript{3} group and the C\textsubscript{6}F\textsubscript{5} substituents at boron atoms B1, B2, and at carbon atom C4 are omitted for clarity: for details see the ESI; † selected bond lengths (Å) and angles (degrees): P1–C6 1.913(10), B1–O1 1.717(13), B2–O2 1.634(13), O2–C6 1.248(12), O1–C6 1.271(12), O1–C6–O2 128.7(9), B2–C1–B1 118.1(9)].

**Fig. 5** Projection of the molecular structures of the FLP/CO\textsubscript{2} addition product cis-13 [left, thermal ellipsoids are shown with a 50% probability level; hydrogen atoms of the P\textsubscript{3}Bu\textsubscript{3} group and the C\textsubscript{6}F\textsubscript{5} substituents at boron atoms B1, B2, and at carbon atom C4 are omitted for clarity: for details see the ESI; † selected bond lengths (Å) and angles (degrees): P1–C6 1.905(2), B1–O1 1.675(2), B2–O2 1.636(2), O2–C6 1.258(2), O1–C6–O2 128.0(2), B2–C1–B1 110.9(2)] and trans-13 [right, independent synthesis of trans-13 is described below; thermal ellipsoids are shown with a 30% probability level; hydrogen atoms of the P\textsubscript{3}Bu\textsubscript{3} group and the C\textsubscript{6}F\textsubscript{5} substituents at boron atoms B1, B2, and at carbon atom C4 are omitted for clarity: for details see the ESI; † selected bond lengths (Å) and angles (degrees): P1–C6 1.913(10), B1–O1 1.717(13), B2–O2 1.634(13), O2–C6 1.248(12), O1–C6 1.271(12), O1–C6–O2 128.7(9), B2–C1–B1 118.1(9)].

**Fig. 6** A view of the molecular structure of the hydridoborate/phosphonium salt trans-12 (thermal ellipsoids are shown with a 50% probability level). Selected bond lengths (Å) and angles (degrees): B1····B2 1.909(5), B2–C1 1.584(5), B1–C1 1.596(4), B1–C4 1.636(5), B2–H1 1.31(3), B1–H1 1.30(4), B2–C1–B1 73.8(2), B1–H1–B2 93.8.

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occurs at δ = 173.4 ppm (1JPC = 90.0 Hz) and compound trans-13 features a total of six o- (two overlapping), four p- and four m-
C6F5 19F NMR signals in d8-THF at 233 K (for further details see the ESI†).

Conclusions

We have shown in this study that the reaction of cyclo-
propylacetylene with two molar equivalents of Piers’ borane
[HB(C6F5)2] takes an unusual course. We assume that initially
the usual two-fold hydromboration reaction of the terminal
alkyne takes place with the anti-Markovnikov orientation
generating the respective geminal bis-boryl compound. This is
apparently not stable under the applied mild reaction condi-
tions, but undergoes an intramolecular rearrangement process
initiated by cyclopropyl ring opening by the adjacent strong
borane Lewis acid. This initiates a series of 1,2-migration
reactions involving the migration of one C6F5 group from boron
to carbon which eventually yields the α-boryl tetrahydroborole
system 9. This is obtained with a rather high diastereoselectivity
from this rearrangement process. The major compound cis-9
is an active FLP dihydrogen cleavage reagent in the presence of the
bulk P3Bu3 Lewis base. The cis-9/P3Bu3 FLP also sequesters CO2
cleanly in a chelate fashion, similar to the here studied more
Lewis acidic geminal R-CH[B(C6F5)2]2 reference systems,
despite the loss of one electron withdrawing C6F5 substituent at a
boron atom. This probably indicates the favourable influence of
the geminal bis-boryl situation for both chelate hydride and
chelate CO2 binding.

Experimental section

Preparation of compound 6a

A solution of 4-phenyl-1-butyne (5a, 65.0 mg, 0.50 mmol) in
toluene (1.0 mL) was added to a suspension of bis(penta-
fluorophenyl)borane (345 mg, 1.00 mmol) and toluene (3.0 mL).
The reaction mixture was stirred at room temperature for 1 hour
and then the suspension was filtered by cannula filtration. The
volatiles of the obtained filtrate were removed in vacuo to give a
colorless oil. Subsequently pentane (4.0 mL) was added and the
mixture was stored at ca. −35 °C overnight. The formed
white powder was isolated by filtration, washed with pentane
(2 × 1 mL) and dried in vacuo to give compound 6a (312 mg,
0.38 mmol, 76%) as a white solid. Anal. calc. for C34H12B2F20: C,
49.68%; H, 1.47%. Found: C, 49.40%; H, 1.40%. For the NMR
data see the ESI†

Preparation of compound 7

A solution of compound 6a (82.2 mg, 0.10 mmol) and tri-tert-
butyolphosphine (20.5 mg, 0.10 mmol) in pentane (3.0 mL) was
exposed to a hydrogen atmosphere (2.0 bar) at room temperature
and stirred overnight. The resulting white precipitate was
collected by cannula filtration and washed with pentane (3 ×
2 mL). After the removal of all volatiles in vacuo, compound 7
was obtained (88.6 mg, 0.087 mmol, 87%) as a white solid. Anal.
calc. for C46H43B2F20P: C, 53.83%; H, 4.03%. Found: C, 53.81%;
H, 4.01%. Single crystals suitable for the X-ray crystal structure
analysis were obtained by the slow diffusion of pentane into
a solution of compound 7 in dichloromethane at −35 °C.

Preparation of compound 8

A solution of compound 6a (123.3 mg, 0.15 mmol) and tri-tert-
butyolphosphine (30.3 mg, 0.15 mmol) in pentane (5.0 mL)
was exposed to CO2 (2.0 bar) at room temperature and then stirred
for 2 hours. The resulting white precipitate was isolated by
cannula filtration and washed with pentane (3 × 1 mL). After
drying the solid in vacuo, compound 8 (129.4 mg, 0.12 mmol,
81%) was obtained as a white powder. Anal. calc. for
C47H39B2F20O2P: C, 52.84%; H, 3.68%. Found: C, 53.21%; H,
3.91%. Single crystals of compound 8 suitable for the X-ray
crystal structure analysis were obtained by the slow diffusion
of pentane into a solution of the white powder in dichloromethane
at −35 °C.

Preparation of compound cis-9

A solution of compound 5b (33.0 mg, 0.50 mmol) in toluene
(1.0 mL) was added to a suspension of bis(pentafluorophenyl) borane (345 mg, 1.00 mmol) and toluene (3.0 mL). After stirring
the reaction mixture at room temperature for 1 hour, the solu-
tion was separated from the resulting suspension by cannula
filtration. Then all volatiles of the filtrate were removed in vacuo
to give a yellow oil, which was dissolved in pentane (2.5 mL) and
stored at −35 °C overnight. The precipitated pale yellow solid
was isolated by filtration and washed with cold pentane (2 ×
0.5 mL). The removal of all volatiles in vacuo gave a pale yellow
solid (253 mg, 0.34 mmol, 67%). Anal. calc. for C29H28B2F20:C,
45.95%; H, 1.06%. Found: C, 45.74%; H, 1.07%. Crystals of
compound cis-9 suitable for the X-ray crystal structure analysis
were obtained from a solution of the yellow solid in pentane at
−35 °C.

Preparation of compound trans-9

TEMPO (16.6 mg, 0.11 mmol) was added to a solution of
compound cis-9 (400 mg, 0.53 mmol) in pentane (15 mL). After
stirring the reaction mixture at r.t. for 4 days, the resulting
suspension was concentrated to about 2.0 mL, and stored in the
fridge (−35 °C) overnight. The precipitated white powder was
isolated via cannula filtration, and washed with cold pentane
(2 × 1.0 mL). The removal of all volatiles under reduced pressure
gave product trans-9 (296 mg, 0.39 mmol, 74%) as a white
solid. Anal. calc. for C29H28B2F20:C, 45.95%; H, 1.06%. Found: C,
45.45%; H, 0.95%. Crystals suitable for the X-ray crystal structure
analysis were obtained from a solution of compound trans-
9 in pentane (1.5 mL) and CH2Cl2 (0.5 mL) at −35 °C.

Preparation of compound cis-12

A solution of compound cis-9 (cis/trans = 96/4, vide supra) (113.7 mg, 0.15 mmol) and tri-tert-butyolphosphine (30.3 mg,
0.15 mmol) in pentane (5.0 mL) was exposed to dihydrogen
(2.0 bar) at room temperature and then stirred overnight. The
formed white precipitate was collected by cannula filtration and

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washed with pentane (3 × 1 mL). After the removal of all volatiles in vacuo, a white solid was obtained (101.4 mg, 0.11 mmol, 71%). Anal. calc. for C_{41}H_{37}B_{2}F_{20}P: C, 51.17%; H, 3.88%. Found: C, 50.96%; H, 3.76%. Single crystals of compound cis-12 suitable for the X-ray crystal structure analysis were obtained by the slow diffusion of n-pentane into a solution of the white solid in dichloromethane at room temperature.

Preparation of compound trans-12

A solution of compound trans-9 (75.8 mg, 0.10 mmol) and tri-tert-butylphosphine (20.2 mg, 0.10 mmol) in pentane (4.0 mL) was exposed to a dihydrogen atmosphere (2.0 bar) and then stirred overnight. The formed white precipitate was collected by cannula filtration and washed with n-pentane (2 × 1 mL). The removal of all volatiles in vacuo gave compound trans-12 (59.2 mg, 0.062 mmol, 62%) as a white solid. Anal. calc. for C_{42}H_{35}B_{2}F_{20}O_{2}P: C, 50.23%; H, 3.51%. Found: C, 50.07%; H, 3.36%. Single crystals suitable for X-ray crystal structure analysis were obtained by the slow diffusion of n-pentane into a solution of compound trans-12 in dichloromethane at room temperature.

Preparation of compound cis-13

A solution of compound cis-9 (cis/trans = 96/4, vide supra) (113.7 mg, 0.15 mmol) and tri-tert-butylphosphine (30.3 mg, 0.15 mmol) in pentane (5.0 mL) was exposed to a CO_{2} atmosphere (2.0 bar) and then stirred overnight at room temperature. The formed white precipitate was collected by cannula filtration and washed with pentane (3 × 1 mL). After the removal of all volatiles in vacuo, a white solid was obtained (108.3 mg, 0.11 mmol, 73%). Anal. calc. for C_{42}H_{35}B_{2}F_{20}O_{2}P: C, 50.23%; H, 3.51%. Found: C, 50.07%; H, 3.36%. Single crystals of compound cis-13 suitable for the X-ray crystal structure analysis were obtained by the slow diffusion of n-pentane into a solution of the obtained white solid in dichloromethane at −35 °C.

Preparation of compound trans-13

A solution of compound trans-9 (75.8 mg, 0.10 mmol) and tri-tert-butylphosphine (20.2 mg, 0.10 mmol) in pentane (5.0 mL) was exposed to CO_{2} (2.0 bar) at room temperature and then stirred overnight. The formed white precipitate was collected by cannula filtration and washed with pentane (3 × 1 mL). After the removal of all volatiles in vacuo, compound trans-13 (76.2 mg, 0.076 mmol, 76%) was obtained as a white solid. Anal. calc. for C_{42}H_{35}B_{2}F_{20}O_{2}P: C, 50.23%; H, 3.51%. Found: C, 49.96%; H, 3.27%. Single crystals of compound trans-13 suitable for the X-ray crystal structure analysis were obtained directly from a reaction solution of compound trans-9 (37.9 mg) and tri-tert-butylphosphine (10.1 mg) in a CO_{2} atmosphere (2.0 bar) at room temperature.

Notes and references


For reviews, see: (a) L. Tebben and A. Studer, Angew. Chem., Int. Ed., 2011, 50, 5034; (b) A. Studer and D. P. Curran, Nat. Chem., 2014, 6, 765; (c) A. Studer and D. P. Curran, Angew. Chem., Int. Ed., 2016, 55, 58.