

# Phosphido- and Amidozirconocene Cation-Based Frustrated Lewis Pair Chemistry

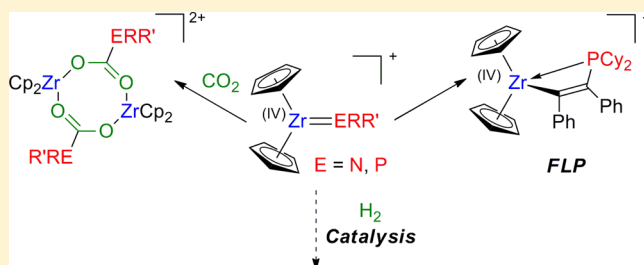
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**S** Supporting Information

**ABSTRACT:** Methyl abstraction from neutral  $[\text{Cp}_2\text{ZrMe}(\text{ERR}')]$  complexes **1** ( $\text{E} = \text{N}, \text{P}$ ;  $\text{R}, \text{R}' = \text{alkyl, aryl}$ ) with either  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]^-$  results in the formation of  $[\text{Cp}_2\text{Zr}(\text{ERR}')][\text{X}]$  complexes **2** ( $\text{X}^- = \text{MeB}(\text{C}_6\text{F}_5)_3^-$ ,  $\text{B}(\text{C}_6\text{F}_5)_4^-$ ). The X-ray structure of amido complexes  $[\text{Cp}_2\text{Zr}(\text{NPh}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**2d**) and  $[\text{Cp}_2\text{Zr}(\text{N}^t\text{BuAr})][\text{B}(\text{C}_6\text{F}_5)_4]$  (**2e'**,  $\text{Ar} = 3,5\text{-C}_6\text{H}_3(\text{CH}_3)_2$ ) is reported, showing a sterically dependent  $\text{Zr}/\text{N}-\pi$  interaction. Complexes **2** catalyze the hydrogenation of electron-rich olefins and alkynes under mild conditions (room temperature, 1.5 bar  $\text{H}_2$ ). Complex **2e** binds  $\text{CO}_2$ , giving  $[\text{Cp}_2\text{Zr}(\text{CO}_2)(\text{N}^t\text{BuAr})_2][\text{MeB}(\text{C}_6\text{F}_5)_3]_2$  (**3e**). Amido complex **2d** reacts with benzaldehyde yielding  $[\text{Cp}_2\text{Zr}(\text{OCH}_2\text{Ph})(\text{OCPhNPh}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7d**). Phosphido complex  $[\text{Cp}_2\text{Zr}(\text{PCy}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**2a**) reacts with diphenylacetylene to yield frustrated Lewis pair  $[\text{Cp}_2\text{Zr}(\text{PhCCPh})(\text{PCy}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**8a**) which further reacts with a range of carbonyl substrates.



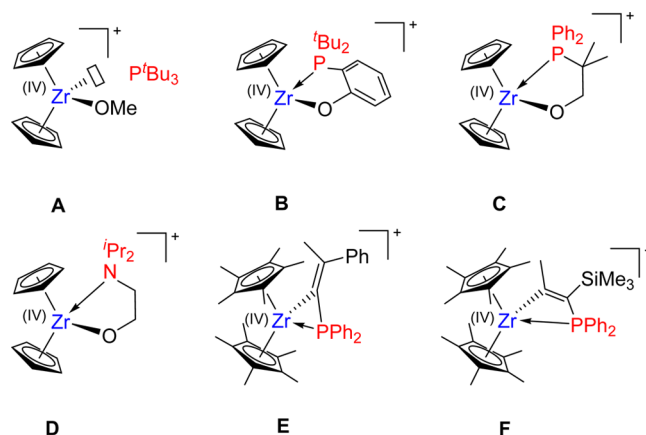
## INTRODUCTION

Frustrated Lewis pairs (FLPs) initially gathered considerable interest due to their potential as transition-metal-free hydrogenation catalysts.<sup>1,2</sup> Exciting new applications of FLPs have since been developed,<sup>3</sup> including catalytic  $\text{CO}_2$  reduction.<sup>4</sup> Organometallic frustrated Lewis pairs (om-FLPs) have recently emerged as a subclass of FLPs with promising properties.<sup>5</sup> These species contain transition metals, mostly as the Lewis acid component,<sup>6</sup> although it was shown that low-valent metals may also be used as Lewis bases.<sup>7</sup>

Lately Stephan, Wass, and Erker have been exploring the FLP behavior of  $d^0$  zirconocene cations (A–F).<sup>6a–c,e,i–n,p</sup> Figure 1 shows representative examples of this useful extension of the FLP concept to transition-metal-based Lewis acids. Some of these systems showed interesting catalytic features, e.g., **B** was reported to catalyze the dehydrogenation of amine boranes with very high turnover frequency,<sup>6c</sup> while **D** is an efficient hydrogenation catalyst.<sup>6n</sup>

There are two ways to synthesize such systems: (i) by protonolysis of  $\text{Cp}^*_2\text{ZrMe}_2$  with an alcohol followed by Me abstraction (A–D) or (ii) by insertion of a functionalized alkyne into the  $\text{Zr}-\text{Me}$  bond of the  $\text{Cp}^*_2\text{ZrMe}^+$  cation (E–F). Both these two methods require prefunctionalized phosphines (or amines), therefore we thought that a methodology using simple secondary phosphines (or amines) to generate analogous systems would be interesting.

In particular we wondered if cationic Zr phosphido (or amido) complexes could undergo formal  $[2 + 2]$  cycloaddition



**Figure 1.** Examples of FLPs with zirconocene cations.  $\text{B}(\text{C}_6\text{F}_5)_4^-$  anion omitted for clarity.

with unsaturated substrates to generate  $\text{Zr}^+/\text{P}$  or  $\text{Zr}^+/\text{N}$  FLPs (Scheme 1).

In this contribution, we report the proof of concept preparation of a new FLP following this approach, along with studies of the structure and fundamental reactivity of  $\text{Cp}_2\text{Zr}=\text{ER}_2^+$  cations ( $\text{E} = \text{N}, \text{P}$ ), including catalytic hydrogenation and  $\text{CO}_2$  activation. Indeed, although neutral Zr

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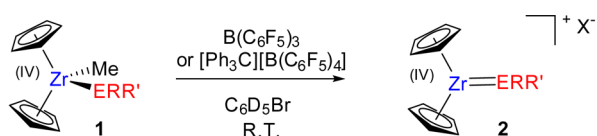
Table 2. Relevant Bond Distances (Å) and Angles (deg) in Compounds 1a–e

	1a	1b	1c <sup>a</sup>	1d	1e	1-P <sup>b</sup>	1-N <sup>c</sup>
Zr–Ct1	2.203	2.208	2.217	2.227	2.268	2.180	2.298
Zr–Ct2	2.213	2.214	2.227	2.233	2.253	2.180	2.313
Ct1–Zr–Ct2	131.7	132.4	127.6	129.0	127.2	127.92	132.82
Zr–Me	2.316(3)	2.319(2)	2.313(2)	2.310(2)	2.304(6)	2.36(6)	2.296(3)
Zr–E	2.553 (1)	2.552(1)	2.735(1)	2.163(1)	2.102(4)	2.629(3)	2.099(2)
Me–Zr–E	101.0(1)	102.9 (1)	99.6(1)	104.2(1)	111.3(2)	97.6(2)	94.1(1)
Σα(E)	358.4	359.5	337.9	357.2	360	349.3	359.9
C21–E–Zr–Ct1 (φ)	–3.8	27.9	49.6	36.6	105.7	–5.2	60.8

<sup>a</sup>Independent molecule a is discussed. <sup>b</sup>Ref 17b. <sup>c</sup>Ref 19.

**Synthesis of the Cationic Complexes.** Cationic complexes **2a,b** and **2d,e** were conveniently prepared *in situ* by reaction of the neutral Zr–Me precursors **1** with 1 equiv of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in C<sub>6</sub>D<sub>5</sub>Br (Scheme 3).<sup>24</sup> Interestingly, reaction of **1c**

Scheme 3



E = P, X<sup>–</sup> = MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>–</sup>

**2a** R = R' = Cy

**2b** R = R' = Mes

E = N, X<sup>–</sup> = MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>–</sup>

**2d** R = R' = Ph

**2e** R = <sup>t</sup>Bu, R' = 3,5-(C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>)

**2e'** X<sup>–</sup> = B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>–</sup>

with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> did not give the expected cationic phosphido complex. Instead, the reaction gave an intractable mixture of products (see Supporting Information).

Evidence for the formation of these species was given by the important downfield shift of the signals observed in the <sup>31</sup>P{<sup>1</sup>H} and <sup>15</sup>N{<sup>1</sup>H} NMR spectra—up to 163.5 ppm for **2a** and 86.3 ppm for **2d**, see Table 1—consistent with much greater interaction of the lone pair of E with Zr.<sup>25</sup> Concomitant formation of the MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>–</sup> anion was also observed, with diagnostic signals in the <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H}, and <sup>19</sup>F{<sup>1</sup>H} NMR spectra of complexes **2** (see Supporting Information). Alternatively, Me abstraction could also be performed with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] for the amido complexes, which gave very similar <sup>1</sup>H NMR signals for the [Zr]<sup>+</sup> moieties.

Since the formation of the cationic complexes was very clean and no degradation was observed in solution over a period of hours (**2a,b**) or days (**2d,e**), we attempted to isolate them. The trityl procedure was used to prepare crystalline **2e'**, while **2d** crystallized with the MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>–</sup> anion. Both these compounds were isolated as air-sensitive solids in 77 and 85% yield, respectively. On the other hand, the phosphido complexes were found to be too reactive for isolation and were used *in situ* for further reactivity studies.

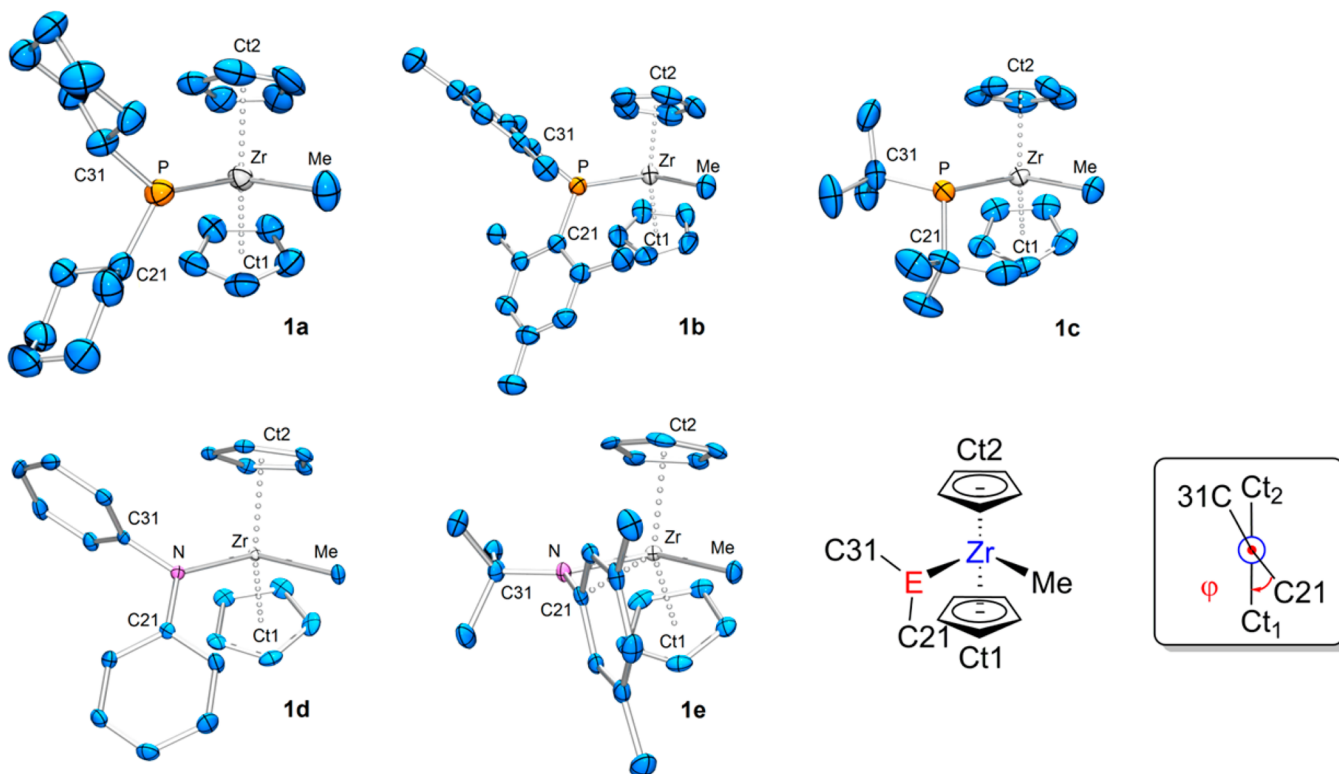
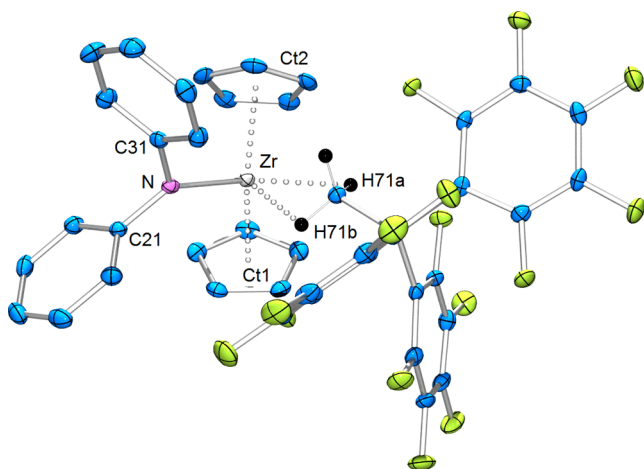


Figure 2. POV-Ray projections of the crystal structures of compounds 1a–e (50% ellipsoids probability) and definition of angle φ.

Single crystal X-ray diffraction analysis of **2d** revealed the solid-state structure of this compound, which consists of an amidozirconocene cation stabilized through electrostatic interactions with the  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  counteranion (Figure 3).<sup>24,26</sup> Two close contacts were found between the Zr center



**Figure 3.** POV-Ray projection of the crystal structure of compound **2d** (50% ellipsoids probability).

and hydrogen atoms of  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  (2.31(2) and 2.40(2) Å). As expected, removal of the Me ligand in **1d** results in much more pronounced  $\pi$  interaction between the Zr and N atoms. The Zr–N distance in **2d** is shorter by 0.075 Å (see Table 3);

**Table 3. Relevant Bond Distances (Å) and Angles (deg) in Compounds **2d** and **2e'****

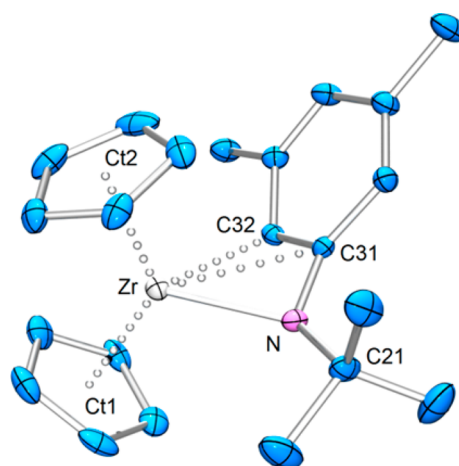
	<b>2d</b>	<b>2e'</b>
Zr–Ct1	2.213	2.222
Zr–Ct2	2.204	2.202
Ct1–Zr–Ct2	127.9	130.2
Zr–N	2.088(2)	2.150(2)
$\Sigma\alpha(\text{N})$	359.8	352.0
C21–N–Zr–Ct1 ( $\varphi$ )	–12.5	–91.4

at 2.088(2) Å it is now halfway between a single (2.25 Å) and a double (1.88 Å) Zr–N bond.<sup>27</sup> Moreover the orientation of the planar  $\text{NPh}_2$  ligand ( $\varphi = -12.5^\circ$ ) is much more favorable to  $p_\pi$ – $d_\pi$  orbital interactions than in **1d**.

The structure of **2e'** is drastically different (Figure 4). No Zr–anion interaction was found; instead the Zr center is stabilized by an interaction with the aromatic ring of the amido ligand. This type of structure is not unprecedented: indeed a similar structure was reported by Norton for compound  $[\text{Cp}_2\text{ZrN}(\text{Ph})\text{CHPh}(\text{CH}_2)_2\text{B}(\text{C}_6\text{F}_5)_3]$  (**2-N**).<sup>9b</sup>

The Zr–N distance in **2e'** is longer than in **1e** by 0.048 Å, and the orientation of the N lone pair ( $\varphi = -91.4^\circ$ ) also precludes  $\pi$  interactions with Zr. Therefore, in the absence of a Me ligand, stabilization of the Zr center occurs by coordination to the C31–C32 double bond (Zr–C31: 2.598(2) Å; Zr–C32: 2.449(2) Å).

Norton reported that compound **2-N** also shows a Zr–Ph interaction in solution, as evidenced by the nonequivalent  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR signals of the coordinated phenyl ring (at low temperature) and the upfield chemical shift of the *ortho* H and C atoms. We did not observe such features in the spectra of **2e/2e'** apart from a significant upfield shift of the *ortho* C from



**Figure 4.** POV-Ray projection of the crystal structure of compound **2e'** (50% ellipsoids probability,  $\text{B}(\text{C}_6\text{F}_5)_4^-$  anion omitted for clarity).

134.9 ppm (**1e**) to 100.8/101.8 ppm (**2e/2e'**). In particular the *ortho* H remained equivalent over the 183–299 K temperature range (see the Supporting Information). Therefore, we conclude that the interaction between Zr and the aromatic ring is not persistent in solution.

Overall, the spectroscopic and X-ray diffraction evidence gathered on complexes **2** indicates that there is a considerable  $\pi$  interaction between Zr and E, provided the E atom substituents are not too bulky (as in the case of **2e/2e'**).

**Catalytic Hydrogenation.** Since the pioneering work of Noyori, it is well-known that metal complexes which possess a ligand with a Lewis basic atom (e.g., N) can activate  $\text{H}_2$  (or a hydrogen donor such as isopropanol) and act as hydrogenation catalysts.<sup>28</sup> Thus, since complexes **2** possess a highly Lewis acidic  $\text{Cp}_2\text{Zr}^+$  center bound to a Lewis basic atom, it was interesting to investigate their behavior in hydrogenation catalysis.

Complexes **2a,b** and **2d,e** were found to catalyze the hydrogenation of cyclohexene (**11**, Figure 5) under mild conditions: 1% loading, room temperature, 1.5 bar of  $\text{H}_2$ , 2 h (entries 2–5, Table 4). Hydrogenation of styrene (**12**) under similar conditions was also effective, giving ethylbenzene (**22a**) in addition to variable amounts of 1,4-diphenylbutane (**22b**) and 1,3-diphenylbutane (**22c**) (entries 6–9). Given the time allowed between the addition of styrene and  $\text{H}_2$  (~20 min), this indicates a weak residual polymerization activity for these complexes.<sup>29</sup> Interestingly, the nature of the ERR' ligand has a strong influence on product distribution, for example **2a** ( $\text{PCy}_2$ ) gives almost exclusively **22a**, while **2b** ( $\text{PMe}_2$ ) affords a roughly 1:1 mixture of **22a** and **22b** (entries 6 and 7).

From the results obtained with **11** and **12**, it became evident that **2a** and **2d** are less active catalysts than **2b** and **2e**. We therefore focused further catalytic studies on the latter. Pentafluorostyrene (**13**) gave poor results even with increased catalyst loading (2%, entries 10 and 11), while 3,3-dimethylbut-1-ene (**14**) and enamine **15** gave complete starting material consumption under similar conditions (entries 12, 13, 15, and 17).<sup>30</sup> The use of **2e'** (generated *in situ* by mixing **1e** and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ) gave identical results (entry 18).

Although the efficient conversion of **15** to **25** seems to imply that nitrogen-containing substrates are well tolerated, imine **16** could not be hydrogenated at all (entries 19 and 20). Finally, diene **17** and alkyne **18** gave satisfactory conversions after 6 h (entries 21–24).



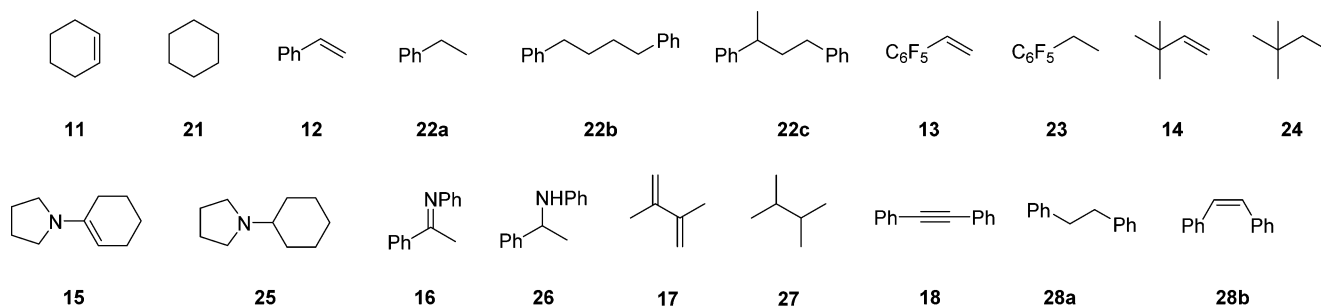


Figure 5. Catalytic hydrogenation substrates (11–18) and products (21–28b).

Table 4. Catalytic Hydrogenation Results<sup>a</sup>

entry	cat.	loading (mol %)	substrate	product	conv. (%)
1	–	–	11	21	0
2	2a	1	11	21	55
3	2b	1	11	21	97
4	2d	1	11	21	55 <sup>b</sup>
5	2e	1	11	21	82 <sup>c</sup>
6	2a	1	12	22a/b/c	60/5/0
7	2b	1	12	22a/b/c	51/43/10
8	2d	1	12	22a/b/c	48/23/7 <sup>b</sup>
9	2e	1	12	22a/b/c	48/43/9 <sup>b</sup>
10	2b	2	13	23	19 <sup>b</sup>
11	2e	2	13	23	20
12	2b	1	14	24	86 <sup>c</sup>
13	2e	1	14	24	65 <sup>c</sup>
14	2a	2	15	25	24
15	2b	2	15	25	100
16	2d	2	15	25	6
17	2e	2	15	25	100
18	2e'	2	15	25	100
19	2b	2	16	26	0
20	2e	2	16	26	0
21	2b	2	17	27	89 <sup>c,d</sup>
22	2e	2	17	27	75 <sup>c,d</sup>
23	2b	2	18	28a/b	92/3 <sup>d</sup>
24	2e	2	18	28a/b	96/2 <sup>d</sup>

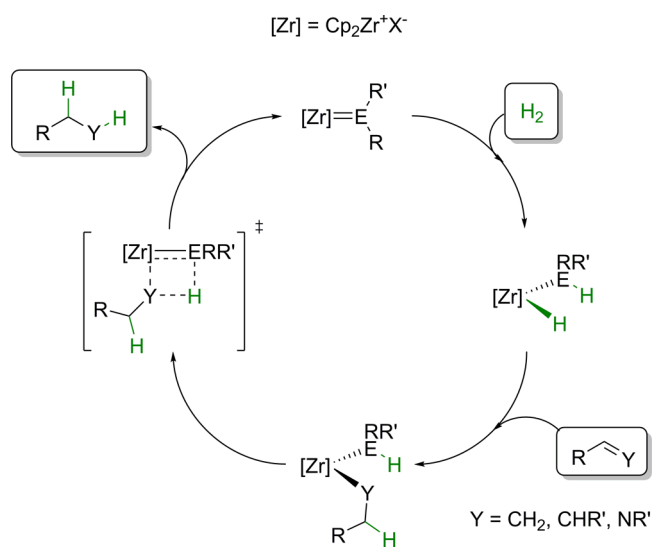
<sup>a</sup>Reagents and conditions: 2 mmol substrate, *x* mol % catalyst, 0.8 mL C<sub>6</sub>D<sub>5</sub>Br, 1.5 bar H<sub>2</sub>, 2 h reaction time. Conversion (average of two runs) determined by integration vs Cp<sub>2</sub>Fe standard. <sup>b</sup>Conversion determined by integration vs starting material. <sup>c</sup>100% conversion of starting material. <sup>d</sup>6 h reaction time.

Following the hypothesis of cooperative H<sub>2</sub> activation across the M=E bond,<sup>31,32</sup> one can draw the catalytic cycle depicted in Scheme 4.

According to this scheme, the unsaturated substrate inserts into the Zr–H bond.<sup>33</sup> This step is followed by product elimination via protonolysis of the Zr–Y bond. Therefore, the low activity (or lack thereof) observed for 13 and 16 could be a result of the lower basicity of the Y ligand compared to other Zr–alkyls (e.g., styryl, cyclohexyl). This could explain for example why enamine 15 is a suitable substrate despite the presence of N, while imine 16 is not.

However, this mechanistic picture remains largely speculative: we did study the stoichiometric reaction of 2b and 2e' with H<sub>2</sub> in the absence of hydrogenation substrate, (see the

Scheme 4. Possible Hydrogenation Mechanism<sup>a</sup>

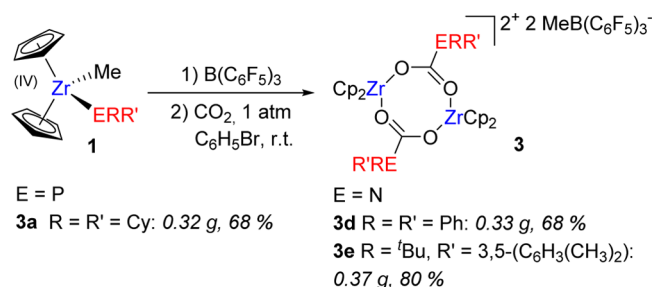


<sup>a</sup>Note: Only olefin-like substrates shown for clarity.

Supporting Information) but several species were observed in both cases and no firm conclusions could be drawn at this stage.

**Reaction with CO<sub>2</sub> and Other Carbonyl Compounds.** The catalytic hydrogenation described above suggested that complexes 2 show nucleophilic reactivity at the pnictogen atom. To confirm this we reacted 2a, 2d, and 2e with CO<sub>2</sub> under mild conditions: room temperature, 1 atm CO<sub>2</sub> (Scheme 5).

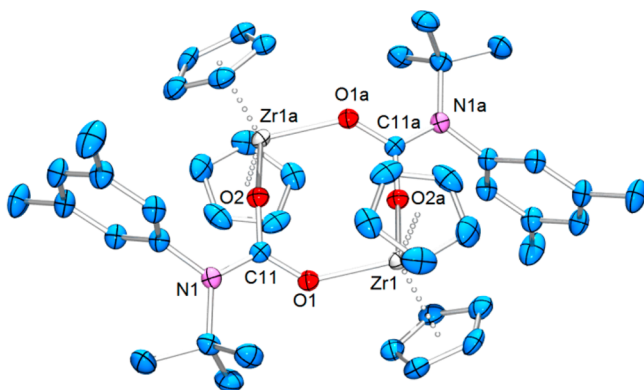
Scheme 5



The homogeneous solutions of 2a and 2e in C<sub>6</sub>H<sub>5</sub>Br reacted almost instantaneously to give a pale suspension, while 2d required 30 min reaction, consistent with the lower Lewis basicity of N in HNPh<sub>2</sub> compared to HN<sup>t</sup>BuAr; compounds 3a, 3d, and 3e were isolated in 68, 68, and 80% yield, respectively.

The solid-state structure of 3e was elucidated by single crystal X-ray diffraction analysis, showing a dimeric structure

with an eight-membered  $(\text{ZrOCO})_2$  core (Figure 6). Bond distances indicate an O–C–O motif with relatively similar



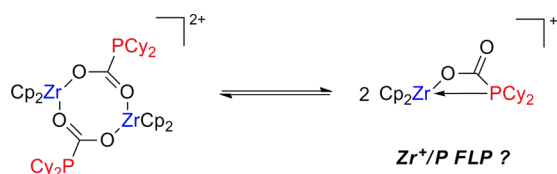
**Figure 6.** POV-Ray projection of the crystal structure of compound **3e** (30% ellipsoids probability,  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  anions omitted for clarity).

$\text{C11-O1}$  and  $\text{C11-O2}$  (1.277(4) vs 1.292(4) Å) bonds. These values are intermediate between those of single and double C–O bonds.<sup>27</sup> Likewise, the  $\text{Zr1-O1}$  and  $\text{Zr1-O2a}$  bonds are quite similar (2.095 vs 2.061(2) Å). Additionally, the  $\text{C11-N1}$  bond is short (1.331(4) Å), and the N atom is trigonal planar ( $\Sigma\alpha = 359.8^\circ$ ). Altogether, these values point to a carbamate ligand with significant  $(\text{Ar}(\text{tBu})\text{N}^+=\text{C}(\text{O}^-)(\text{O}^-))$  character, consistent with the oxophilicity of Zr.

Once isolated, these compounds are scarcely soluble in  $\text{CH}_2\text{Cl}_2$  or  $\text{C}_6\text{H}_5\text{Br}$ , probably as a consequence of their dimeric structure; thus, NMR spectra were recorded in  $d_8$ -THF (**3a**) or  $d_5$ -pyridine (**3d** and **3e**). The  $^{13}\text{C}\{^1\text{H}\}$  chemical shift of the  $\text{CO}_2$  moiety was observed at 168.0 ppm for **3a** ( $^1J_{\text{PC}} = 40.4$  Hz), at 160.7 ppm for **3d**, and 162.7 ppm for **3e**. The  $^{31}\text{P}\{^1\text{H}\}$  chemical shift of **3a** (12.1 ppm) is consistent with an O-bridged dimer with a pendant phosphine, rather than a P-bridged dimer.<sup>34</sup> The FTIR spectra showed C=O absorption bands at 1759 (**3a**), 1761 (**3d**), and 1757 (**3e**)  $\text{cm}^{-1}$ , respectively.<sup>35</sup>

Despite the wealth of studies on metal phosphido complexes, the insertion of  $\text{CO}_2$  into M–PR<sub>2</sub> bonds has only been reported in three instances (M = Hf, Mo, W),<sup>34,36</sup> therefore we were intrigued by compound **3a**. As suggested by the observed low field  $^{31}\text{P}\{^1\text{H}\}$  NMR signal (*vide supra*) and by the lower tendency of P for lone pair delocalization into the  $\text{CO}_2$  moiety,<sup>34</sup> we reasoned that this complex could potentially act as a  $\text{Zr}^+/\text{P}$  FLP, or as a  $\text{Zr}^+/\text{P}$  ambiphilic ligand, in its monomeric form (Scheme 6).

#### Scheme 6



However, reacting **3a** with 2 equiv of  $\text{PhCHO}$  or  $[\text{Pd}(\text{C}_6\text{H}_5)_2\text{Cl}]_2$  in  $\text{CD}_2\text{Cl}_2$  gave complex mixtures. By contrast, reaction with 2 equiv of chalcone afforded complex **4a** along with another, as yet nonidentified compound; **4a** was also obtained (albeit more cleanly) by reacting **2a** with 2 equiv of chalcone (Scheme 7). After isolation, **4a** was characterized by

NMR and FTIR spectroscopy, elemental analysis and high-resolution mass spectrometry (see the Supporting Information).

The  $^1\text{H}$  NMR spectrum of **4a** indicates a  $\text{C}_2$ -symmetric structure, which could result from a stereoselective sequence of either (i) two 1,2- additions or (ii) two 1,4-additions of  $\text{Zr}^+/\text{P}$  compounds onto chalcone. The signature  $^{13}\text{C}\{^1\text{H}\}$  NMR signals of the chalcone moiety at 92.3 ppm ( $^2J_{\text{PC}} = 7.1$  Hz) and 42.3 ppm ( $^1J_{\text{PC}} = 34.1$  Hz) indicate that two 1,4 additions took place; indeed we have previously reported similar 1,4-addition of  $\text{M}^+/\text{P}$  onto chalcone (M = Ti, Zr).<sup>6i,o</sup> It became evident that the other compound observed along with **4a** was an intermediate and that the reaction needed 2 equiv of chalcone per Zr in order to proceed to completion. Indeed, when we reacted **3a** with 4 equiv of chalcone we obtained almost exclusively **4a**.

Given the fast reaction of **2a** with  $\text{CO}_2$  and the fact that we never observed any traces of **2a** in solutions of **3a**,<sup>37</sup> it seems highly unlikely that a pre-equilibrium involving **2a** would take place prior to reaction of **3a** with chalcone. Instead, an FLP-like behavior of monomeric **3a** to generate intermediate **5a** seems more likely; although we could not isolate the second compound present in the reaction mixture of **3a** with 2 equiv of chalcone, the  $^1\text{H}$  NMR spectrum indicates that one chalcone moiety is present and its  $^{31}\text{P}\{^1\text{H}\}$  signal (30.0 ppm) is in the range of other phosphonium enolates reported in this paper. Therefore, we assume that this compound is **5a**.

On the other hand, the direct reaction of **2a** with chalcone did not proceed through a detectable intermediate: when 1 equiv of chalcone was used, a 1:1 mixture of **2a** and **4a** was obtained. It seems reasonable to postulate a reaction pathway going through intermediate **6a**; this complex would then react with a further equivalent of chalcone in an FLP-like manner.

We wondered if this scheme could be generalized to generate  $\text{Zr}^+/\text{E}$  FLPs by reaction of carbonyl compounds with complexes **2** (Scheme 1). We first tested this hypothesis with chalcone, but only complex mixtures resulted (except for **2a**).

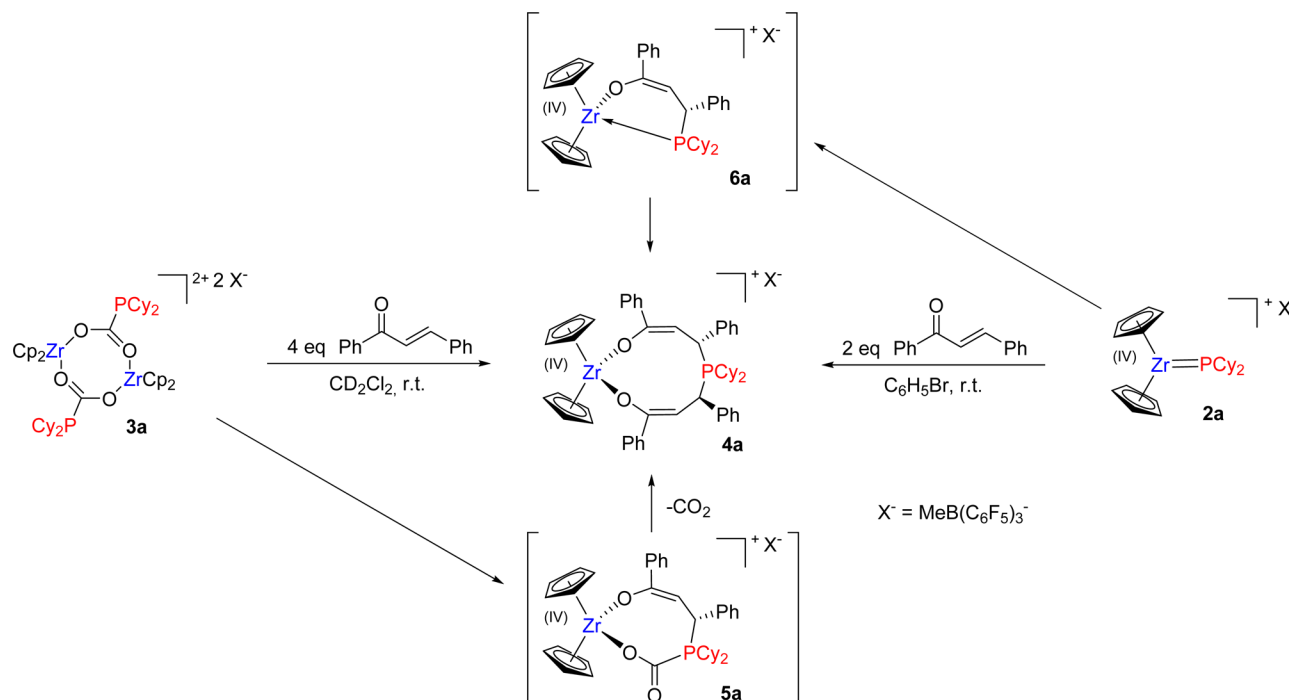
We next turned our attention to benzaldehyde. For **2a,b** and **2e**, the reactions with 1 or 2 equiv resulted in complex mixtures; however, a cleaner reaction was observed when **2d** was reacted with 2 equiv of benzaldehyde. Initially the reaction mixture was complex, but then it evolved to give a single major product, as evidenced by the single Cp signal in the  $^1\text{H}$  NMR spectrum. After workup and salt metathesis with  $\text{NaBAr}^{\text{F}}_4$  ( $\text{Ar}^{\text{F}} = 3,5\text{-}(\text{C}_6\text{H}_3(\text{CF}_3)_2)$ ) compound **7d** was isolated in 45% yield (Scheme 8).

Single crystal X-ray diffraction analysis revealed the structure of this compound in which the  $\text{Cp}_2\text{Zr}^+$  fragment is coordinated to  $\text{Ph}(\text{CO})\text{NPh}_2$  and  $\text{PhCH}_2\text{O}^-$  ligands (Figure 7).

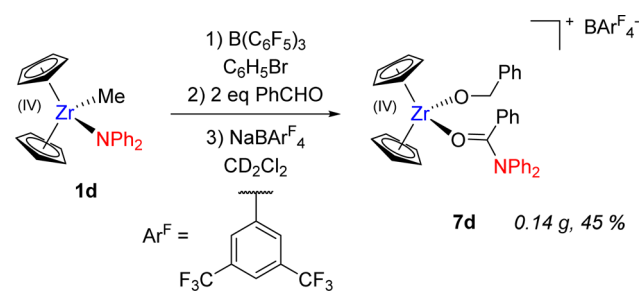
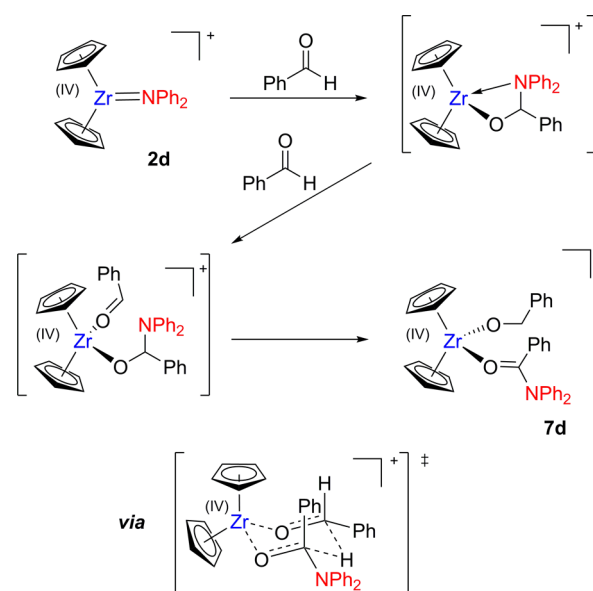
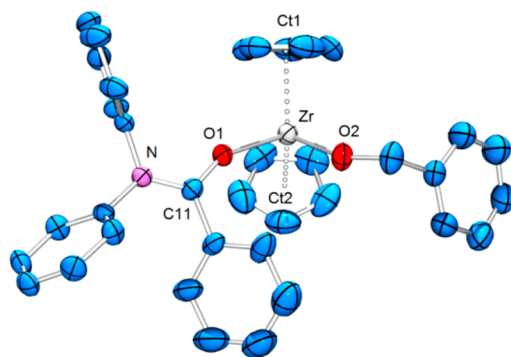
Multinuclear NMR spectroscopy confirmed the structure of **7d**; in particular the  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  shows the presence of a singlet at 5.05 ppm with an integration of two, which corresponds to the benzylic hydrogens. Interestingly, the high-resolution mass spectrum of **7d** principally gave two clusters of peaks: one at 600.14746 Da corresponding to the cationic part of **7d**, and the other at 510.10051 Da corresponding to the replacement of the benzylate ligand by  $\text{OH}^-$ . This suggests that the amide ligand binds more strongly to Zr than the benzylate.

A possible mechanism for the formation of **7d** is shown in Scheme 9: according to this mechanism, initial benzaldehyde insertion would be followed by hydride transfer to a second

Scheme 7. Formation of Compound 4a Starting From 2a or 3a, along with Possible Intermediates



Scheme 8

Scheme 9. Formation of 7d via a MPV-Type Mechanism<sup>a</sup><sup>a</sup>Note: Anions omitted for clarity.Figure 7. POV-Ray projection of the crystal structure of 7d (30% ellipsoids probability,  $\text{BARF}_4^-$  anion omitted for clarity).

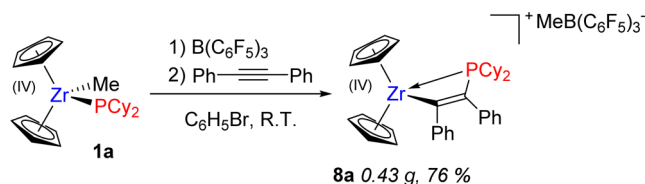
benzaldehyde moiety via a transition state akin to that of the Meerwein Ponndorf Verley (MPV) reduction.<sup>38</sup>

**Synthesis and Reactivity of a Zr/P FLP.** We had originally envisioned exploiting the reactivity of complexes **2** to prepare new FLPs (Scheme 1). The reactions of **2** with carbonyl compounds ( $\text{CO}_2$ , chalcone) described above indeed suggested that insertion of unsaturated substrates into the Zr–E bond is a suitable entry into FLP chemistry, but the elusive nature of the species thus generated (**6a**, monomeric **3a**) called

for another approach. We therefore reacted diphenylacetylene with **2a,b** and **2d,e** in the hope that the formed products would be more stable.<sup>39</sup> While **2d,e** did not react and **2b** gave an unidentified mixture, **2a** reacted cleanly in  $\text{C}_6\text{D}_5\text{Br}$  to give a new species with a  $^{31}\text{P}\{^1\text{H}\}$  signal at  $-12.4$  ppm.<sup>40</sup> Complex **8a** was obtained on preparative scale in 76% yield (Scheme 10) and was characterized by elemental analysis and multinuclear NMR spectroscopy.

A distinctive feature of the  $^1\text{H}$  NMR spectrum of **8a** is the presence of a small coupling constant (0.7 Hz) between the Cp hydrogens and the P atom, indicative of a residual Zr/P interaction despite the insertion of diphenylacetylene. Note-

Scheme 10



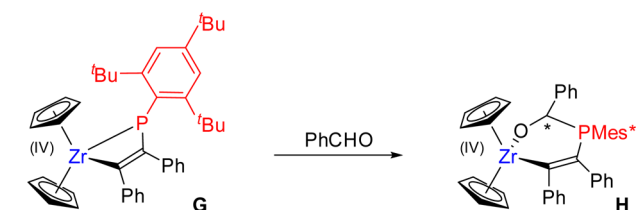
worthy, the reactivity of **2a** resembles that of terminal phosphinidenes, which typically undergo [2 + 2] cycloadditions with alkynes.<sup>41</sup> This analogy highlights the double bond character of the Zr–P interaction in **2a**; by contrast, the neutral precursor **1a** did not react with diphenylacetylene.

Although **8a** is stable in  $\text{C}_6\text{D}_5\text{Br}$ , it degrades after a few hours in the solid state, even when stored at  $-35^\circ\text{C}$ . However, it can be conveniently prepared *in situ*, and this method was used to assess its reactivity with typical FLP substrates. Thus, reaction with benzaldehyde, ferrocene carboxaldehyde, chalcone, and  $\text{CO}_2$  afforded compounds **9a** to **12a** (Scheme 11). All reactions proceeded to completion at room temperature with 100% selectivity. Compounds **9a** to **11a** were isolated and characterized by elemental analysis, NMR (in  $\text{CD}_2\text{Cl}_2$ ) and FTIR spectroscopy, and high-resolution mass spectrometry. Compound **12a** could only be characterized by NMR spectroscopy (in  $\text{C}_6\text{D}_5\text{Br}$ ) due to its labile nature.

Reaction with benzaldehyde afforded the 1,2 addition complex **9a**. This compound was obtained in 75% yield after workup. The  $^{31}\text{P}\{^1\text{H}\}$  spectrum gives a singlet at 27.0 ppm. A characteristic doublet is observed at 6.40 ppm in the  $^1\text{H}$  spectrum for the CHO hydrogen ( $^2J_{\text{PH}} = 3.4$  Hz) and the Cp hydrogens now resonate as two separate singlets (6.36 and 6.34 ppm) due to the chirality of the aldehyde carbon atom. The ESI mass spectrum of **9a** shows clearly the Zr cation (701.24989 Da) along with a small cluster of peaks corresponding to the cation of **8a** (595.20764 Da).

Noteworthy, the reactivity of **8a** is reminiscent of that of the neutral phosphido complex **G** with carbonyl compounds, as reported by Stephan et al. (Scheme 12).<sup>41b,c</sup> They reported the system **G** adding, e.g., acetone to give the respective six-membered heterocyclic carbonyl insertion product into the Zr–

Scheme 12



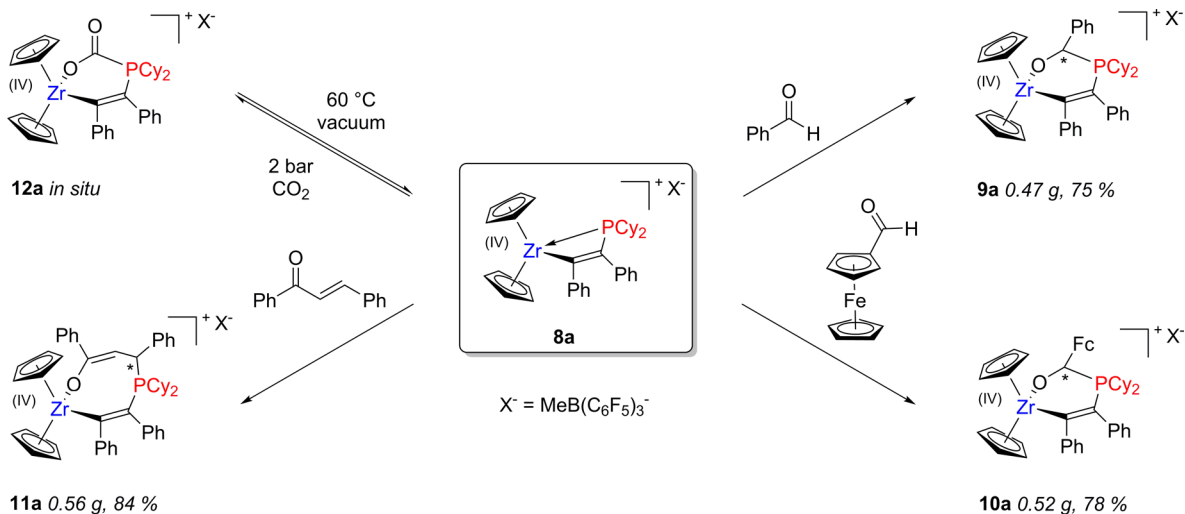
P bond. Subsequent treatment with benzaldehyde found the acetone addition reaction reversible and eventually gave complex **H**. The authors discussed a possible [4 + 2] cycloaddition pathway for this transformation.

Reaction of **8a** with ferrocene carboxaldehyde (FcCHO) also gave 1,2-addition, and compound **10a** was isolated in 78% yield. A singlet at 27.2 ppm was observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy, while the CHO hydrogen resonates as a singlet at 5.95 ppm in the  $^1\text{H}$  NMR spectrum. As in the case of **9a** the Cp rings bound to Zr are nonequivalent (6.43 and 6.38 ppm), and those bound to Fe are visible at lower field as a cluster of three multiplets (FeCpCHO: 4.47–4.33 ppm region) and one singlet (FeCp: 4.27 ppm). The ESI mass spectrum shows the Zr cation of **10a** (809.21593 Da) along with that of **8a** (595.20709 Da) and ferrocene (III) carboxaldehyde (214.00769 Da).

Single crystals suitable for X-ray diffraction analysis were obtained after salt metathesis with  $\text{KB}(\text{C}_6\text{F}_5)_4$  in  $\text{CD}_2\text{Cl}_2$ , thus confirming the structure derived from spectroscopic data (compound **10a'**, Figure 8).<sup>42</sup>

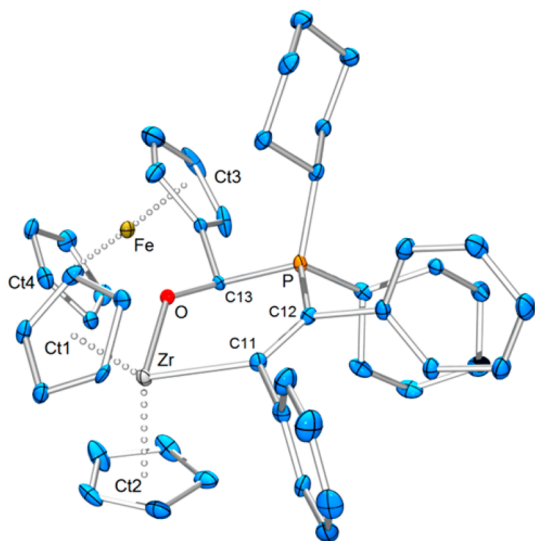
The C11–C12 distance (1.352(4) Å) is consistent with a C=C double bond.<sup>27</sup> The main feature of the Zr cation is the presence of two metallocene systems with bent (Ct1–Zr–Ct2:  $131.9^\circ$ ) and linear geometries (Ct3–Fe–Ct4:  $176.9^\circ$ ). Interestingly the Fe–O distance (3.569(4) Å) is well below the sum of van der Waals radii of both atoms (3.94 Å).<sup>23</sup> This interaction could explain the difference in hybridization for the O atom between **10a'** and **11a'** (*vide infra*): indeed the Zr–O–C13 angle in **10a'** ( $134.7(4)^\circ$ ) considerably deviates from linearity.

While the reactions with aldehydes show that **8a** can activate carbonyl compounds by 1,2-addition, reaction with chalcone

Scheme 11. Reactivity of FLP **8a**<sup>a</sup>

<sup>a</sup>Note: all reactions performed at room temperature in  $\text{C}_6\text{H}_5\text{Br}$  or  $\text{C}_6\text{D}_5\text{Br}$ .

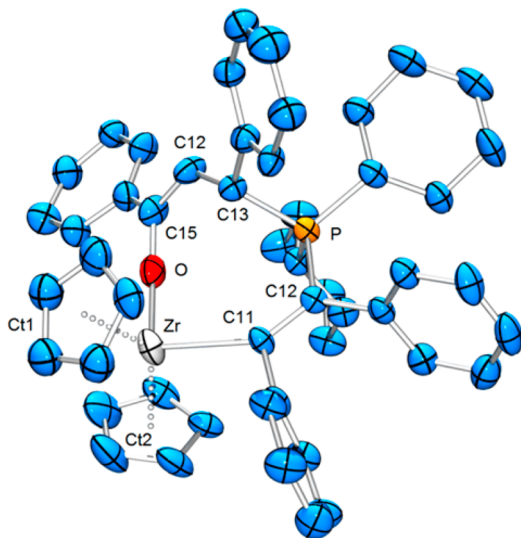




**Figure 8.** POV-Ray projection of the crystal structure of **10a'** (30% ellipsoids probability,  $B(C_6F_5)_4^-$  anion omitted for clarity).

resulted in 1,4-addition. Compound **11a** was obtained in 84% yield after workup. A singlet at 28.5 ppm is observed in the  $^{31}P\{^1H\}$  NMR spectrum. As in the case of **9a** and **10a**, nonequivalent Cp ligands are also observed by  $^1H$  NMR spectroscopy (6.39 and 6.32 ppm), and the typical pattern of  $Zr^+/P$  1,4-addition is diagnosed by  $^{13}C\{^1H\}$  NMR spectroscopy: the carbon  $\alpha$  to P resonates at 45.3 ppm ( $^1J_{PC} = 35.5$  Hz) and the  $\beta$  carbon at 95.8 ( $^2J_{PC} = 8.2$  Hz).

Compound **11a** gave crystals suitable for X-ray diffraction analysis after salt metathesis with  $NaBAR_4^F$  in  $CD_2Cl_2$  (compound **11a'**, Figure 9).<sup>42</sup> The structure of **11a'** reveals



**Figure 9.** POV-Ray projection of the crystal structure of **11a'** (30% ellipsoids probability,  $BAR_4^F^-$  anion omitted for clarity).

an eight-membered Zr macrocycle with two double bonds: C11–C12 (1.369(8) Å) and C14–C15 (1.333(10) Å). The high value of the Zr–O–C15 angle (160.8(5)°) indicates partial  $sp$  hybridization of the O atom.

Finally, **8a** reacted with  $CO_2$ , although in this case the product was unstable and released  $CO_2$  upon workup or when heated under vacuum. Therefore, **12a** was characterized

spectroscopically. A singlet at 6.00 ppm (vs 6.23 ppm for **8a**) corresponding to the Cp rings was observed by  $^1H$  NMR spectroscopy, indicating clean formation of a new species. This was confirmed by the presence of a single signal at 20.6 ppm (vs –12.4 ppm for **8a**) in the  $^{31}P\{^1H\}$  spectrum. Definitive evidence for the formation of a  $CO_2$  adduct came in the shape of a new doublet at 162.6 ppm ( $^1J_{PC} = 37.7$  Hz) in the  $^{13}C\{^1H\}$  NMR spectrum.

## CONCLUSION

We have presented a wide-ranging experimental study of a new class of cationic Zr amido and phosphido complexes (**2**) that possess a very reactive Zr–E bond (E = N, P). X-ray diffraction studies of the amido complexes indicate that the Zr center may be stabilized by  $\pi$  donation from the amido ligand, depending on the size of the substituents on N. For the phosphido complexes, spectroscopic evidence and reactivity with diphenylacetylene also suggest considerable  $\pi$  interaction between Zr and P. Reactivity studies conducted with both classes of complexes showed that the E atom possesses a marked nucleophilic character. Coupled with the strong Lewis acid properties of the  $Cp_2Zr^+$  fragment, this feature enables the activation of  $CO_2$  and  $H_2$  in a cooperative fashion. As a notable consequence, complexes **2** are rather active hydrogenation catalysts under very mild conditions.

An interesting application of the phosphido complexes is the expedient synthesis of  $Zr^+/P$  FLPs. This concept was illustrated by the preparation of a new FLP (**8a**) by formal [2 + 2] cycloaddition with diphenylacetylene. If extended, this methodology would have the advantage of using commercially available precursors (secondary phosphines, alkynes) and could be a powerful tool for the synthesis of FLPs with controlled steric and electronic properties.

## EXPERIMENTAL SECTION

For general information and the spectroscopic and structural data of the new compounds see the Supporting Information.

**Preparation of Compound 1a.**  $Cp_2ZrMeCl$  (1.996 g, 7.3 mmol) and  $LiPCy_2$  (1.654 g, 7.3 mmol) were dissolved separately in THF (20 and 30 mL respectively). Both solutions were cooled to ca.  $-80^\circ C$ , and the phosphide solution was added to zirconium by cannula transfer. Immediate color change was observed. The cold bath was removed after 5 min, and the solution was stirred for 45 min, then evaporated to dryness. The residue was taken up in toluene (20 mL) and filtered over Celite, then concentrated under vacuum to ca. 5 mL. Pentane (80 mL) was added, and a precipitate appeared. The suspension was sonicated briefly, agitated at ca.  $-80^\circ C$  for 10 min, filtered with a borosilicate filter mounted on a cannula stick, rinsed twice with 15 mL of pentane, and dried *in vacuo* to give complex **1a** as a yellow powder (2.69 g, 85% yield). Complex **1a** is stable in the solid state but slowly decomposes in solution. Crystals suitable for X-ray single crystal structure analysis were grown by diffusion of pentane into a toluene solution of **1a**. Elemental Analysis: calcd for  $C_{23}H_{35}PZr$ : C, 63.69; H, 8.13. Found: C, 63.27; H, 7.97.

**Preparation of Compound 1b.**  $Cp_2ZrMeCl$  (1.088 g, 4.0 mmol) and  $LiPMes_2(OEt)_2$  (1.342 g, 4.0 mmol) were dissolved separately in THF (10 and 15 mL respectively). Both solutions were cooled to ca.  $-80^\circ C$ , and the phosphide solution was added to zirconium by cannula transfer. Immediate color change was observed. The cold bath was removed after 5 min, and the solution was stirred for 45 min, then evaporated to dryness. The residue was taken up in toluene (10 mL) and filtered over Celite, then concentrated under vacuum to ca. 1 mL. Pentane (20 mL) was added, and a precipitate appeared. The suspension was sonicated briefly, agitated at ca.  $-70^\circ C$  for 10 min, filtered with a borosilicate filter mounted on a cannula stick, rinsed twice with 10 mL of pentane, and dried *in vacuo* to give complex **1b** as

a red-orange powder (1.37 g, 67% yield). The material thus prepared contained small amounts of impurities (mostly free PHMe<sub>2</sub>); an analytically pure sample was prepared in low yield by recrystallization from toluene/pentane. Crystals suitable for X-ray single crystal structure analysis were grown by diffusion of pentane into a toluene solution of **1b**. Elemental Analysis: calcd for C<sub>29</sub>H<sub>35</sub>PZr: C, 68.87; H, 6.97. Found: C, 68.50; H, 7.05.

**Preparation of Compound 1c.** Cp<sub>2</sub>ZrMeCl (1.088 g, 4.0 mmol) and LiP<sup>t</sup>Bu<sub>2</sub>(OEt)<sub>2</sub> (0.727 g, 4.0 mmol) were dissolved separately in THF (10 and 7 mL respectively). Both solutions were cooled to ca. -80 °C, and the phosphide solution was added to zirconium by cannula transfer. Immediate color change to deep blue was observed. The cold bath was removed after 5 min, and the solution was stirred for 45 min, then evaporated to dryness. The residue extracted with three 15 mL portions of pentane and filtered over Celite, then concentrated under vacuum to ca. 20 mL. The solution was stirred at ca. -80 °C for 10 min, filtered with a borosilicate filter mounted on a cannula stick, rinsed twice with 5 mL of pentane, and dried *in vacuo* to give complex **1c** as a deep blue powder (0.94 g, 61% yield). The material thus prepared was ca. 90% pure based on integration of the <sup>1</sup>H NMR signals in the Cp region (the main impurity was presumably [Cp<sub>2</sub>ZrMe]<sub>2</sub>O); filtration and recrystallization from pentane afforded somewhat cleaner material (ca. 95%), although the μ-oxo impurity remained. Crystals suitable for X-ray single crystal structure analysis were grown by cooling a saturated pentane solution of **1c** at -35 °C. Elemental Analysis: calcd for C<sub>19</sub>H<sub>31</sub>PZr: C, 59.79; H, 8.19. Found: C, 57.60; H, 8.22.

**Preparation of Compound 1d.** Cp<sub>2</sub>ZrMeCl (2.175 g, 8.0 mmol) and diphenylamine (1.354 g, 8.0 mmol) were dissolved separately in THF (20 mL each). Both solutions were cooled to ca. -80 °C, and a 1.6 M solution of <sup>t</sup>BuLi in hexane (5.0 mL, 8 mmol) was added to diphenylamine. The mixture was removed from the cold bath and warmed up to room temperature over 30 min. Upon cooling again to -80 °C the lithium amide solution was added to zirconium by cannula transfer. A yellow color was observed. The cold bath was removed after 5 min, and the solution was stirred for 30 min, then evaporated to dryness. The residue was taken up in toluene (30 mL) and filtered over Celite, then concentrated under vacuum to ca. 5 mL. Pentane (50 mL) was added, and a precipitate appeared. The suspension was stirred at -70 °C for 10 min, filtered with a borosilicate filter mounted on a cannula stick, rinsed twice with 10 mL of pentane, and dried *in vacuo* to give complex **1d** as a yellow-orange powder (2.42 g, 75% yield). Crystals suitable for X-ray single crystal structure analysis were grown by diffusion of pentane into a toluene solution of **1d**. Elemental Analysis: calcd for C<sub>23</sub>H<sub>23</sub>NZr: C, 68.27; H, 5.73; N, 3.46. Found: C, 67.88; H, 5.59; N, 3.58.

**Preparation of Compound 1e.** Cp<sub>2</sub>ZrMeCl (1.730 g, 6.37 mmol) and *N*-*tert*-butylaniline (1.13 g, 6.37 mmol) were dissolved separately in THF (20 mL each). Both solutions were cooled to ca. -80 °C, and a 1.6 M solution of <sup>t</sup>BuLi in hexane (4.0 mL, 6.37 mmol) was added to *N*-*tert*-butylaniline. The mixture was removed from the cold bath and warmed up to room temperature over 30 min. Upon cooling again to -80 °C the lithium amide solution was added to zirconium by cannula transfer. An orange color was observed. The cold bath was removed after 5 min, and the solution was stirred for 30 min, during which time it turned orange-green, then evaporated to dryness. The residue was taken up in toluene (30 mL) and filtered over Celite, then concentrated under vacuum to ca. 5 mL. Pentane (50 mL) was added, and a precipitate appeared. The suspension was stirred at -70 °C for 10 min, filtered with a borosilicate filter mounted on a cannula stick, rinsed twice with 10 mL of pentane, and dried *in vacuo* to give complex **1e** as an olive green powder (1.50 g, 57% yield). The material thus obtained was suitable for synthesis, although small quantities pure enough for elemental analysis were obtained by recrystallization from pentane at -35 °C. Crystals suitable for X-ray single crystal structure analysis were grown by cooling a saturated pentane solution of **1e** to -35 °C. Elemental Analysis: calcd for C<sub>23</sub>H<sub>31</sub>NZr: C, 66.93; H, 7.57; N, 3.39. Found: C, 66.74; H, 7.66; N, 3.34.

**In Situ Characterization of Complex 2a.** In an Ar glovebox, complex **1a** (43.4 mg, 0.1 mmol) and tris(pentafluorophenyl)-borane

(51.2 mg, 0.1 mmol) were dissolved in C<sub>6</sub>D<sub>5</sub>Br (0.8 mL) in an NMR tube. The tube was flame-sealed and the compound immediately characterized by NMR spectroscopy. The compound decomposes slowly over days in solution.

**In Situ Characterization of Complex 2b.** In an Ar glovebox, complex **1b** (50.6 mg, 0.1 mmol) and tris(pentafluorophenyl)-borane (51.2 mg, 0.1 mmol) were dissolved in C<sub>6</sub>D<sub>5</sub>Br (0.8 mL) in a J-Young NMR tube. The compound immediately characterized by NMR spectroscopy. The compound decomposes slowly over days in solution.

**Preparation of Complex 2d.** In an Ar glovebox, complex **1d** (101 mg, 0.25 mmol) and tris(pentafluorophenyl)borane (128 mg, 0.25 mmol) were dissolved in C<sub>6</sub>H<sub>5</sub>Br (1.5 mL). The reaction mixture was precipitated by addition to 25 mL of vigorously stirred pentane. A yellow solid precipitated, which was filtered and rinsed with plenty of pentane. The extremely air-sensitive product was dried quickly under vacuum, giving **2d** as a yellow powder (177 mg, 77% yield) which was stored at -35 °C in the glovebox. The compound is stable over days in solution. Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of heptane into a chlorobenzene solution of **2d** at room temperature. Elemental Analysis: calcd for C<sub>41</sub>H<sub>23</sub>BF<sub>15</sub>NZr: C, 53.72; H, 2.53; N, 1.53. Found: C, 53.75; H, 2.66; N, 1.50.

**In Situ Characterization of Complex 2e.** In an Ar glovebox, complex **1e** (41.3 mg, 0.1 mmol) and tris(pentafluorophenyl)-borane (51.2 mg, 0.1 mmol) were dissolved in C<sub>6</sub>D<sub>5</sub>Br (0.8 mL) in an NMR tube, resulting in a green solution of **2e**. The tube was flame-sealed and the compound immediately characterized by <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, and <sup>19</sup>F NMR spectroscopy. The experiment was repeated on 0.5 mmol scale in 1 mL C<sub>6</sub>D<sub>5</sub>Br for <sup>15</sup>N NMR spectroscopic characterization. The compound is stable over days in solution.

**Preparation of Complex 2e'.** In an Ar glovebox, complex **1d** (103 mg, 0.25 mmol) and trityl tetrakis(pentafluorophenyl)-borate (231 mg, 0.25 mmol) were dissolved in C<sub>6</sub>H<sub>5</sub>Br (1.5 mL). The reaction mixture was precipitated by addition to 25 mL of vigorously stirred pentane. A sticky green solid precipitated, which turned into a powder upon discarding the supernatant solution and triturating in pentane. After filtration and rinsing with pentane, the extremely air-sensitive product was dried quickly under vacuum, giving **2e'** as a green powder (217 mg, 85% yield), which was stored at -35 °C in the glovebox. The compound is stable over days in solution in CD<sub>2</sub>Cl<sub>2</sub>. Material suitable for elemental analysis was obtained by removing small amounts of paramagnetic impurities by trituration in toluene followed by rinsing with pentane and drying under vacuum. Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of heptane into a chlorobenzene solution of **2e'** at room temperature. Elemental Analysis: calcd for C<sub>46</sub>H<sub>28</sub>BF<sub>20</sub>NZr: C, 51.31; H, 2.62; N, 1.30. Found: C, 49.84; H, 2.49; N, 1.11.

**Preparation of Complex 3a.** In an Ar glovebox, complex **1a** (217 mg, 0.5 mmol) and tris(pentafluorophenyl)borane (256 mg, 0.5 mmol) were mixed in C<sub>6</sub>H<sub>5</sub>Br (5 mL). The red mixture was placed into a Schlenk vessel, evacuated, and exposed to a CO<sub>2</sub> atmosphere. A precipitate appeared almost immediately, which was filtered after addition of pentane (15 mL), rinsed with pentane and dried *in vacuo*. Complex **3a** was obtained as a white powder (320 mg, 68%). Elemental Analysis: calcd for C<sub>84</sub>H<sub>70</sub>B<sub>2</sub>F<sub>30</sub>O<sub>4</sub>P<sub>2</sub>Zr<sub>2</sub>: C, 50.97; H, 3.56. Found: C, 50.93; H, 3.38. IR (KBr): 1759 (w, C=O).

**Preparation of Complex 3d.** In an Ar glovebox, complex **1d** (202 mg, 0.5 mmol) and tris(pentafluorophenyl)borane (256 mg, 0.5 mmol) were mixed in C<sub>6</sub>H<sub>5</sub>Br (5 mL). The pale brown mixture was placed into a Schlenk vessel, evacuated, and exposed to a CO<sub>2</sub> atmosphere. A precipitate appeared over 30 min, which was filtered after addition of pentane (30 mL), rinsed with pentane, and dried *in vacuo*. Complex **3d-I** was obtained as a pink powder (329 mg, 68%). Elemental Analysis: calcd for C<sub>84</sub>H<sub>46</sub>B<sub>2</sub>F<sub>30</sub>N<sub>2</sub>O<sub>4</sub>Zr<sub>2</sub>: C, 52.51; H, 2.41; N, 1.46. Found: C, 51.97; H, 2.32; N, 1.32. IR (KBr): 1761 (br, m, C=O) cm<sup>-1</sup>.

**Preparation of Complex 3e.** In an Ar glovebox, complex **1e** (206 mg, 0.5 mmol) and tris(pentafluorophenyl)borane (256 mg, 0.5 mmol) were mixed in C<sub>6</sub>H<sub>5</sub>Br (5 mL). The green mixture was placed into a Schlenk vessel, evacuated, and exposed to a CO<sub>2</sub> atmosphere. A

precipitate appeared almost immediately, which was filtered after addition of pentane (15 mL), suspended in  $\text{CH}_2\text{Cl}_2$ /pentane, rinsed with pentane, and dried *in vacuo*. Complex **3e** was obtained as a pale pink powder (370 mg, 80%). Single crystals suitable for X-ray diffraction were grown by diffusion of pentane into a saturated solution of **3e** in  $\text{CH}_2\text{Cl}_2$  at room temperature. Elemental Analysis: calcd for  $\text{C}_{84}\text{H}_{62}\text{B}_2\text{F}_{30}\text{N}_2\text{O}_4\text{Zr}_2$ : C, 52.07; H, 3.23; N, 1.45. Found: C, 50.63; H, 3.08; N, 1.38. IR (KBr): 1757 (m, C=O).

**Preparation of Complex 4a.** In an Ar glovebox, complex **1a** (217 mg, 0.5 mmol) and tris(pentafluorophenyl)borane (256 mg, 0.5 mmol) were dissolved in  $\text{C}_6\text{H}_5\text{Br}$  (1.5 mL). The solution was added to *trans*-chalcone (208 mg, 1 mmol), and the mixture was stirred for 30 min, then added to 50 mL of pentane. The resulting yellow oil was washed three times with 5 mL of pentane and dried *in vacuo* outside the box. This operation was repeated two more times until a yellow powder was obtained. Finally, the powder was triturated in 20 mL of pentane, and the supernatant was filtered off. Complex **4a** was obtained as a yellow powder (0.49 g, 72%) containing 100 mol % of pentane. This compound was also obtained and characterized *in situ* by reacting **3a** with 2–4 equiv of chalcone in  $\text{CD}_2\text{Cl}_2$ . Elemental Analysis: calcd for  $\text{C}_{71}\text{H}_{59}\text{BF}_{15}\text{O}_2\text{PZr}(\text{C}_5\text{H}_{12})$ : C, 63.64; H, 4.99. Found: C, 62.59; H, 5.01. HRMS (ESI-pos): calcd for  $\text{C}_{52}\text{H}_{56}\text{O}_2\text{PZr}[\text{M}-\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ : 833.30595. Found: 833.30682 (rel. ab. 100%, + 1.0 ppm).

**Preparation of Complex 7d.** In an Ar glovebox, complex **1d** (81 mg, 0.2 mmol) and tris(pentafluorophenyl)borane (256 mg, 0.5 mmol) were mixed in  $\text{C}_6\text{H}_5\text{Br}$  (2 mL). Benzaldehyde (42.4 mg, 0.2 mmol) was added to the reaction mixture, and the solution was stirred for 36 h, during which a color change from red to green was observed. The reaction mixture was added to 15 mL of vigorously stirred pentane, causing the precipitation of a green oil which was further rinsed with pentane, then taken up in 2 mL of  $\text{CD}_2\text{Cl}_2$  and stirred with 213 mg (0.24 mmol) of  $\text{NaBAR}_4^{\text{F}}$ . The reaction mixture was filtered over a borosilicate filter and precipitated by addition to 15 mL of vigorously stirred pentane. A green precipitate was obtained, which was rinsed with pentane, yielding complex **7d** as a pale green powder (135 mg, 45%) containing <10% of  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  anion. Single crystals suitable for X-ray diffraction were grown by diffusion of pentane into a  $\text{CD}_2\text{Cl}_2$  solution of **7d** at  $-35^\circ\text{C}$ . Elemental Analysis: calcd for  $\text{C}_{68}\text{H}_{44}\text{BF}_{24}\text{NO}_2\text{Zr}$ : C, 55.75; H, 3.03; N, 0.96. Found: C, 54.93; H, 2.90; N, 0.93. HRMS (ESI-pos): calcd for  $\text{C}_{36}\text{H}_{32}\text{NO}_2\text{Zr}[\text{M}-\text{BAR}_4^{\text{F}}]^-$ : 600.14746. Found: 600.14723 (rel. ab. 90%,  $-0.4$  ppm).

**Preparation of Complex 8a.** In an Ar glovebox, complex **1a** (217 mg, 0.5 mmol), tris(pentafluorophenyl)borane (256 mg, 0.5 mmol) and diphenylacetylene (90 mg, 0.5 mmol) were dissolved in  $\text{C}_6\text{H}_5\text{Br}$  (3 mL). The mixture was stirred for 5 min, then added to 50 mL of vigorously stirred pentane. The resulting red oil was washed three times with 5 mL pentane, after which a further 30 mL of pentane was added, and the mixture was stirred for 2 h in the glovebox. The supernatant was removed, and the oil rinsed with 5 mL of pentane. The resulting crusty solid was soaked in 5 mL of pentane for 10 min, the supernatant was discarded, and the oily solid was dried *in vacuo* for 25 min in the box antechamber. Complex **8a** was obtained as a red powder (0.43 g, 76%). The compound degrades within several hours when stored at  $-35^\circ\text{C}$  under Ar. Elemental Analysis: calcd for  $\text{C}_{55}\text{H}_{45}\text{BF}_{15}\text{PZr}$ : C, 58.77; H, 4.04. Found: C, 57.90; H, 4.46.

**Preparation of Complex 9a.** In an Ar glovebox, complex **1a** (217 mg, 0.5 mmol), tris(pentafluorophenyl)borane (256 mg, 0.5 mmol) and diphenylacetylene (89 mg, 0.5 mmol) were dissolved in  $\text{C}_6\text{H}_5\text{Br}$  (3 mL) to give a brown-red solution. Benzaldehyde (53 mg, 0.5 mmol) was added, and the solution turned bright yellow instantaneously. It was then added to 50 mL of vigorously stirred pentane. The resulting yellow oil was washed three times with 3 mL pentane and dried *in vacuo* outside the box. Pentane (10 mL) was added, the mixture was stirred for 10 min, and the supernatant solution was discarded. The residue was taken up in 1.5 mL of  $\text{CH}_2\text{Cl}_2$ , and the solution was added to 50 mL of vigorously stirred pentane to give a yellow oil. The supernatant solution was discarded, and residue was dried *in vacuo* for 1 h. Complex **4a-I** was obtained as a

pale yellow foam (0.47 g, 75%). Elemental Analysis: calcd for  $\text{C}_{62}\text{H}_{51}\text{BF}_{15}\text{OPZr}$ : C, 60.54; H, 4.18. Found: C, 61.09; H, 4.21. HRMS (ESI-pos): calcd for  $\text{C}_{43}\text{H}_{48}\text{OPZr}[\text{M}-\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ : 701.24843. Found: 701.24989 (rel. ab. 100%, + 2.1 ppm).

**Preparation of Complex 10a.** In an Ar glovebox, complex **1b** (217 mg, 0.5 mmol), tris(pentafluorophenyl)borane (256 mg, 0.5 mmol) and diphenylacetylene (89 mg, 0.5 mmol) were dissolved in  $\text{C}_6\text{H}_5\text{Br}$  (3 mL) to give a brown-red solution. Ferrocene carboxaldehyde (107 mg, 0.5 mmol) was added and the solution darkened slightly. It was then added to 50 mL of vigorously stirred pentane. The resulting brown oil was washed three times with 3 mL pentane, taken up in 2 mL of  $\text{CH}_2\text{Cl}_2$ , and added to 50 mL of vigorously stirred pentane. The resulting brown oil solidified upon trituration with pentane, and **10a** was obtained as an ochre powder containing 25% of pentane after drying *in vacuo* (0.52 g, 78%). Single crystals suitable for X-ray diffraction were obtained after overnight ion exchange of 0.1 mmol of **10a** with 0.12 mmol of  $\text{KB}(\text{C}_6\text{F}_5)_4$  in  $\text{CD}_2\text{Cl}_2$  (1.5 mL) and subsequent crystallization by diffusion of pentane at  $-35^\circ\text{C}$ . Multinuclear 1D NMR ( $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{19}\text{F}$ ) of **10a'** performed before crystallization indicated >90% anion exchange. Analytical data follow for **10a**. Elemental Analysis: calcd for  $\text{C}_{66}\text{H}_{55}\text{BF}_{15}\text{FeOPZr}(\text{C}_5\text{H}_{12})_{0.25}$ : C, 59.57; H, 4.31. Found: C, 58.81; H, 4.27. HRMS (ESI-pos): calcd for  $\text{C}_{47}\text{H}_{52}\text{OPFeZr}[\text{M}-\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ : 809.21493. Found: 809.21593 (rel. ab. 100%, + 1.2 ppm).

**Preparation of Complex 11a.** In an Ar glovebox, complex **1a** (217 mg, 0.5 mmol), tris(pentafluorophenyl)borane (256 mg, 0.5 mmol) and diphenylacetylene (89 mg, 0.5 mmol) were dissolved in  $\text{C}_6\text{H}_5\text{Br}$  (3 mL) to give a brown-red solution. Chalcone (104 mg, 0.5 mmol) was added, and the solution turned bright yellow over 2 min. It was then added to 50 mL of vigorously stirred pentane. The resulting yellow oil was washed three times with 10 mL pentane outside the box and dried *in vacuo*. The residue was taken up in 4 mL of  $\text{CH}_2\text{Cl}_2$ , and the solution was added to 50 mL of vigorously stirred pentane to give a yellow oil. The supernatant solution was discarded, and residue was dried *in vacuo* for 1 h. Complex **11a** was obtained as a bright yellow crusty solid containing 100 mol % of pentane (0.56 g, 84%). Single crystals suitable for X-ray diffraction were obtained after overnight ion exchange of 0.1 mmol of **11a** with 0.12 mmol of  $\text{NaBAR}_4^{\text{F}}$  in  $\text{CD}_2\text{Cl}_2$  (1.5 mL) and subsequent crystallization by diffusion of pentane at  $-35^\circ\text{C}$ . Multinuclear 1D NMR ( $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{19}\text{F}$ ) performed before crystallization indicated >90% anion exchange. Analytical data follow for **11a**. Elemental Analysis: calcd for  $\text{C}_{70}\text{H}_{57}\text{BF}_{15}\text{OPZr}(\text{C}_5\text{H}_{12})$ : C, 64.14; H, 4.95. Found: C, 63.23; H, 5.66. HRMS (ESI-pos): calcd for  $\text{C}_{51}\text{H}_{54}\text{OPZr}[\text{M}-\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ : 803.29538. Found: 803.29883 (rel. ab. 100%, + 4.3 ppm).

**In Situ Characterization of Complex 12a.** In an Ar glovebox, complex **1a** (43.4 mg, 0.1 mmol), tris(pentafluorophenyl)borane (51.2 mg, 0.1 mmol) and diphenylacetylene (17.8 mg, 0.1 mmol) were dissolved in  $\text{C}_6\text{D}_5\text{Br}$  (0.8 mL) in an NMR tube fitted with a pressure valve. The tube was evacuated and refilled with 2 bar of  $\text{CO}_2$ . It was then closed and shaken periodically over 5 min until the red-brown mixture turned bright yellow. Complex **12a** was characterized *in situ* and showed no decomposition over several days. The NMR tube was then heated to  $60^\circ\text{C}$  for 4 h under dynamic vacuum. Solvent level was restored, and the mixture was analyzed again, showing a 2/5 mixture of **12a** and **8a**.

**Procedure for Catalytic Hydrogenation (NMR Scale).** In an argon glovebox, a 0.1 M stock solution of catalyst (typically 0.1 mmol of Zr complex **1a–e** and  $\text{B}(\text{C}_6\text{F}_5)_3$  in 1.0 mL  $\text{C}_6\text{D}_5\text{Br}$ ) was prepared, and a 0.2 mL aliquot was added to a solution of  $\text{Cp}_2\text{Fe}$  (standard; 9.3 mg, 0.05 mmol) and the substrate (1.0 or 2.0 mmol) in  $\text{C}_6\text{D}_5\text{Br}$  (0.6 mL). The Schlenk vessel was frozen with liquid nitrogen and was evacuated. After thawing, it was refilled with 1.5 bar of  $\text{H}_2$ . The reaction mixture was stirred for the indicated time at room temperature. Product conversion was estimated by  $^1\text{H}$  NMR after dilution with  $\text{C}_6\text{D}_5\text{Br}$  (integration of a suitable signal vs  $\text{Cp}_2\text{Fe}$  or remaining starting material).

**Procedure for Catalytic Hydrogenation of Styrene (Preparative Scale).** In an argon glovebox, a 0.1 M stock solution of catalyst (0.1 mmol of Zr complex **1e** and  $\text{B}(\text{C}_6\text{F}_5)_3$  in 1 mL  $\text{C}_6\text{D}_5\text{Br}$ ) was



prepared, and this was added to a solution of styrene (10 mmol) in  $C_6D_5Br$  (3 mL). The Schlenk vessel was evacuated and refilled with 1.5 bar of  $H_2$ . The reaction mixture was stirred for 2 h at room temperature. Product distribution was estimated by  $^1H$  NMR as previously. The crude reaction mixture was filtered through a plug of silica gel and eluted with  $CH_2Cl_2$ . After evaporation the residue was distilled at 60 °C/0.3 mbar, and the residue was analyzed by  $^1H$  NMR in  $CDCl_3$  and GCMS, revealing the presence of a 5/1 mixture of 1,4-diphenylbutane and 1,3-diphenylbutane (373 mg, 36%) with traces of a third product arising from the coupling of three styrene moieties ( $M_w = 314$ ).

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06551.

Details about the experimental procedures, characterization of all new compounds (PDF)

Crystal structure data (CIF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) (a) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124–1126. (b) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072–5074.
- (2) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76.
- (3) (a) *Frustrated Lewis Pair Chemistry I: Uncovering and Understanding*; Erker, G.; Stephan, D. W., Eds.; Springer: Heidelberg, 2013; Vol. 332. (b) *Frustrated Lewis Pair Chemistry II: Expanding the Scope*; Erker, G.; Stephan, D. W., Eds.; Springer: Heidelberg, 2013; Vol. 334. (c) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2015**, *54*, 6400–6441.
- (4) Fontaine, F.-G.; Courtemanche, M.-A.; Légaré, M.-A. *Chem. - Eur. J.* **2014**, *20*, 2990–2996.
- (5) Flynn, S. R.; Wass, D. F. *ACS Catal.* **2013**, *3*, 2574–2581.
- (6) (a) Neu, R. C.; Otten, E.; Lough, A.; Stephan, D. W. *Chem. Sci.* **2011**, *2*, 170–176. (b) Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* **2011**, *133*, 18463–18478. (c) Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* **2011**, *133*, 8826–8829. (d) Chapman, A. M.; Wass, D. F. *Dalton Trans.* **2012**, *41*, 9067–9072. (e) Chapman, A. M.; Haddow, M. F.; Wass, D. F. *Eur. J. Inorg. Chem.* **2012**, *2012*, 1546–1554. (f) Sgro, M. J.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 11343–11345. (g) Sgro, M. J.; Stephan, D. W. *Chem. Commun.* **2013**, *49*, 2610–2612. (h) Kalz, K. F.; Brinkmeier, A.; Dechert, S.; Mata, R. A.; Meyer, F. *J. Am. Chem. Soc.* **2014**, *136*, 16626–16634. (i) Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2013**, *135*, 6465–6476. (j) Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *Organometallics* **2013**, *32*, 7306–7311. (k) Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 13629–13632. (l) Fromel, S.; Kehr, G.; Fröhlich, R.; Daniliuc, C. G.; Erker, G. *Dalton Trans.* **2013**, *42*, 14531–14536. (m) Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2014**, *136*, 12431–12443. (n) Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2015**, *137*, 4550–4557. (o) Normand, A. T.; Richard, P.; Balan, C.; Daniliuc, C. G.; Kehr, G.; Erker, G.; Le Gendre, P. *Organometallics* **2015**, *34*, 2000–2011. (p) Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *Organometallics* **2015**, *34*, 2655–2661.
- (7) (a) Podiyanchari, S. K.; Fröhlich, R.; Daniliuc, C. G.; Petersen, J. L.; Mück-Lichtenfeld, C.; Kehr, G.; Erker, G. *Angew. Chem., Int. Ed.* **2012**, *51*, 8830–8833. (b) Forrest, S. J. K.; Clifton, J.; Fey, N.; Pringle, P. G.; Sparkes, H. A.; Wass, D. F. *Angew. Chem., Int. Ed.* **2015**, *54*, 2223–2227.
- (8) (a) Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661–1717. (b) Stephan, D. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 314–329. (c) Waterman, R. *Dalton Trans.* **2009**, 18–26. (d) Rosenberg, L. *Coord. Chem. Rev.* **2012**, *256*, 606–626.
- (9) (a) Temme, B.; Erker, G. *J. Organomet. Chem.* **1995**, *488*, 177–182. (b) Harlan, C. J.; Bridgewater, B. M.; Hascall, T.; Norton, J. R. *Organometallics* **1999**, *18*, 3827–3834.
- (10) (a) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336–5337. (b) Weng, W.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4700–4705. (c) Kamitani, M.; Pinter, B.; Chen, C.-H.; Pink, M.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 10913–10915.
- (11) For a discussion of the “carbene analogy”, see ref 8d.
- (12) (a) Douglass, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 1824–1825. (b) Douglass, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221–10238. (c) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108–4109. (d) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673–686. (e) Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 12764–12765. (f) Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 6311–6324.
- (13) Hultzsich has reported a Zr system for hydroamination which was claimed to involve an active catalyst of general formula  $Cp_2Zr=NR^+$ : Gribkov, D. V.; Hultzsich, K. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5542–5546.
- (14) (a) Bailey, J. A.; Pringle, P. G. *Coord. Chem. Rev.* **2015**, *297–298*, 77–90. (b) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. *Chem. Rev.* **2010**, *110*, 4023–4078.
- (15) (a) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. *J. Am. Chem. Soc.* **2008**, *130*, 12632–12633. (b) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem.* **2011**, *50*, 336–344.
- (16) (a) Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1987**, 1604–1604. (b) Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *Polyhedron* **1988**, *7*, 2083–2086. (c) Hey-Hawkins, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Dalton Trans.* **1991**, 939–948. (d) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914–11921. (e) Breen, T. L.; Stephan, D. W. *Organometallics* **1996**, *15*, 4509–4514.
- (17) (a) Coles, N.; Harris, M. C. J.; Whitby, R. J.; Blagg, J. *Organometallics* **1994**, *13*, 190–199. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729–8731.
- (18) Novarino, E.; Guerrero Rios, I.; van der Veer, S.; Meetsma, A.; Hessen, B.; Bouwkamp, M. W. *Organometallics* **2011**, *30*, 92–99.
- (19) Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reyes, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.
- (20) Feldman, J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 1042–1044.
- (21) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.
- (22) Due to the considerable pyramidalization of P in **1c** and **1-P**, the  $\varphi$  values do not reflect the favorable geometry for orbitals overlap.
- (23) Alvarez, S. *Dalton Trans.* **2013**, *42*, 8617–8636.
- (24) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623–3625.
- (25)  $^{31}P$  NMR spectroscopy is an effective tool to diagnose planar (downfield signal) vs pyramidalized (highfield signal)  $PR_2$  ligands, see ref 8d and references cited therein.
- (26) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235–2243.
- (27) Pyykkö, P.; Atsumi, M. *Chem. - Eur. J.* **2009**, *15*, 12770–12779.



(28) (a) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97–102.  
(b) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393–406.

(29) This contrasts with the high activity of an analogous Y complex [Cp\*<sub>2</sub>YPh<sub>2</sub>] reported by Marks, see ref 12a.

(30) Product conversion is somewhat low in the case of 3,3-dimethylbut-1-ene (**14**) due to the volatility of 2,2-dimethylbutane (**24**).

(31) For a review, see: Grützmacher, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1814–1818.

(32) For selected examples of cooperative catalysts see: (a) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790–792.  
(b) Kashiwame, Y.; Kuwata, S.; Ikariya, T. *Chem. - Eur. J.* **2010**, *16*, 766–770. (c) Espinosa-Jalapa, N. Á.; Ke, D.; Nebra, N.; Le Goanvic, L.; Mallet-Ladeira, S.; Monot, J.; Martin-Vaca, B.; Bourissou, D. *ACS Catal.* **2014**, *4*, 3605–3611.

(33) Troutman, M. V.; Appella, D. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4916–4917.

(34) Buhro, W. E.; Chisholm, M. H.; Martin, J. D.; Huffman, J. C.; Folting, K.; Streib, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8149–8156.

(35) Szalay, R.; Knausz, D.; Szakács, L.; Újszászy, K.; Sohár, P. *J. Organomet. Chem.* **1995**, *487*, 267–271.

(36) (a) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 1760–1765. (b) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1987**, *26*, 3087–3088.

(37) Reaction of **2a** with 1 equiv of THF yielded a labile adduct with a <sup>31</sup>P NMR signal of 340.5 ppm, see [Supporting Information](#); this compound was never observed in THF solutions of **3a**.

(38) The MPV reaction has precedents in Zr chemistry, see: (a) Ishii, Y.; Nakano, T.; Inada, A.; Kishigami, Y.; Sakurai, K.; Ogawa, M. *J. Org. Chem.* **1986**, *51*, 240–242. (b) Nakano, T.; Umano, S.; Kino, Y.; Ishii, Y.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3752–3757.

(39) Insertion of phenylacetylene into the Zr–P bond of [Cp<sub>2</sub>Zr(Cl)(P(SiMe<sub>3</sub>)<sub>2</sub>)] was previously reported by Hey–Hawkins: Hey-Hawkins, E.; Lindenberg, F. *Chem. Ber.* **1992**, *125*, 1815–1819.

(40) Complexes **2** were generated in situ by the reaction of **1** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

(41) (a) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445–451.  
(b) Breen, T. L.; Stephan, D. W. *Organometallics* **1996**, *15*, 5729–5737. (c) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1996**, *118*, 4204–4205.

(42) The integrity of the Zr cation after anion exchange was assessed by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy.