# Carbonylation Reactions of Intramolecular Vicinal Frustrated Phosphane/Borane Lewis Pairs

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**S** *Supporting Information*

**ABSTRACT:** The intramolecular frustrated Lewis pair (FLP) $Mes_2PCH_2CH_2B(C_6F_5)_2$ **4** adds cooperatively to carbon monoxide to form the five-membered heterocyclic carbonyl compound **5**. The intramolecular FLP **7** contains an *exo*-3-$B(C_6F_5)_2$ Lewis acid and an *endo*-2-$PMes_2$ Lewis base



functionality coordinated at the norbornane framework. This noninteracting FLP adds carbon monoxide in solution at −35 °C cooperatively to yield a five-membered heterocyclic FLP-carbonyl compound **8**. In contrast, FLP **7** is carbonylated in a CO-doped argon matrix at 25 K to selectively form a borane carbonyl **9** without involvement of the adjacent phosphanyl moiety. The free FLP **7** was generated in the gas phase from its $FLPH_2$ product **10**. A DFT study has shown that the phosphonium hydrido borate zwitterion **10** is formed exergonically in solution but tends to lose $H_2$ when brought into the gas phase.
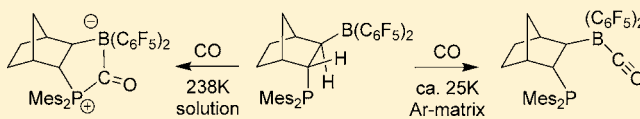
## INTRODUCTION

There have been interesting developments in recent years in small molecule binding and activation by frustrated Lewis pairs (FLPs).[1] Intra- as well as intermolecular FLP examples[2] were used in binding of alkenes and alkynes,[3] carbonyl compounds including carbon dioxide,[3f,s,4] sulfur dioxide,[5] nitrogen oxides,[6] and other small molecules.[7] FLPs have served as templates for CO reduction.[8] Most remarkable is the metal-like ability to heterogeneously split dihydrogen[9,10] and to use the activated hydrogen for catalytic hydrogenation reactions of various substrates under metal-free conditions.[11,12]

Intramolecular FLPs contain a donor center (usually phosphane[10,13] or amine[11d,14]) and an acceptor center (mostly a borane) that are spatially separated. Such situations have allowed for binding of FLPs as ligands to metal centers,[15] giving rise to coordination schemes remotely reminiscent to metal–ligand bonding as it is described by, e.g., the Dewar–Chatt–Duncanson model.[16] Many of such complexes have become known in the past. Some typical examples are depicted in Scheme 1.

In principle, it could be envisioned that this coordination situation could be reversed, namely that the FLP takes up a metal-like role in a Dewar–Chatt–Duncanson reminiscent situation by using its available donor/acceptor pair, only that these two functions are not localized at a single center (as in the real metal complex cases) but residing on different atoms in a single molecule.

We recently found a few examples that could be described in this way. We had observed that the FLP **1** reacted with some alkyl isocyanides to give equilibrium mixtures that contained

**Scheme 1**
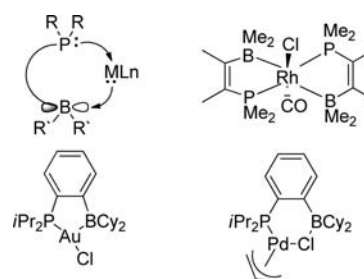


the starting material, the conventional isonitrile–borane adduct **2** and the five-membered heterocycle **3** featuring cooperative binding of both the phosphorus donor and the borane acceptor to the isonitrile "ligand" (see Scheme 2).[17] This may be regarded as an example of a metal-reminiscent ("inverse" Dewar–Chatt–Duncanson-type) coordination behavior of a frustrated Lewis pair.

**Scheme 2**
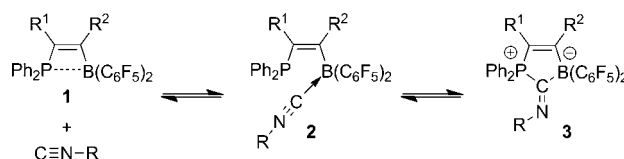
Isonitriles are rather special ligands. It would be interesting to learn whether this unsusual FLP–"ligand" coordination could also be observed in the related FLP/CO systems, thereby building up a remote relation of FLP coordination chemistry to the chemistry of the ubiquitous metal carbonyls. Here, we present first examples of the coordination behavior of a pair of intramolecular vicinal frustrated phosphane/borane Lewis pairs with carbon monoxide. We carried out these reactions in solution at low temperature and also for a comparison under ultracold conditions in CO-doped argon matrices. The thermochemistry of these processes has been studied by state-of-the-art dispersion corrected density functional theory including solvation effects.

### ■ RESULTS AND DISCUSSION

**FLP-Carbonylation in Solution.** For this study, we selected the FLPs **4** and **7** as the substrates for the carbonylation reactions. We first reacted the ethylene-bridged intramolecular FLP $Mes_2PCH_2CH_2B(C_6F_5)_2$ (**4**)[10] with carbon monoxide (2.0 bar); crystallization at −40 °C under a CO atmosphere (5 d) eventually gave the FLP-carbonyl compound **5** as a yellow crystalline solid in 74% yield. Compound **5** was characterized by spectroscopy [IR: $\tilde{\nu}/cm^{-1}$ (C=O) = 1757 cm$^{-1}$, $^{11}$B NMR: $\delta$ = −13.3, $^{31}$P NMR: $\delta$ = −2.3, $^{13}$C NMR: $\delta$ = 228.9 ($^{1}J_{PC}$ = 98 Hz, CO)].

The X-ray crystal structure analysis of compound **5** (see Figure 1) shows a five-membered heterocyclic core in a
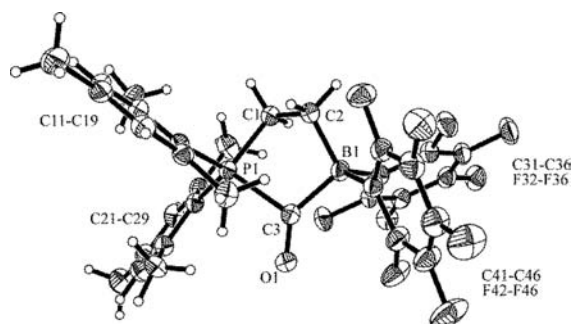


**Figure 1.** Molecular structure of compound **5** (thermal ellipsoids are shown with 30% probability).

distorted twistlike conformation. It contains the [P]−CH$_2$−CH$_2$−[B] unit in a staggered conformation [P1−C1: 1.819(2) Å, C1−C2: 1.544(3) Å, C2−B1: 1.624(3) Å, P1−C1−C2−B1: 58.5(2)°, C1−P1−C3: 91.3 (1)°, C2−B1−C3: 103.5(1)°]. The boron atom is found bonded to the carbonyl carbon atom (B1−C3: 1.662(3) Å; DFT-D3: 1.655 Å). Carbon atom C3 is also bonded to phosphorus, although the phosphorus−C(=O) linkage is rather long at 2.036(2) Å (P1−C3; DFT-D3: 2.154 Å). The O1−C3 bond is short (1.191(2) Å; DFT-D3: 1.181 Å). The carbonyl carbon atom shows a trigonal planar coordination geometry (Σ C3$^{BOP}$ = 360.1°) with individual bond angles of 105.2(1)° (B1−C3−P1), 135.7(2)° (B1−C3−O1), and 119.2(1)° (P1−C3−O1), respectively.

The FLP **7** was prepared by HB(C$_6$F$_5$)$_2$ hydroboration of the phosphinonorbornene **6** starting material as we had previously described.[18] Compound **7** features the B(C$_6$F$_5$)$_2$ group in the 3-exo-position and the bulky −PMes$_2$ Lewis base substituent 2-endo oriented at the norbornane framework. In this situation, there is hardly any residual intramolecular P···B contact observable. Consequently, the FLP **7** is very reactive. It reacts

with carbon monoxide at low temperature (at ca. 2.5 bar) to give the 1,1-addition product **8** (see Scheme 3). The

**Scheme 3**
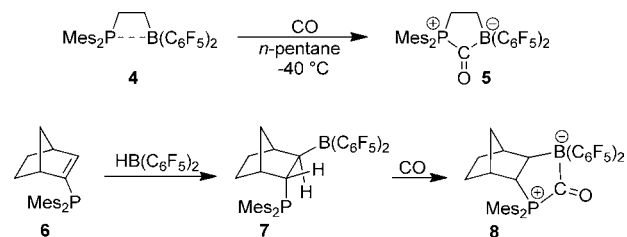


carbonylation reaction was shown to be reversible at the temperatures above ca. 243 K (for details see the Supporting Information). Therefore, we isolated the product **8** by low temperature crystallization (<−35 °C) and obtained it as a yellow crystalline solid in ca. 63% yield.

Compound **8** was also characterized by X-ray diffraction (see Figure 2). The structure shows the norbornane framework to
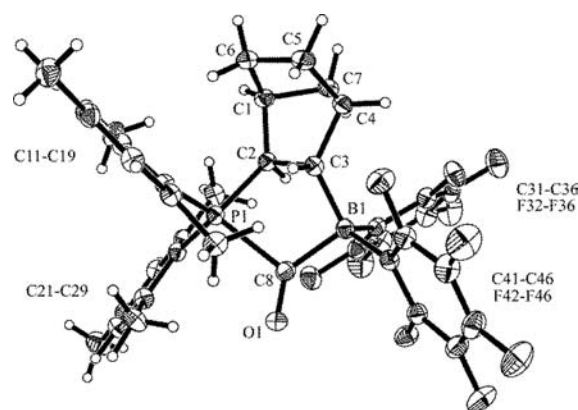


**Figure 2.** View of the molecular structure of the FLP−CO addition product **8** (thermal ellipsoids are shown with 30% probability).

which the boryl substituent is exo attached at the 3-position and the phosphanyl substituent is found endo-2-bonded. The CO molecule has added to the boron Lewis acid (B1−C8: 1.684(2) Å; DFT-D3: 1.675 Å), and the carbonyl carbon atom also features a phosphanyl contact, although the resulting phosphorus−carbon bond is quite long (P1−C8: 2.104(2) Å; DFT-D3: 2.215 Å). As a comparison, the P1−C2 bond length amounts to typical 1.810(2) Å and the pair of P−C(aryl) bonds are only slightly longer (P1−C11: 1.823(2), P1−C21: 1.825(2) Å). Consequently, the C8−O1 bond is very short (1.174(2) Å; DFT-D3: 1.177 Å) and the coordination geometry around the carbonyl carbon atom is quite unsymmetrical [Σ C8$^{BOP}$ = 360.0°, angle B1−C8−O1: 135.3(2)°, P1−C8−O1: 118.3(2)°, P1−C8−B1: 106.4(1)°].

Compound **8** features an IR (C=O) stretching vibration at $\tilde{\nu}$ = 1791 cm$^{-1}$. In solution it shows a $^{13}$C NMR carbonyl carbon resonance at $\delta$ = 224.7 ($^{1}J_{PC}$ ∼ 111 Hz) and heteronuclear magnetic resonance signals at $\delta$ = −12.8 ($^{11}$B) and $\delta$ = −6.4 ($^{31}$P). Compound **8** shows a total of six $^{1}$H NMR methyl resonances of the pair of diastereotopic mesityl substituents on phosphorus at 233 K (CD$_2$Cl$_2$) and at the same temperature a total of 10 $^{19}$F NMR signals originating from the pair of diastereotopic C$_6$F$_5$ groups at boron.

**Reactions in the Gas Phase and in an Argon Matrix.** The above results posed the question if the formation of the cyclic CO addition product is preceded by the formation of a labile borane-carbonyl intermediate (such as **9**) that rapidly cyclizes via intramolecular addition of the phosphane nucleophile (Scheme 4). Since we were not able to observe

**Scheme 4**
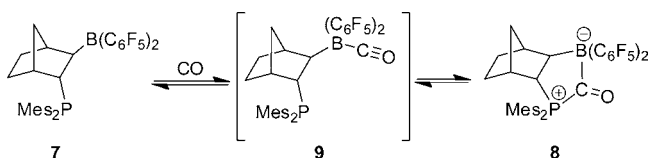


such a [B]—C≡O intermediate in solution, we tried to find evidence for the occurrence of the borane carbonyl **9** by matrix isolation techniques by reacting the FLP **7** with carbon monoxide in a CO-doped argon matrix at 10−35 K. In addition, DFT calculations were used to localize intermediates during the reaction between FLPs and CO.

For this purpose, a DFT study using state-of-the-art quantum chemical methods was conducted[27] (for details see the Supporting Information). First, gas-phase structure optimizations at the dispersion-corrected DFT level using large triple-$\zeta$ AO basis sets (TPSS-D3/def2-TZVP)[20−22] followed by single-point energy calculations at the high double-hybrid density functional level (B2PLYP-D3/def2-TZVP)[23] were performed. These calculations were performed with the TURBOMOLE 6.3 suite of programs.[24] In addition, thermo-statistical corrections from ZPVE-exclusive energy ($\Delta E$) to free energy ($\Delta G$; at various temperatues $T$, 1 atm pressure) were calculated. Because of the extremely high computational cost for the many necessary frequency calculations, these were performed at the semiempircal PM6-D3H level which was validated carefully recently for supramolecular complexes.[25] Corrections for solvation free energy were applied by the accurate (DFT-based) COSMO-RS model in the parametrization for dichloromethane.[26] The estimated accuracy of this approach, which has been successfully applied in FLP chemistry in recent years,[27,28] is about 2−3 kcal/mol for absolute free reaction enthalpies, and relative values for different systems should be accurate to about 1 kcal/mol. In general, we find all structures shown in Schemes 3−5 to be minima on the corresponding DFT hypersurfaces.

**Scheme 5**
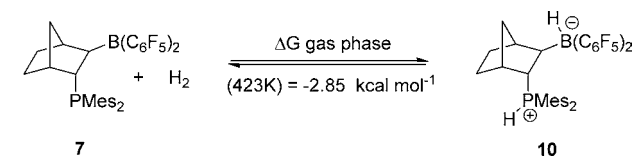


The DFT calculations were carried out for the carbonylation reaction of **7** (see Table 1, for details see the Supporting Information). These results reveal that the formation of **8** in the gas phase is slightly exergonic at all but the highest investigated reaction temperatures.

The reaction energies of the carbonylation reaction are slightly more favorable in solution. Nevertheless, the calculated $\Delta G_{solution}$ value of the formation of the cyclic five-membered FLP-CO product **8** indicates that this product might be

**Table 1. DFT (B2PLYP-D3)-Calculated Reaction Free Enthalpies for the Carbonylation of 7**

| phase | $T$ (K) | $\Delta G$ (kcal/mol) of 9 | $\Delta G$ (kcal/mol) of 8 |
|---|---|---|---|
| gas phase | 423 | +11.1 | +2.8 |
| | 298 | +5.7 | −3.0 |
| | 238 | +3.1 | −5.8 |
| | 10 | −6.3 | −15.3 |
| | 0 | −7.1[a] | −17.0[a] |
| solution (CH$_2$Cl$_2$) | 298 | +2.4 | −9.0 |
| | 238 | +1.3 | −10.4 |

[a]Reaction enthalpy $\Delta H$.

thermally sensitive with regard to CO loss, a feature that we have observed experimentally.

According to the DFT calculations, the formation of borane carbonyl **9** is endergonic in the gas phase and in dichloromethane solution under "normal" laboratory conditions. However, since the dissociation of **9** back to **7** and CO is driven by entropy, at very low temperatures (e.g., 10 K, typical temperature used in matrix isolation experiments), the formation of **9** becomes exergonic. Therefore, **9** can serve as a model for an encounter complex in FLP-carbonylation reactions. In confined environments, **9** could also be involved as reactive intermediate at higher temperatures (Figure 3).
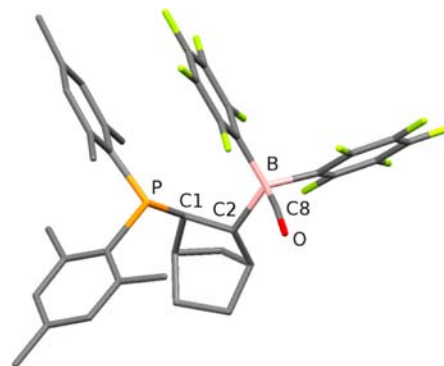


**Figure 3.** View of the DFT (TPSS-D3/def2-TZVP)-optimized structure of the FLP−CO addition product **9**. In this structure, the boron atom is found bonded to the carbon atom of CO (B1−C8: 1.591 Å, C8−O1: 1.136 Å) with a bent B−C−O bond (B1−C8−O1: 167.05°), and the phosphorus atom is not involved in bonding with the carbonyl carbon atom (P1−C8: 4.21 Å). The structure optimizations and all frequency calculations were conducted at the TPSS-D3 (BJ)/def2-TZVP level, while all computed reaction free enthalpies are based on more accurate single-point B2PLYP-D3 (BJ)/def2-TZVP.

It was tempting to use matrix isolation spectroscopy to learn about these interesting FLP-derived borane carbonyl species by an experimental approach. This technique allows synthesis and isolation of weakly bound intermolecular complexes by annealing inert gas matrices (argon in most cases) doped with small amounts of the components.[19] The idea was to isolate FLPs in a large excess of solid argon doped with 1% CO at 10 K and subsequently anneal the matrix at temperatures up to 35 K to enable the diffusion of CO in the matrix and thus the formation of bimolecular complexes between the FLPs and CO. This posed the problem of transporting an active FLP **7** through the gas phase into an argon matrix. We first tried the direct sublimation of **7** at temperatures between 70 and 100 °C

and trapping the product with a large excess of argon on top of a cold (10 K) spectroscopic window. However, analysis of the matrix IR spectra revealed that under these conditions only pentafluorobenzene and other fragments are trapped, which demonstrates that the FLPs are not sufficiently thermally stable to "survive" these sublimation conditions.

In contrast, when we sublimed the dihydrogen activation product **10** at 120−150 °C we eventually found that the frustrated Lewis pair **7** was trapped in the argon matrix (Figures 4 and 5). That means that while in the solid state **10** is
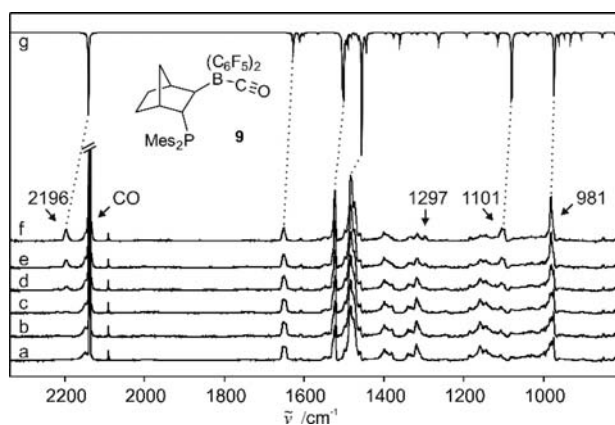


**Figure 4.** Annealing of a 1% CO-doped argon matrix containing FLP **7**. The matrix was produced by sublimation of **10** at 150 °C and trapping the matrix at 10 K. While the matrix was warmed from 10 to 35 K with a rate of approximately 1 K/min, IR spectra were taken every 5 min (a−f, all spectra in absorbance). Bands at 2196, 1297, 1101, and 981 cm$^{-1}$ are assigned to the CO adduct **9**. The calculated spectrum (harmonic PBE0-D3/def2-TZVP level) is included (g) for comparison.
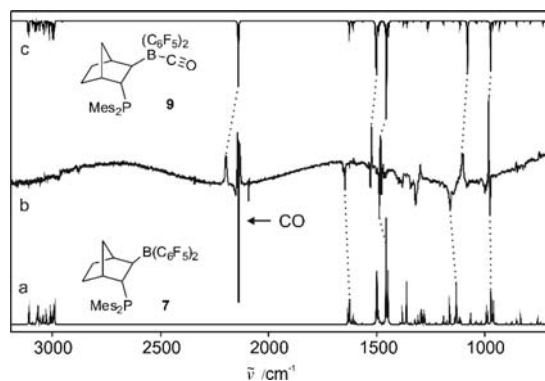


**Figure 5.** (a) IR spectrum of **7**, calculated at the PBE0-D3/def2-TZVP level of theory. (b) Difference IR spectrum of **7**, matrix-isolated in 1% CO-doped argon before and after annealing at 35 K. (c) IR spectrum of **9** calculated at the PBE0-D3/def2-TZVP level of theory. All spectra are shown in absorbance.

thermally more stable than **7**, in the gas phase **10** loses 1 equiv of dihydrogen to form **7**. A DFT study gave us an explanation for this unexpected effect. It revealed a remarkable general solvent influence on the thermodynamic stability of the FLPH$_2$ products (see Table 2 and compare ref 27). Thus, the sublimation of the H$_2$ adducts of FLPs seems to be a general way to bring FLPs into the gas phase without decomposition.

In solution, the FLP (**7**) + H$_2$ ⇋ FLPH$_2$ (**10**) equilibrium lies on the side of the H$_2$-addition product. Solvation in general seems to stabilize the zwitterionic product side. This situation is

**Table 2. DFT (B2PLYP-D3)-Calculated $\Delta G$ Values of the FLP (7) + H$_2$ ⇋ FLPH$_2$ (10) Equilibrium in Solution and in the Gas Phase**[a]

| temp (K) | CH$_2$Cl$_2$ | gas phase |
|---|---|---|
| 10 | b | −16.7 |
| 238 | −19.3 | −9.8 |
| 298 | −17.4 | −6.5 |
| 423 | b | −2.9 |

[a]$\Delta G$ values in kcal/mol [b]Values in solution at 10 and 423 K are not included as the solvent is solid or gaseous at these temperatures.

different in the gas phase. As can be seen from the $\Delta G$ values listed in Table 2, the DFT calculation indicates a much smaller exergonicity of the **7** + H$_2$ ⇋ **10** reaction. At 238 K the product (**10**) is by ca. 9.5 kcal/mol less stable in the gas phase than in solution, at 298 K the difference is ca. 11 kcal/mol, but at 423 K this equilibrium system is almost thermoneutral.

Looking at the polarity of the molecules (e.g., as indicated by their dipole moments), this observation makes sense; for the zwitterionic reaction product **10** a comparatively high dipole moment of 16.5 D was calculated (on the TPSS-D3 level). Naturally, such a molecule is more stabilized in a polar environment like a CH$_2$Cl$_2$ solution. For the CO reaction products this effect is slightly less pronounced, but dipole moments of 11.5 and 10.8 D for **5** and **8**, respectively, are computed. In comparison, the boron−CO adduct **9** has only a dipole moment of 4.1 D and would not experience as much stabilization from a polar solvent.

Under our experimental conditions, it is well conceivable that H$_2$-cleavage of **10** has become a good method to generate the respective FLP **7** in the gas phase. In a way, we have used the H$^+$/H$^-$ attachment as a protective measure for the free FLP **7**.

The next experiment was to matrix-isolate FLP **7** in argon doped with 1% CO at 10 K. Under these conditions, we observe for **7** the same IR spectrum as in pure argon and in addition the expected very strong band of CO at $\tilde{\nu}$ = 2138 cm$^{-1}$. Warming this matrix with a rate of approximately 1 K/min from 10 to 35 K results in a decrease of all bands assigned to **7** and the formation of new bands (Figure 4). Most of these bands are only slightly shifted with respect to that of **7**; however, a new strong band at $\tilde{\nu}$ = 2196 cm$^{-1}$ clearly indicates the formation of a complex between CO and **7** (Figure 5, Table 3). Other bands with a larger shift are all related to C−B stretching vibrations, indicating that the CO is strongly interacting with the boron atom. The IR spectra of compounds **7** and **9** were calculated applying the hybrid-GGA functional PBE0-D3[31] together with the large Gaussian AO-basis set def2-TZVP[21] and the numerical quadrature grid $m5$ as implemented in the TURBOMOLE 6.3 program package.[22] By comparison of the experimental IR spectrum with the results from DFT calculation, the newly formed product was assigned to CO adduct **9**. The blue-shift of the CO stretching vibration in complex **9** compared to free CO is characteristic of borane−CO complexes.[29] This computed shift is quite sensitive to the density functional employed, and we find in test calculations that a hybrid functional like the applied PBE0 is necessary for accurate results.

## ■ CONCLUSIONS

It is well-known that intramolecular phosphane/borane systems may serve as combined donor/acceptor ligands in $d$-metal coordination chemistry.[15] We had discussed the possibility that

**Table 3. Experimental and Calculated (PBE0-D3/def2-TZVP; Index Calcd) Vibrational Frequencies of FLP 7 and the FLP−CO Adduct 9**

| 7 | | 9 | | | | |
|---|---|---|---|---|---|---|
| $\nu_{calcd}$ (cm$^{-1}$) | $\nu_{exp}{}^a$ (cm$^{-1}$) | $\nu_{calcd}$ (cm$^{-1}$) | $\nu_{exp}{}^b$ (cm$^{-1}$) | assignment | calcd shift $\Delta\nu$ (cm$^{-1}$) | exptl shift $\Delta\nu$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| | | 2261 (vs) | 2196 (vs) | C−O str | | +58$^c$ |
| 1704 (w) | 1653 (w) | 1699 (w) | 1653 (w) | C=C ring str (C$_6$F$_5$) | −5 | 0 |
| 1696 (m) | 1649 (m) | 1691 (m) | 1649 (m) | C=C ring str (C$_6$F$_5$) | −15 | 0 |
| 1670 (w) | 1623 (w) | 1670 (w) | 1623 (w) | C=C ring str (Mes) | 0 | 0 |
| 1573 (s) | 1523 (s) | 1576 (s) | 1522 (s) | C=C ring str (C$_6$F$_5$) | +3 | −1 |
| 1575 (vs) | 1484 (vs) | 1533 (vs) | 1480 (vs) | C=C ring str (C$_6$F$_5$) | −2 | −4 |
| 1525 (s) | 1475 (s) | 1521 (s) | 1469 (s) | C=C ring str (C$_6$F$_5$) | −4 | −6 |
| 1370 (vs) | 1380 (w) | 1393 (w) | 1379 (w) | CH$_3$ bending | +23 | −1 |
| 1203 (s) | 1318 (m) | 1202 (vw) | 1297 (m) | C−B str (aliphatic) | −1 | −21 |
| 1185 (w) | 1180 (w) | 1181 (w) | 1127 (w) | C−B str (C$_6$F$_5$ ring) | −4 | −50 |
| 1181 (s) | 1159 (s) | 1139 (vs) | 1101 (vs) | C−B str (C$_6$F$_5$ ring) | −42 | −58 |
| 971 (m) | 974 (s) | 973 (s) | 981 (vs) | CH o.o.p bend (bridge head C−H, CH$_2$) | +2 | +7 |

$^a$Argon matrix at 10 K. $^b$1% CO-doped argon matrix at 10 K. $^c$From free CO.

P/B-frustrated Lewis pairs might engage themselves in a formally reversed role, namely to serve as bifunctional main group element systems mimicking transition metal coordination behavior to typical small ligand systems. We previously noted that the P/B FLP **4** and some of its relatives cleanly added cooperatively to nitrogen monoxide to yield the unique persistent FLPNO radicals **11** (see Scheme 6).[6] The unsaturated FLP **1** had been shown to add n-butyl isocyanide similarly to give the five-membered heterocyclic product **3** (see Scheme 2).[17]

**Scheme 6**
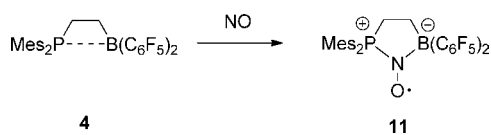


It seems that we have now observed two examples of a FLP reaction remotely resembling metal carbonyl coordination, the "archetypical" feature in the Dewar−Chatt−Dunanson coordination scheme.[16] One might be tempted to describe this CO binding to the FLPs **4** and **7** similarly by a combination of two formal coordination components, namely the binding of the CO donor to the borane acceptor which is strengthened and augmented by the phosphane donor to interact with the activated borane carbonyl function via the antibonding carbon monoxide $\pi^*$ orbital (Scheme 7). It may even be that the slight unsymmetry found in the bonding situation of the CO molecule in both the synergistic P/B−CO adducts (**5** and **8**),

**Scheme 7**
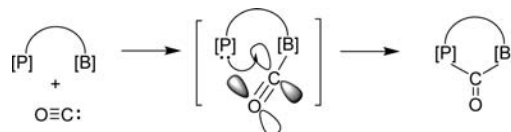


featuring relatively large B−C−O angles, might be reminiscent of this specific cooperative bonding arrangement.

We have no direct experimental evidence that the thermodynamically unfavorable borane−carbonyl compound (**9**) might actually be serving as reactive high energy intermediate in the FLP carbonylation under our actual preparative conditions. We noticed that the parent borane-carbonyl H$_3$B-CO, which has been known since 1937,[29] is kinetically stabilized by the reluctance of CO to insert into B−H bonds. H$_3$B−CO features a IR (C≡O) stretching band at $\tilde{\nu}$ = 2164 cm$^{-1}$, above the free CO value (2143 cm$^{-1}$) as expected for a Lewis acid to carbon monoxide adduct.[30] In our matrix isolation experiments we have observed the respective borane-carbonyl **9**, albeit under quite different conditions from our solution chemistry.

We conclude that intramolecular frustrated phosphane−borane Lewis pairs react cooperatively with carbon monoxide to form the five-membered heterocyclic carbonyl compounds. This FLP coordination behavior remotely resembles the bonding situation in metal−carbonyl complexes, as it is described by, e.g., the classical Dewar−Chatt−Duncanson model. We do not want to stretch this analogy too far, but it seems that we are finding interesting remarkable new chemical FLP behavior. Some FLPs are showing chemical reactions, such as, e.g., H$_2$-spliting and activation,[9−12] that had previously been thought to be a dominant domain of transition metal systems. Now it seems that FLPs may even exhibit a remotely metal-reminiscent behavior to coordination chemistry.

## ■ EXPERIMENTAL SECTION

**General Procedures.** All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glovebox) under an atmosphere of argon. Solvents were dried prior to use. For X-ray diffraction, data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN;[32] absorption correction, Denzo;[33] structure solution SHELXS-97;[34] structure refinement SHELXL-97[35] and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, $R$-values are given for observed reflections, and wR2 values are given for all reflections.

**Synthesis of Compound 8.** Compound **7** was prepared by dissolving equivalent amounts of dimesitylnorbornenylphosphane (97.3 mg, 0.268 mmol) and HB(C$_6$F$_5$)$_2$ (92.6 mg, 0.268 mmol) in n-pentane (15 mL) and stirring at rt for 30 min. The solution was degassed, and CO gas (2.5 bar) was pressed to it at rt. The reaction mixture was kept at −35 °C, and within 4 days a yellowish crystalline solid was formed. The reaction mixture was cooled to −78 °C, and the solvent was removed via a filter canula. The obtained residue was dried in vacuo at −78 °C to give compound **8** as a yellow crystalline solid (119 mg, 63% yield). The obtained crystals were suitable for the X-ray single crystal structure analysis. IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 1791 (s, C=O). Melting point (DSC): 87.7 °C. Anal. Calcd for C$_{38}$H$_{32}$PBF$_{10}$O: C, 61.98; H, 4.38. Found: C, 62.71; H, 5.04. X-ray crystal structure analysis of compound **8**: formula C$_{38}$H$_{32}$BF$_{10}$OP, $M$ = 736.42, colorless crystal, 0.28 × 0.20 × 0.16 mm, $a$ = 16.4396(3) Å, $b$ = 17.2702(3) Å, $c$ = 23.2971(5) Å, $V$ = 6614.4(2) Å$^3$, $\rho_{calc}$ = 1.479 g

cm$^{-3}$, $\mu$ = 1.529 mm$^{-1}$, empirical absorption correction (0.674 ≤ T ≤ 0.792), Z = 8, orthorhombic, space group Pbca (No. 61), $\lambda$ = 1.54178 Å, T = 223(2) K, $\omega$ and $\varphi$ scans, 57347 reflections collected ($\pm h, \pm k, \pm l$), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 5836 independent ($R_{int}$ = 0.047) and 5299 observed reflections [$I > 2\sigma(I)$], 466 refined parameters, R = 0.037, wR$^2$ = 0.097, max (min) residual electron density 0.22 (−0.34) e Å$^{-3}$; hydrogen atoms were calculated and refined as riding atoms.

**In Situ Generation of the Adduct 8.** Dimesitylnorbornenylphosphane (40.0 mg, 0.11 mmol) and HB(C$_6$F$_5$)$_2$ (38.1 mg, 0.11 mmol) in CD$_2$Cl$_2$ (0.7 mL) at rt gave a bright yellow solution. The obtained solution was transferred into a Young NMR tube which was evacuated by a freeze−pump−thaw cycle. Then the solution was cooled to −78 °C, and CO gas (3.0 bar) was applied. The Young NMR tube was closed (CO atmosphere ca. 3.0 bar), and the obtained reaction mixture was characterized by NMR experiments at 233 K. $^1$H NMR (600 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 7.02 (s, 1H, m-Mes$^A$), 6.96 (d, $^4J_{PH}$ = 4.3 Hz, 1H, m-Mes$^B$), 6.90 (br s, 1H, m′-Mes$^B$), 6.87 (s, 1H, m′-Mes$^B$), 2.92 (br, 1H, H-1)$^t$, 2.61 (br, 1H, H-4)$^t$, 2.53 (s, 3H, o-CH$_3^{MesA}$), 2.36 (dd, $^2J_{PH}$ = 13.8 Hz, $^3J_{HH}$ = 5.9 Hz, 1H, PCH), 2.29 (s, 3H, o-CH$_3^{MesB}$), 2.28 (s, 3H, p-CH$_3^{MesA}$), 2.26 (s, 3H, p-CH$_3^{MesB}$), 2.13 (s, 3H, o′-CH$_3^{MesB}$), 1.96 (s, 3H, o′-CH$_3^{MesA}$), 1.56 (m, 1H, BCH), 1.38/1.10 (each m, each 1H, H-5)$^t$, 1.28/0.79 (each m, each 1H, H-6)$^t$, 1.26/0.74 (each m, each 1H, H-7)$^t$, [$^t$ tentatively assigned]. $^{13}$C{$^1$H} NMR (151 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 224.7 (br d, $^1J_{PC}$ ~ 111 Hz, CO), 143.9 (d, $^2J_{PC}$ = 2.9 Hz, o′-Mes$^B$), 143.4 (d, $^4J_{PC}$ = 2.5 Hz, p-Mes$^B$), 143.2 (d, $^2J_{PC}$ = 15.9 Hz, o-Mes$^B$), 142.4 (d, $^2J_{PC}$ = 6.8 Hz, o′-Mes$^A$), 142.3 (d, $^4J_{PC}$ = 2.9 Hz, p-Mes$^A$), 141.5 (d, $^2J_{PC}$ = 3.3 Hz, o-Mes$^A$), 131.3 (d, $^3J_{PC}$ = 9.2 Hz, m-Mes$^A$), 131.0 (d, $^3J_{PC}$ = 11.1 Hz, m′-Mes$^A$), 130.6 (d, $^3J_{PC}$ = 11.7 Hz, m-Mes$^B$), 130.3 (d, $^3J_{PC}$ = 6.6 Hz, m′-Mes$^B$), 121.2 (d, $^1J_{PC}$ = 33.5 Hz, i-Mes$^B$), 120.0 (d, $^1J_{PC}$ = 43.2 Hz, i-Mes$^A$), 48.4 (d, $^1J_{PC}$ = 38.4 Hz, PCH), 42.2 (br, BCH), 41.94 (d, $^2J_{PC}$ = 16.0 Hz, C-1)$^t$, 41.91 (d, $^3J_{PC}$ = 10.5 Hz, C-7)$^t$, 37.3 (br, C-4)$^t$, 34.9 (C-5)$^t$, 25.0 (d, $^3J_{PC}$ = 6.5 Hz, o-CH$_3^{MesA}$), 23.1 (o-CH$_3^{MesA}$), 21.8 (d, $^3J_{PC}$ = 3.1 Hz, o′-CH$_3^{MesB}$), 21.7 (d, $^3J_{PC}$ = 5.0 Hz, o′-CH$_3^{MesA}$), 21.3 (C-6)$^t$, 21.0 (d, $^5J_{PC}$ = 1.0 Hz, p-CH$_3^{MesB}$), 20.9 (d, $^5J_{PC}$ = 1.4 Hz, p-CH$_3^{MesA}$), [C$_6$F$_5$ not listed; $^t$ tentatively assigned]. $^{11}$B NMR (192 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = −12.8 ($\nu_{1/2}$ ≈ 400 Hz). $^{31}$P NMR (242 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = −6.4 ($\nu_{1/2}$ ≈ 60 Hz). $^{19}$F NMR (564 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = −126.5 (m, 1F, o-C$_6$F$_5^A$), −130.76, (m, 1F, o-C$_6$F$_5^B$), −130.85 (m, 1F, o′-C$_6$F$_5^A$), −135.8 (m, 1F, o′-C$_6$F$_5^B$), −159.1 (t, $^3J_{FF}$ = 20.5 Hz, 1F, p-C$_6$F$_5^A$), −159.4 (t, $^3J_{FF}$ = 21.0 Hz, 1F, p-C$_6$F$_5^B$), −163.3 (m, 1F, m′-C$_6$F$_5^A$), −163.9 (m, 1F, m-C$_6$F$_5^A$), −164.5 (m, 1F, m-C$_6$F$_5^B$), −164.8 (m, 1F, m′-C$_6$F$_5^B$). $\Delta\delta$ $^{19}$F(m,p) = 4.8, 4.2, 4.7, 5.4.

**Synthesis of Compound 5.** Dimesitylvinylphosphane (296 mg, 1.00 mmol) and HB(C$_6$F$_5$)$_2$ (346 mg, 1.00 mmol) were dissolved in n-pentane (20 mL), and the mixture was stirred for 15 min at room temperature. After the solution was degassed, carbon monoxide (2 bar) was introduced at room temperature for 10 min. After the reaction mixture was kept at −40 °C for 5 days, a yellow crystalline solid precipitated. The liquid part was removed by filter cannula at −78 °C, and the residue was dried under vacuum to obtain **5** (476 mg, 74%) as a yellow crystalline solid. Crystals suitable for the X-ray single-crystal structure analysis were grown from n-pentane solution under CO (2 bar) at −40 °C. IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 1757 (s, C═O). Melting point (DSC): 70.5 °C. Anal. Cacld for C$_{33}$H$_{26}$PBF$_{10}$O: C, 59.13; H, 3.91. Found: C, 59.46; H, 4.13. X-ray crystal structure analysis of **5**: formula C$_{33}$H$_{26}$BF$_{10}$OP, M = 670.32, pale yellow crystal, 0.33 × 0.15 × 0.10 mm, a = 22.3190(7) Å, b = 14.9283(5) Å, c = 20.1500(10) Å, $\beta$ = 115.062(5) °, V = 6081.6(4) Å$^3$, $\rho_{calc}$ = 1.464 g cm$^{-3}$, $\mu$ = 1.603 mm$^{-1}$, empirical absorption correction (0.619 ≤ T ≤ 0.856), Z = 8, monoclinic, space group C2/c (No. 15), $\lambda$ = 1.54178 Å, T = 223(2) K, $\omega$ and $\varphi$ scans, 23316 reflections collected ($\pm h, \pm k, \pm l$), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 5273 independent ($R_{int}$ = 0.036) and 4808 observed reflections [$I > 2\sigma(I)$], 421 refined parameters, R = 0.041, wR$^2$ = 0.112, max (min) residual electron density 0.23 (−0.32) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**In Situ Generation of Compound 5.** The reaction was carried out using a Young's NMR tube. Dimesitylvinylphosphane (44.5 mg, 0.15 mmol) and HB(C$_6$F$_5$)$_2$ (51.9 mg, 0.15 mmol) were dissolved in

CD$_2$Cl$_2$ (0.6 mL), and the mixture was reacted for 15 min at room temperature. After the solution was degassed, carbon monoxide (2.0 bar) was introduced at −78 °C. The Young's NMR tube was taken out of the cooling bath and shaken well, and then it was cooled again at −78 °C under CO pressure. This procedure was repeated four times. Subsequently, the reaction mixture was characterized by NMR experiments at −60 °C. $^1$H NMR (500 MHz, 213 K, CD$_2$Cl$_2$): $\delta$ = 6.94 (d, $^4J_{PH}$ = 3.6 Hz, 2H, m-Mes), 2.82 (br m, 1H, PCH$_2$), 2.26 (s, 3H, p-CH$_3^{Mes}$), 2.22 (s, 6H, o-CH$_3^{Mes}$), 1.65 (br d, $^3J_{PH}$ = 21.0 Hz, 2H, BCH$_2$). $^{13}$C{$^1$H} NMR (126 MHz, 213 K, CD$_2$Cl$_2$): $\delta$ = 228.9 (br d, $^1J_{PC}$ ~ 98 Hz, C═O), 146.9 (dm, $^1J_{FC}$ ~ 237 Hz, C$_6$F$_5$), 143.1 (d, $^4J_{PC}$ = 2.9 Hz, p-Mes), 142.3 (d, $^2J_{PC}$ = 7.4 Hz, o-Mes), 138.7 (dm, $^1J_{FC}$ ~ 254 Hz, C$_6$F$_5$), 136.4 (dm, $^1J_{FC}$ ~ 248 Hz, C$_6$F$_5$), 130.9 (d, $^3J_{PC}$ = 10.0 Hz, m-Mes), 121.0 (br, i-C$_6$F$_5$), 120.3 (d, $^1J_{PC}$ = 42.9 Hz, i-Mes), 28.4 (d, $^1J_{PC}$ = 42.8 Hz, PCH$_2$), 23.1 (br, o-CH$_3^{Mes}$), 20.8 (s, p-CH$_3^{Mes}$), 16.6 (br, BCH$_2$). $^{11}$B{$^1$H} NMR (160 MHz, 213 K, CD$_2$Cl$_2$): $\delta$ = −13.3 ($\nu_{1/2}$ ≈ 300 Hz). $^{31}$P{$^1$H} NMR (202 MHz, 213 K, CD$_2$Cl$_2$): $\delta$ = −2.3 ($\nu_{1/2}$ ≈ 110 Hz). $^{19}$F NMR (470 MHz, 213 K, CD$_2$Cl$_2$): $\delta$ = −131.4 (br, 2F, o-C$_6$F$_5$), −159.4 (t, $^3J_{FF}$ = 21.0 Hz, 1F, p-C$_6$F$_5$), −164.3 (m, 2F, m-C$_6$F$_5$). $\Delta\delta^{19}$F(m, p) = 4.8.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information**

Experimental and computational details, UV/vis spectra, IR spectra, X-ray crystallographic details, $^1$H NMR and $^{13}$C NMR spectra, and two-dimensional data of compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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**Notes**
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## ■ ACKNOWLEDGMENTS

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