

Phosphido- and Amidozirconocene Cation Based Frustrated Lewis Pair Chemistry

Adrien T. Normand,^{§†} Constantin G. Daniliuc,[§] Birgit Wibbeling,[§] Gerald Kehr,[§] Pierre Le Gendre*[†] and Gerhard Erker.*[§]

[§] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany.

[†] Institut de Chimie Moléculaire de l'Université de Bourgogne, ICMUB UMR6302, CNRS, Univ. Bourgogne Franche-Comté, F-21000 Dijon, France.

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 Zr/N π interaction. Complexes **2** catalyze the hydrogenation of electron-rich olefins and alkynes under mild conditions (room temperature, 1.5 bar H_2). Complex **2e** binds 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.^{1,2} Exciting new applications of FLPs have since been developed,³ including catalytic CO_2 reduction.⁴ Organometallic frustrated Lewis pairs (om-FLPs) have recently emerged as a sub-class of FLPs with promising properties.⁵ These species contain transition metals, mostly as the Lewis acid component,⁶ although it was shown that low-valent metals may also be used as Lewis bases.⁷

Lately Stephan, Wass and Erker have been exploring the FLP behavior of d^0 zirconocene cations (**A-F**).^{6a-c,6e,6i-n,6p} 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,^{6c} while **D** is an efficient hydrogenation catalyst.⁶ⁿ

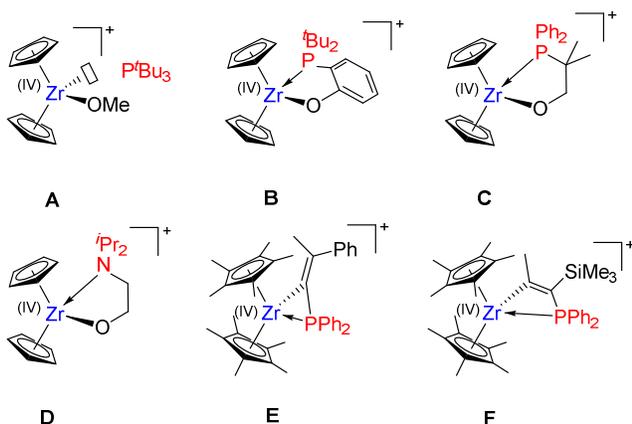
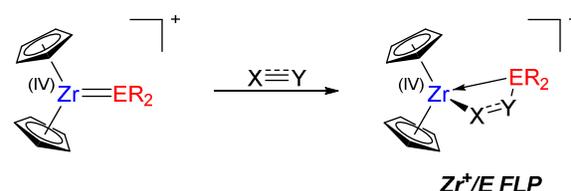


Figure 1. Examples of FLPs with zirconocene cations. $\text{B}(\text{C}_6\text{F}_5)_4^-$ anion omitted for clarity.

There are two ways to synthesize such systems: *i*) by protonolysis of $\text{Cp}^R_2\text{ZrMe}_2$ with an alcohol followed by Me abstraction (**A-D**) or *ii*) by insertion of a functionalized alkyne into the Zr-Me bond of the $\text{Cp}^R_2\text{ZrMe}^+$ cation (**E-F**). Both these two methods require pre-functionalized 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 with unsaturated substrates to generate Zr^+/P or Zr^+/N FLPs (Scheme 1).

Scheme 1.



$\text{E} = \text{N}, \text{P}$

$\text{X}\equiv\text{Y}$: alkene, alkyne, ketone, aldehyde, imine...

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 CO_2 activation. Indeed, although neutral Zr phosphido and amido complexes have been extensively studied,⁸ to the best of our knowledge there are no reported examples of cationic complexes outside two brief reports by Norton and Erker with $\text{E} = \text{N}$.⁹ Therefore we feel that the current interest in FLPs calls for a reappraisal of the properties of these compounds within the context of FLP chemistry.

It is also worth noting the broader context of this work, in that $\text{Cp}_2\text{Zr}=\text{ER}_2^+$ cations can be considered as *i*) pnictogen analogues of Zr alkylidene complexes;^{10,11} *ii*) Zr analogues of the d^0 lanthanocene catalysts described by Marks for hydroamination, hydrophosphination and ethylene polymerization;^{12,13} *iii*) Zr analogues of amine- and phosphine-boranes.¹⁴ The latter were shown by Stephan to cooperatively cleave H_2 , a process related to H_2 activation by FLPs.¹⁵

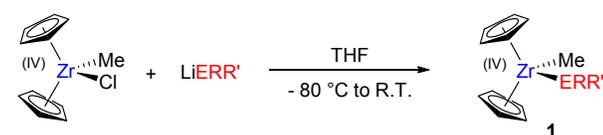
RESULTS AND DISCUSSION

Synthesis of the neutral precursors

In order to prepare $\text{Cp}_2\text{Zr}=\text{ER}_2^+$ cations we synthesized a range of neutral Zr-Me precursors by a well-established procedure involving salt metathesis of LiERR' with Cp_2ZrMeCl (Scheme 2).^{16,9a,17}

Complexes **1** were obtained as air sensitive solids in 57 to 85 % yield; they showed high solubility in most hydrocarbon solvents. Proton NMR spectroscopy of the phosphido complexes revealed $^1\text{H}/^{31}\text{P}$ coupling with both the Cp rings and the methyl hydrogens (see constants in Table 1), whereas imido complexes only displayed $^1\text{H}/^{15}\text{N}$ coupling at the *ortho* position of the aromatic ring attached to N (see 2D spectra in the Supporting Information).

Scheme 2.



E = P

1a R = R' = Cy: 2.69 g, 85 %

1b R = R' = Mes: 1.37 g, 67 %

1c R = R' = ^tBu: 0.94 g, 61 %

E = N

1d R = R' = Ph: 2.42 g, 75 %

1e R = ^tBu, R' = 3,5-(C₆H₃(CH₃)₂):

1.50 g, 57 %

Table 1. Relevant NMR chemical shifts and coupling constants for compounds 1a-e and 2a-e.

	Cp (ppm)	³ J _{PH} Cp/P (Hz)	Me ^a (ppm)	³ J _{PH} Me/P (Hz)	¹⁵ N/ ³¹ P (ppm)
1a	5.91	1.2	-0.54	7.8	233.1
1b	5.79	1.7	-0.28	6.4	136.9
1c	6.27	0.8	0.13	2.1	83.0
1d	5.92	N.A.	0.09	N.A.	-199.7
1e	5.80	N.A.	0.27	N.A.	-214.9
2a	5.87	0	1.09	N.A.	396.6
2b	5.71	0	1.07	N.A.	298.6
2d	5.78	N.A.	0.97	N.A.	-113.4
2e	6.09	N.A.	1.11	N.A.	-169.2

1a-d analyzed in d_8 -THF, **1e** in C_6D_6 , **2a-e** in $\text{C}_6\text{D}_5\text{Br}$. ^a: Zr-Me for **1a-e**, B-Me for **2a-e**.

The isolation of pure **1c** proved problematic outside the glovebox: only recrystallization from cold pentane in the box could afford ~95 % pure material. Compound **1c** is a purple-blue solid giving similarly colored solutions in THF, toluene or pentane. Thus, an absorption maximum was observed in the

visible spectrum at $\lambda = 592$ nm in THF, whereas **1a** and **1b** (orange-red solutions) gave 391 and 442 nm respectively.

Single crystals suitable for X-ray diffraction were obtained for **1a-e**. For comparison purposes, relevant metric parameters are included in Table 2 for two known compounds: $\text{Cp}_2\text{ZrMeP}(\text{SiMe}_3)_2$ (**1-P**) and $\text{Cp}^*_2\text{ZrMeN}(\text{Et})_2$ (**1-N**).^{16b,16c,18} The analysis reveals a strong interaction between E and Zr, as evidenced both by the trigonal planar geometry around the pnictogen atom and the relatively short Zr-E distances, well below the sum of covalent radii (E = P: 2.82(10) Å; E = N: 2.46(8) Å).¹⁹ Noteworthy, compounds **1c** and **1-P** are clear outliers in this series and display considerable pyramidalization of the P atom, with sums of angles around P of 337.9 and 349.3 respectively. This, along with the elongated Zr-P bonds (**1c**: 2.735(1) Å; **1-P**: 2.629(3) Å) is likely the result of the increased steric pressure of the ^tBu₂/P(SiMe₃)₂ moiety.

The above remarks concerning the geometry around E and the Zr-E distance seem to suggest partial double bond character of the Zr-E bond for **1a-b** and **1d-e**; however, one should exert caution when making assumptions relative to bond orders based purely on structural data.

Indeed, Feldman has shown that the d^1 complex $\text{Cp}^*_2\text{TiN}(\text{MePh})$ contains a Ti-N single bond despite the trigonal planar geometry around N.²⁰ In Feldman's case there is no possible bonding interaction between the filled p_π orbital of N, on the one hand, and the partially occupied $1a_1$ and b_2 orbitals of Ti, on the other hand, because they are oriented orthogonally.²¹

With this in mind, it is interesting to note the value of the C21-E-Zr-Ct1 torsion angle in complexes **1a-d**, and thus the orientation of the lone pair of E with respect to the Me-Zr-E plane (angle φ , Table 2). Indeed, while such an interaction is favored for **1a**, **1b**, and **1d** ($\varphi = -3.8$, 27.9 and 36.6 °),²² the situation is completely different for **1e**: in this complex the alignment of the lone pair of N with the Zr-Ct1 vector ($\varphi = 105.7$ °) considerably reduces the overlap with the empty orbitals on Zr (which lie in the Me-Zr-E plane). Clearly, given the respective geometries of **1d** and **1e** there must be a steric effect of the ^tBu group in the latter, which enforces the best orientation of the amido ligand in order to minimize steric interactions between ^tBu and the Cp rings. Probably because of this sterically more favorable conformation, the amido ligand in **1e** is closer to Zr than in **1d** (Zr-N: 2.102(4) vs 2.1625(15) Å), and the distance between Zr and the *ipso* carbon atom of the aryl ring is shorter than the sum of van der Waals radii (Zr-C21: 2.704(5) Å).²³ Thus, much like in Feldman's case one observes trigonal planar geometry around N in the absence of $p\pi$ - $d\pi$ interactions between N and the metal, this time in a d^0 complex.

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 eq of $\text{B}(\text{C}_6\text{F}_5)_3$ in $\text{C}_6\text{D}_5\text{Br}$ (Scheme 3).²⁴ Interestingly, reaction of **1c** with $\text{B}(\text{C}_6\text{F}_5)_3$ 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 $^{31}\text{P}\{^1\text{H}\}$ and $^{15}\text{N}\{^1\text{H}\}$ NMR spectra —up to 163.5 ppm for **2a**

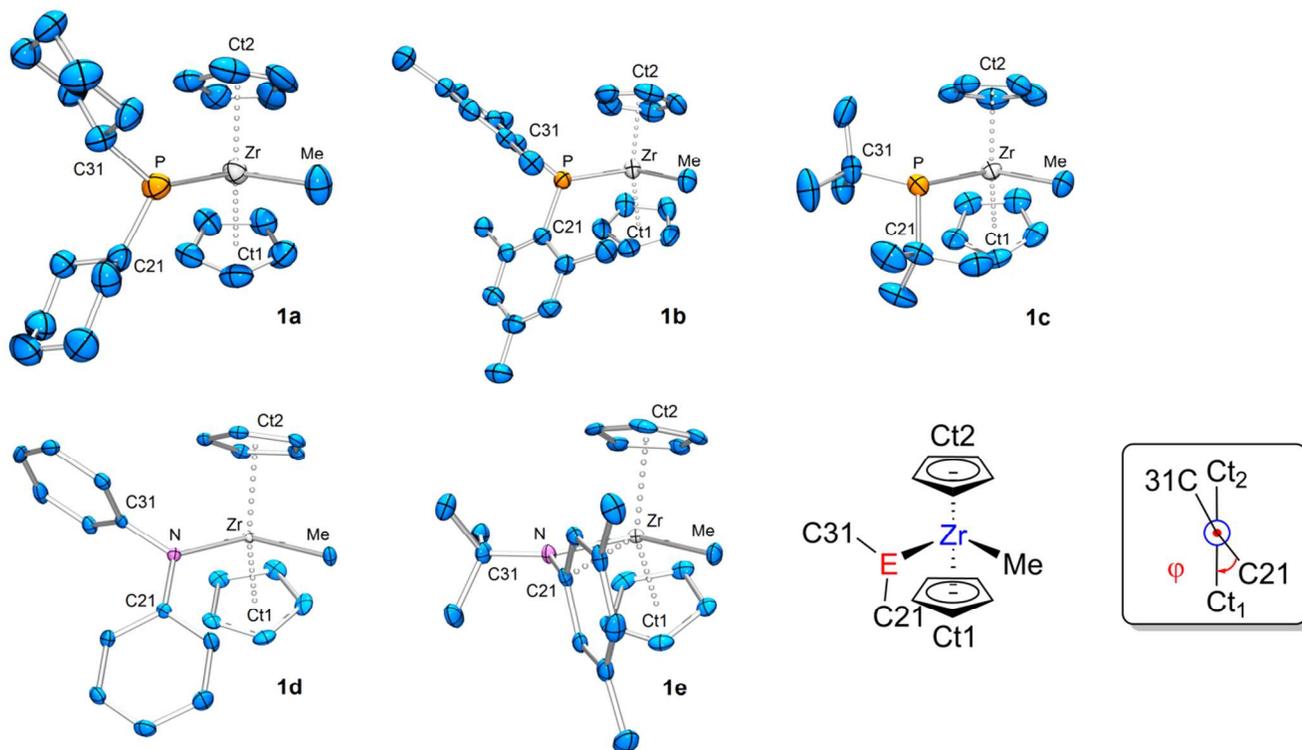


Figure 2. POV-ray projections of the crystal structures of compounds **1a-e** (50 % ellipsoids probability) and definition of angle ϕ .

Table 2. Relevant bond distances (Å) and angles (°) in compounds 1a-e.

	1a	1b	1c^a	1d	1e	1-P^b	1-N^c
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)
$\Sigma\alpha(E)$	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

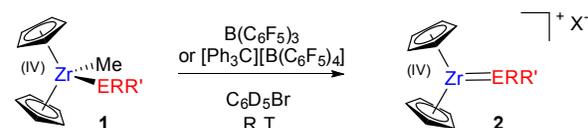
^a: independent molecule a is discussed ^b: ref. 17b,c. ^c: ref 19.

and 86.3 ppm for **2d**, see Table 1— consistent with much greater interaction of the lone pair of E with Zr.²⁵ Concomitant formation of the $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ anion was also observed, with diagnostic signals in the ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of complexes **2** (see Supporting Information). Alternatively, Me abstraction could also be performed with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ for the amido complexes, which gave very similar ^1H NMR signals for the $[\text{Zr}]^+$ 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 $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ anion. Both these compounds were isolated as air-sensitive solids in 77 and 85 % yield respectively. On the other hand, the phosphido complex-

es were found to be too reactive for isolation and were used *in situ* for further reactivity studies.

Scheme 3.



E = P, X⁻ = $\text{MeB}(\text{C}_6\text{F}_5)_3^-$

2a R = R' = Cy

2b R = R' = Mes

E = N, X⁻ = $\text{MeB}(\text{C}_6\text{F}_5)_3^-$

2d R = R' = Ph

2e R = ^tBu, R' = 3,5-(C₆H₃(CH₃)₂)

2e' X⁻ = $\text{B}(\text{C}_6\text{F}_5)_4^-$

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).^{24,26} Two close contacts were found between the Zr center 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 π interaction between the Zr and N atoms. The Zr-N distance in **2d** is shorter by 0.075 Å (see Table 3); at 2.088(2) Å it is now halfway between a single (2.25 Å) and a double (1.88 Å) Zr-N bond.²⁷ Moreover the orientation of the planar NPh_2 ligand ($\varphi = -12.5^\circ$) is much more favorable to π -d π orbital interactions than in **1d**.

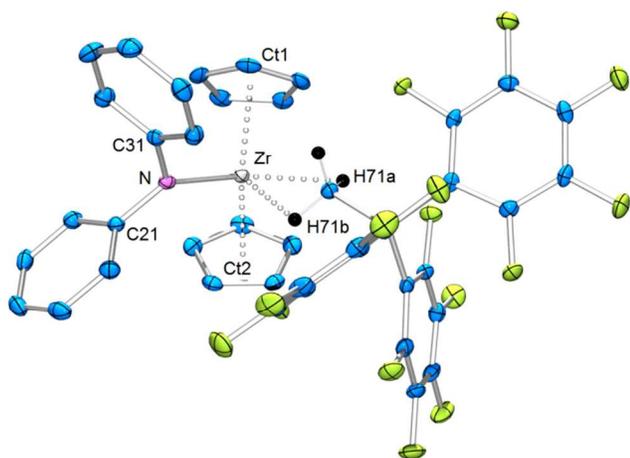


Figure 3. POV-Ray projection of the crystal structure of compound **2d** (50 % ellipsoids probability).

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**).^{9b}

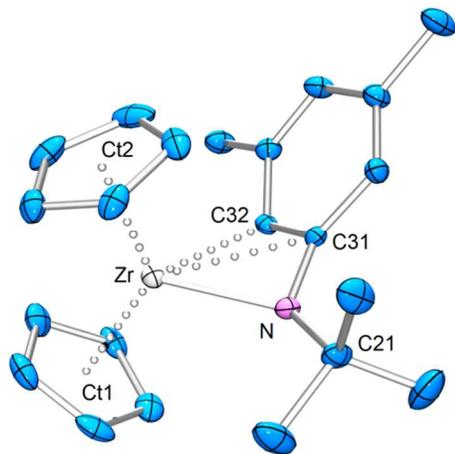


Figure 4. POV-Ray projection of the crystal structure of compound **2e'** (50 % ellipsoids probability, $\text{B}(\text{C}_6\text{F}_5)_4^-$ anion omitted for clarity).

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 π

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 non-equivalent ^1H and $^{13}\text{C}\{\text{H}\}$ 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 134.9 ppm (**1e**) to 100.8/101.8 ppm (**2e/2e'**). In particular the *ortho* H remained equivalent over the 183-299K temperature range (see the Supporting Information). Therefore we conclude that the interaction between Zr and the aromatic ring is not persistent in solution.

Table 3. Relevant bond distances (Å) and angles ($^\circ$) in compounds **2d** and **2e'**.

	2d	2e'
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 (φ)	-12.5	-91.4

Overall, the spectroscopic and X-ray diffraction evidence gathered on complexes **2** indicate that there is a considerable π 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 H_2 (or a hydrogen donor such as isopropanol) and act as hydrogenation catalysts.²⁸ Thus, since complexes **2** possess a highly Lewis acidic Cp_2Zr^+ 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 H_2 , 2 hours (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 H_2 (~20 min), this indicates a weak residual polymerization activity for these complexes.²⁹ Interestingly, the nature of the ERR' ligand has a strong influence on product distribution, for example **2a** (PCy_2) gives almost exclusively **22a**, while **2b** (PMes_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

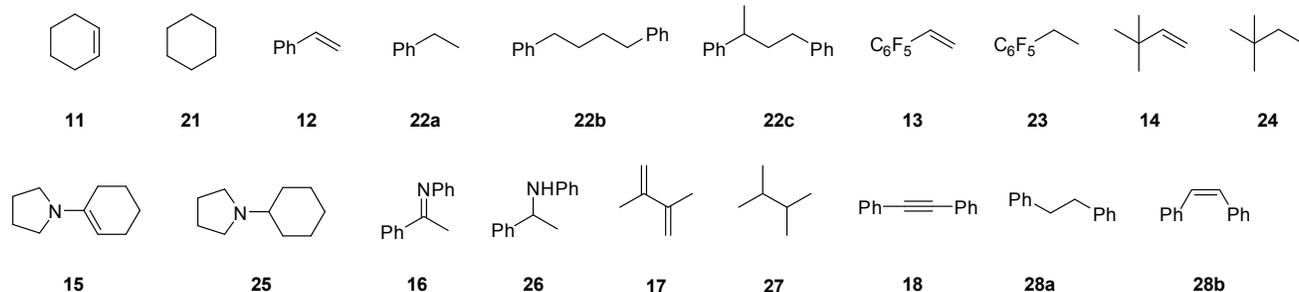


Figure 5. Catalytic hydrogenation substrates (11-18) and products (21-28b).

The homogeneous solutions of **2a** and **2e** in C_6H_5Br reacted almost instantaneously to give a pale suspension, while **2d** required 30 min reaction, consistent with the lower Lewis basicity of N in $HNPh_2$ compared to HN^tBuAr ; compounds **3a**, **3d** and **3e** were isolated in 68, 68 and 80 % yield respectively.

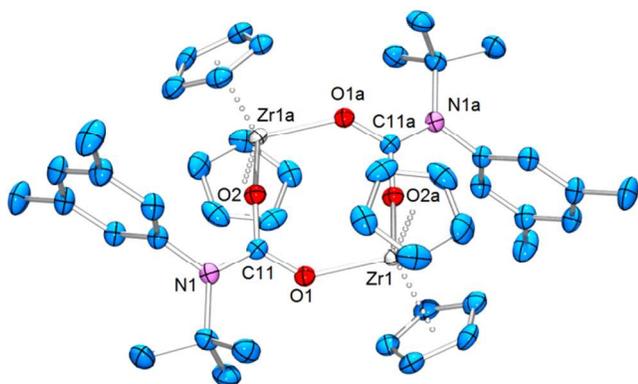


Figure 6. POV-Ray projection of the crystal structure of compound **3e** (30 % ellipsoids probability, $MeB(C_6F_5)_3^-$ anions omitted for clarity).

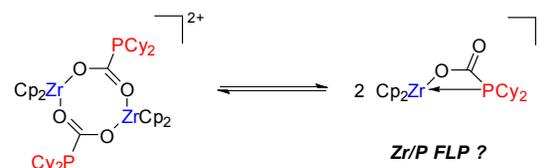
The solid state structure of **3e** was elucidated by single crystal X-ray diffraction analysis, showing a dimeric structure with an 8-membered $(ZrOCO)_2$ core (Figure 6). Bond distances indicate an O-C-O motif with relatively similar C11-O1 and C11-O2 (1.277(4) Å vs 1.292(4) Å) bonds. These values are intermediate between those of single and double C-O bonds.²⁷ Likewise, the Zr1-O1 and Zr1-O2a bonds are quite similar (2.095 Å vs 2.061(2) Å). Additionally, the 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 $(Ar^tBu)N^+=C(O^-)(O^-)$ character, consistent with the oxophilicity of Zr.

Once isolated, these compounds are scarcely soluble in CH_2Cl_2 or C_6H_5Br , 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 $^{13}C\{^1H\}$ chemical shift of the CO₂ moiety was observed at 168.0 ppm for **3a** ($^1J_{PC} = 40.4$ Hz), at 160.7 ppm for **3d** and 162.7 ppm for **3e**. The $^{31}P\{^1H\}$ chemical shift of **3a** (12.1 ppm) is consistent with an O-bridged dimer with a pendant phosphine, rather than a P-bridged dimer.³⁴ The FTIR spectra showed C=O absorption

bands at 1759 (**3a**), 1761 (**3d**) and 1757 (**3e**) cm^{-1} respectively.³⁵

Despite the wealth of studies on metal phosphido complexes, the insertion of CO₂ into M-PR₂ bonds has only been reported in three instances (M = Hf, Mo, W),^{34,36} therefore we were intrigued by compound **3a**. As suggested by the observed low field $^{31}P\{^1H\}$ NMR signal (*vide supra*) and by the lower tendency of P for lone pair delocalization into the CO₂ moiety,³⁴ we reasoned that this complex could potentially act as a Zr/P FLP—or as a Zr/P ambiphilic ligand—in its monomeric form (Scheme 6).

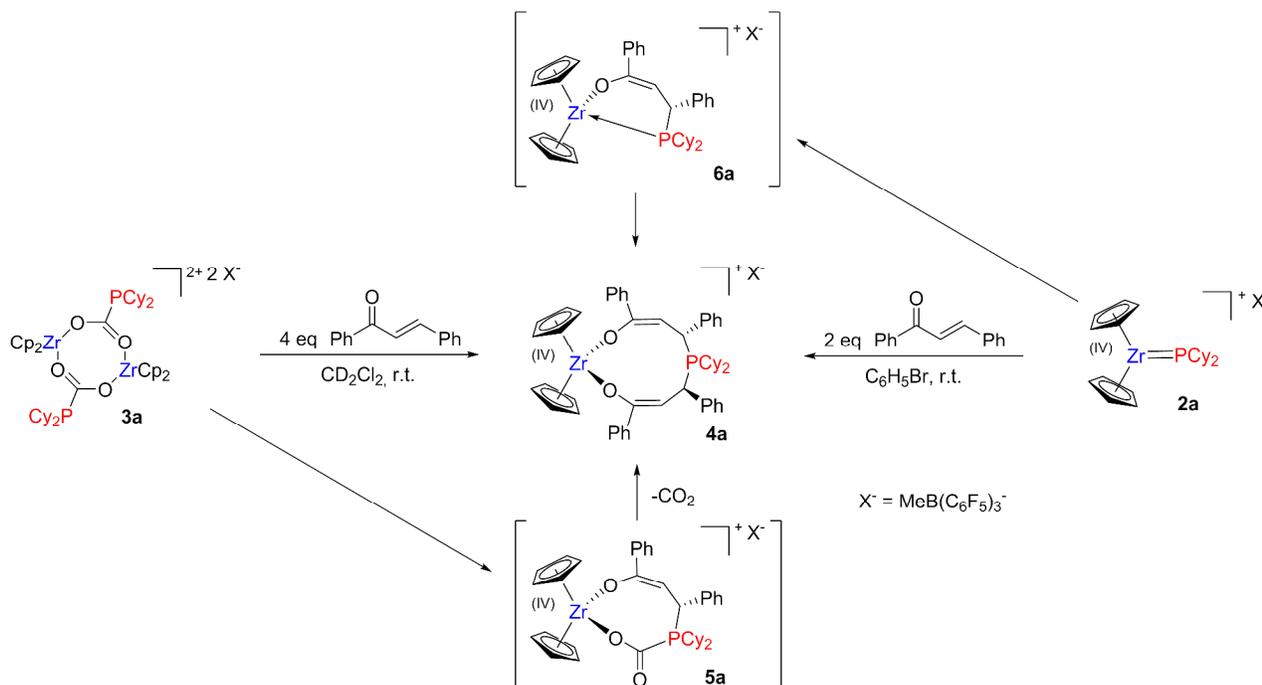
Scheme 6.



However, reacting **3a** with 2 eq of PhCHO or $[Pd(C_3H_5)Cl]_2$ in CD_2Cl_2 gave complex mixtures. By contrast, reaction with 2 eq of chalcone afforded complex **4a** along with another, as yet non-identified compound; **4a** was also obtained (albeit more cleanly) by reacting **2a** with 2 eq 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 1H NMR spectrum of **4a** indicates a C₂-symmetric structure, which could result from a stereoselective sequence of either *i*) two 1,2- additions or *ii*) two 1,4-additions of Zr/P compounds onto chalcone. The signature $^{13}C\{^1H\}$ NMR signals of the chalcone moiety at 92.3 ppm ($^2J_{PC} = 7.1$ Hz) and 42.3 ppm ($^1J_{PC} = 34.1$ Hz) indicate that two 1,4 additions took place; indeed we have previously reported similar 1,4-addition of M/P onto chalcone (M = Ti, Zr).^{61,60} It became evident that the other compound observed along with **4a** was an intermediate and that the reaction needed 2 eq of chalcone per Zr in order to proceed to completion. Indeed, when we reacted **3a** with 4 eq of chalcone we obtained almost exclusively **4a**.

Given the fast reaction of **2a** with CO₂ and the fact that we never observed any traces of **2a** in solutions of **3a**,³⁷ 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 eq of chalcone, the ^1H 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 eq 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 Zr/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 equivalents resulted in complex mixtures; however, a cleaner reaction was observed when **2d** was reacted with 2 eq 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 ^1H 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 Cp_2Zr^+ fragment is coordinated to $\text{Ph}(\text{CO})\text{NPh}_2$ and PhCH_2O^- ligands (Figure 7).

Multinuclear NMR spectroscopy confirmed the structure of **7d**; in particular the ^1H NMR spectrum in CD_2Cl_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 OH^- . This suggests that the amide ligand binds more strongly to Zr than the benzylate.

Scheme 8.

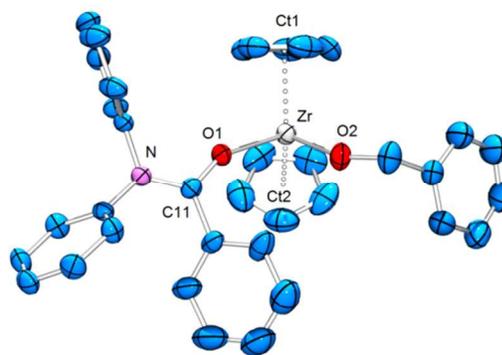
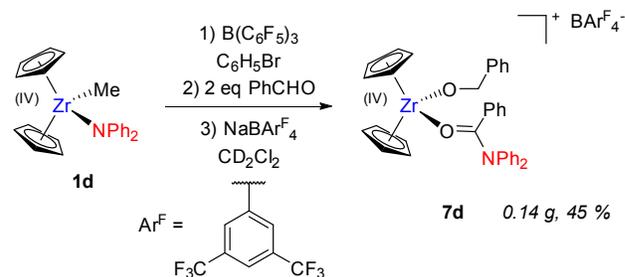
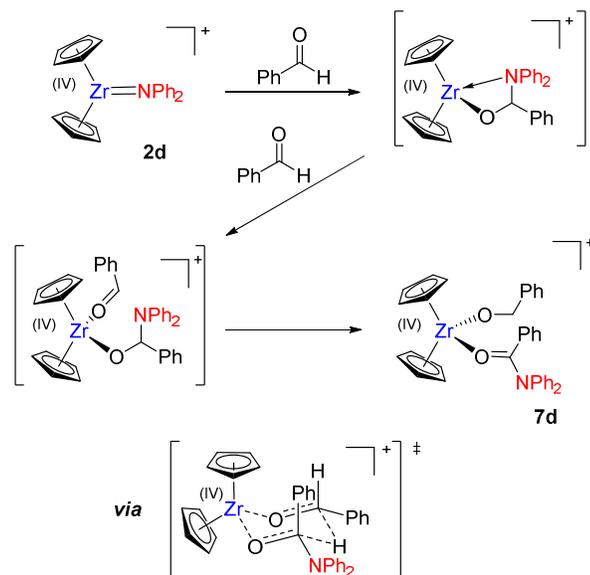


Figure 7. POV-Ray projection of the crystal structure of **7d** (30 % ellipsoids probability, $\text{BAR}^{\text{F}}_4^-$ anion omitted for clarity).

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

Scheme 9. Formation of **7d** via a MPV-type mechanism.



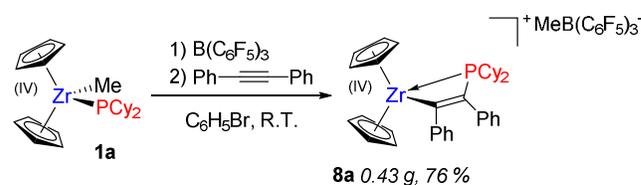
Note: Anions omitted for clarity.

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 (CO₂, 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

nylacetylene with **2a,b** and **2d,e** in the hope that the formed products would be more stable.³⁹ While **2d,e** did not react and **2b** gave an unidentified mixture, **2a** reacted cleanly in C₆D₅Br to give a new species with a ³¹P{¹H} signal at -12.4 ppm.⁴⁰ Complex **8a** was obtained on preparative scale in 76 % yield (Scheme 10) and was characterized by elemental analysis and multinuclear NMR spectroscopy.

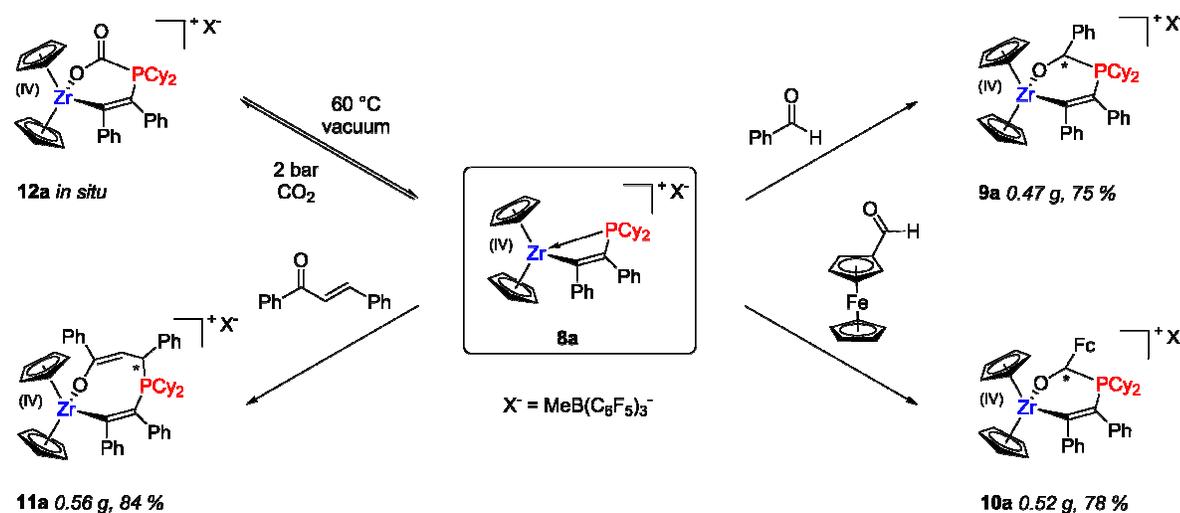
Scheme 10.



A distinctive feature of the ¹H 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. Noteworthy, the reactivity of **2a** resembles that of terminal phosphinidenes, which typically undergo [2+2] cycloadditions with alkynes.⁴¹ 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 C₆D₅Br, it degrades after a few hours in the solid state, even when stored at -35 °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 CO₂ 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 CD₂Cl₂) and FTIR spectroscopy, and high resolution mass spectrometry. Compound

Scheme 11. Reactivity of FLP **8a**.



Note: all reactions performed at room temperature in C₆H₅Br or C₆D₅Br.

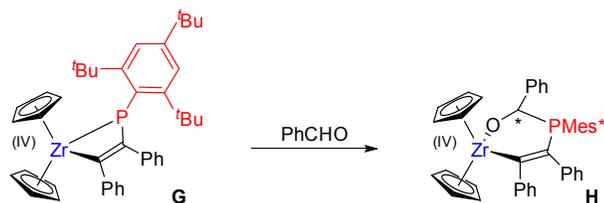
3a) called for another approach. We therefore reacted diphe-

12a could only be characterized by NMR spectroscopy (in C_6D_5Br) 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 $^{31}P\{^1H\}$ spectrum gives a singlet at 27.0 ppm. A characteristic doublet is observed at 6.40 ppm in the 1H spectrum for the CHO hydrogen ($^2J_{PH} = 3.4$ 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).^{41b,41c} They reported the system **G** adding e.g. acetone to give the respective six-membered heterocyclic carbonyl insertion product into the Zr-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.

Scheme 12.



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 $^{31}P\{^1H\}$ NMR spectroscopy, while the CHO hydrogen resonates as a singlet at 5.95 ppm in the 1H NMR spectrum. As in the case of **9a** the Cp rings bound to Zr are non-equivalent (6.43 and 6.38 ppm) and those bound to Fe are visible at lower field as a cluster of three multiplets (FcCpCHO: 4.47-4.33 ppm region) and one singlet (FcCp: 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 $KB(C_6F_5)_4$ in CD_2Cl_2 , thus confirming the structure derived from spectroscopic data (compound **10a'**, Figure 8).⁴²

The C11-C12 distance (1.352(4) Å) is consistent with a C=C double bond.²⁷ The main feature of the Zr cation is the presence of two metallocene systems with bent (Ct1-Zr-Ct2: 131.9 °) and linear geometries (Ct3-Fe-Ct4: 176.9 °). 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).²³ 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) °) considerably deviates from linearity.

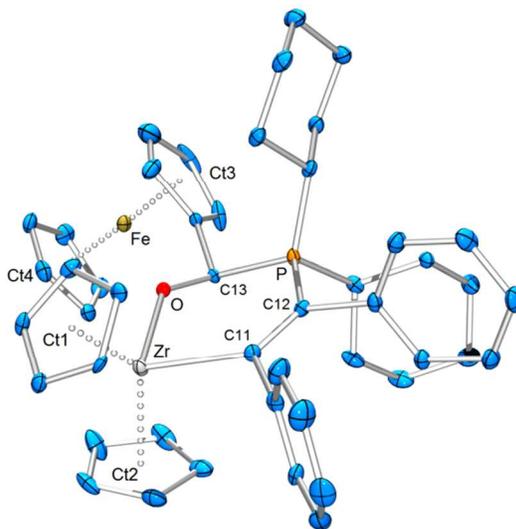


Figure 8. POV-Ray projection of the crystal structure of **10a'** (30 % ellipsoids probability, $B(C_6F_5)_4^-$ anion omitted for clarity).

While the reactions with aldehydes show that **8a** can activate carbonyl compounds by 1,2 addition, reaction with chalcone 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**, non-equivalent 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 α to P resonates at 45.3 ppm ($^1J_{PC} = 35.5$ Hz), and the β 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).⁴² The structure of **11a'** reveals an 8-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.

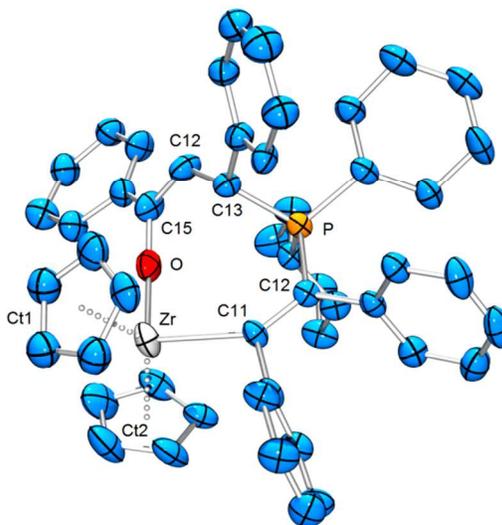


Figure 9. POV-Ray projection of the crystal structure of **11a'** (30 % ellipsoids probability, $BAR_4^F^-$ anion omitted for clarity).

1
2
3
4
5
6
7
8
9
10
Finally, **8a** reacted with CO₂, although in this case the product was unstable and released CO₂ 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 ³¹P{¹H} spectrum. Definitive evidence for the formation of a CO₂ adduct came in the shape of a new doublet at 162.6 ppm (¹J_{PC} = 37.7 Hz) in the ¹³C{¹H} NMR spectrum.

11 CONCLUSION

12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
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 π 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 π 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 Cp₂Zr⁺ fragment, this feature enables the activation of CO₂ and H₂ in a cooperative fashion. As a notable consequence, complexes **2** are rather active hydrogenation catalysts under very mild conditions.

27
28
29
30
31
32
33
34
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.

35 EXPERIMENTAL SECTION

36
37
38
For general information and the spectroscopic and structural data of the new compounds see the Supporting Information.

39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Preparation of compound 1a. Cp₂ZrMeCl (1.996 g, 7.3 mmol) and LiPCy₂ (1.654 g, 7.3 mmol) were dissolved separately in THF (20 and 30 mL resp.). Both solutions were cooled to ca -80 °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 °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 C₂₃H₃₅PZr: C, 63.69; H, 8.13. Found: C, 63.27; H, 7.97.

Preparation of compound 1b. Cp₂ZrMeCl (1.088 g, 4.0 mmol) and LiPMes₂(OEt₂)_{0,9} (1.342 g, 4.0 mmol) were dissolved separately in THF (10 and 15 mL resp.). Both solutions were cooled to ca -80 °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 °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 PHMes₂); 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 C₂₉H₃₅PZr: C, 68.87; H, 6.97. Found: C, 68.50; H, 7.05.

Preparation of compound 1c. Cp₂ZrMeCl (1.088 g, 4.0 mmol) and Li^tBu₂(OEt₂)_{0,4} (0.727 g, 4.0 mmol) were dissolved separately in THF (10 and 7 mL resp.). 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 = 90 % pure based on integration of the ¹H NMR signals in the Cp region (the main impurity was presumably [Cp₂ZrMe]₂O); filtration and recrystallization from pentane afforded somewhat cleaner material (= 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 C₁₉H₃₁PZr: C, 59.79; H, 8.19. Found: C, 57.60; H, 8.22.

Preparation of compound 1d. Cp₂ZrMeCl (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 ⁿBuLi 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 C₂₃H₂₃NZr: C, 68.27; H, 5.73; N, 3.46. Found: C, 67.88; H, 5.59; N, 3.58.

Preparation of compound 1e. Cp₂ZrMeCl (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 ^tBuLi 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 C₂₃H₃₁NZr: 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 C₆D₅Br (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 C₆D₅Br (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 C₆H₅Br (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 C₄₁H₂₃BF₁₅NZr: 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 C₆D₅Br (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 ¹H, ¹¹B, ¹³C and ¹⁹F NMR spectroscopy. The exper-

iment was repeated on 0.5 mmol scale in 1 mL C₆D₅Br for ¹⁵N 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 C₆H₅Br (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 CD₂Cl₂. 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 C₄₆H₂₈BF₂₀NZr: 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 C₆H₅Br (5 mL). The red mixture was placed into a schlenk vessel, evacuated and exposed to a CO₂ 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 C₈₄H₇₀B₂F₃₀O₄P₂Zr₂: 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 C₆H₅Br (5 mL). The pale brown mixture was placed into a schlenk vessel, evacuated and exposed to a CO₂ 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 C₈₄H₄₆B₂F₃₀N₂O₄Zr₂: 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⁻¹.

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 C₆H₅Br (5 mL). The green mixture was placed into a schlenk vessel, evacuated and exposed to a CO₂ atmosphere. A precipitate appeared almost immediately, which was filtered after addition of pentane (15 mL), suspended in CH₂Cl₂ / 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 CH₂Cl₂ at room temperature. Elemental Analysis: calcd for C₈₄H₆₂B₂F₃₀N₂O₄Zr₂: 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 C₆H₅Br (1.5 mL). The solution was added to *trans*-chalcone (208 mg, 1 mmol) and the

1 mixture was stirred for 30 min, then added to 50 mL of pen-
2 tane. The resulting yellow oil was washed three times with 5
3 mL of pentane and dried *in vacuo* outside the box. This opera-
4 tion was repeated two more times until a yellow powder was
5 obtained. Finally, the powder was triturated in 20 mL of pen-
6 tane and the supernatant was filtered off. Complex **4a** was
7 obtained as a yellow powder (0.49 g, 72 %) containing 100
8 mol% of pentane. This compound was also obtained and char-
9 acterized *in situ* by reacting **3a** with 2-4 eq of chalcone in
10 CD₂Cl₂. Elemental Analysis: calcd for
11 C₇₁H₅₉BF₁₅O₂PZr(C₅H₁₂): C, 63.64; H, 4.99. Found: C, 62.59;
12 H, 5.01. HRMS (ESI-pos): calcd for C₅₂H₅₆O₂PZr [M-
13 CH₃B(C₆F₅)₃]⁺: 833.30595. Found: 833.30682 (rel. ab. 100 %, +1.0 ppm).

14 **Preparation of complex 7d.** In an Ar glovebox, complex **1d**
15 (81 mg, 0.2 mmol) and tris(pentafluorophenyl)borane (256
16 mg, 0.5 mmol) were mixed in C₆H₅Br (2 mL). Benzaldehyde
17 (42.4 mg, 0.2 mmol) was added to the reaction mixture and the
18 solution was stirred for 36 hours, during which a color change
19 from red to green was observed. The reaction mixture was
20 added to 15 mL of vigorously stirred pentane, causing the
21 precipitation of a green oil which was further rinsed with
22 pentane, then taken up in 2 mL of CD₂Cl₂ and stirred with 213
23 mg (0.24 mmol) of NaBAR₄^F. The reaction mixture was filtered
24 over a borosilicate filter and precipitated by addition to 15
25 mL of vigorously stirred pentane. A green precipitate was
26 obtained, which was rinsed with pentane, yielding complex **7d**
27 was obtained as a pale green powder (135 mg, 45 %) contain-
28 ing <10 % of MeB(C₆F₅)₃⁻ anion. Single crystals suitable for
29 X-ray diffraction were grown by diffusion of pentane into a
30 CD₂Cl₂ solution of **7d** at -35 °C. Elemental Analysis: calcd for
31 C₆₈H₄₄BF₂₄NO₂Zr: C, 55.75; H, 3.03; N, 0.96. Found: C,
32 54.93; H, 2.90; N, 0.93. HRMS (ESI-pos): calcd for
33 C₃₆H₃₂NO₂Zr [M-BAR₄^F]⁺: 600.14746. Found: 600.14723 (rel.
34 ab. 90 %, -0.4 ppm).

35 **Preparation of complex 8a.** In an Ar glovebox, complex **1a**
36 (217 mg, 0.5 mmol), tris(pentafluorophenyl)borane (256 mg,
37 0.5 mmol) and diphenylacetylene (90 mg, 0.5 mmol) were
38 dissolved in C₆H₅Br (3 mL). The mixture was stirred for 5
39 min, then added to 50 mL of vigorously stirred pentane. The
40 resulting red oil was washed three times with 5 mL pentane,
41 after which a further 30 mL of pentane was added and the
42 mixture was stirred for 2 hrs in the glovebox. The supernatant
43 was removed, the oil rinsed with 5 mL of pentane and. The
44 resulting crusty solid was soaked in 5 mL of pentane for 10
45 min, the supernatant was discarded and the oily solid was
46 dried *in vacuo* for 25 min in the box antechamber. Complex **8a**
47 was obtained as a red powder (0.43 g, 76 %). The compound
48 degrades within several hours when stored at -35 °C under Ar.
49 Elemental Analysis: calcd for C₅₅H₄₅BF₁₅PZr: C, 58.77; H,
50 4.04. Found: C, 57.90; H, 4.46.

51 **Preparation of complex 9a.** In an Ar glovebox, complex **1a**
52 (217 mg, 0.5 mmol), tris(pentafluorophenyl)borane (256 mg,
53 0.5 mmol) and diphenylacetylene (89 mg, 0.5 mmol) were
54 dissolved in C₆H₅Br (3 mL) to give a brown-red solution.
55 Benzaldehyde (53 mg, 0.5 mmol) was added, and the solution
56 turned bright yellow instantaneously. It was then added to 50
57 mL of vigorously stirred pentane. The resulting yellow oil was
58 washed three times with 3 mL pentane and dried *in vacuo*
59 outside the box. Pentane (10 mL) was added, the mixture was

60 stirred for 10 min and the supernatant solution was discarded.
The residue was taken up in 1.5 mL of CH₂Cl₂, and the solu-
tion was added to 50 mL of vigorously stirred pentane to give
a yellow oil. The supernatant solution was discarded and resi-
due was dried *in vacuo* for 1 hr. Complex **4a-I** was obtained as
a pale yellow foam (0.47 g, 75 %). Elemental Analysis: calcd
for C₆₂H₅₁BF₁₅OPZr: C, 60.54; H, 4.18. Found: C, 61.09; H,
4.21. HRMS (ESI-pos): calcd for C₄₃H₄₈OPZr [M-
CH₃B(C₆F₅)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 C₆H₅Br (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
CH₂Cl₂ 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 KB(C₆F₅)₄ in
CD₂Cl₂ (1.5 mL) and subsequent crystallization by diffusion
of pentane at -35 °C. Multinuclear 1D NMR (¹H, ³¹P {¹H}, ¹⁹F)
of **10a** performed before crystallization indicated >90 %
anion exchange. Analytical data follow for **10a**. Elemental
Analysis: calcd for C₆₆H₅₅BF₁₅FeOPZr.(C₅H₁₂)_{0.25}: C, 59.57;
H, 4.31. Found: C, 58.81; H, 4.27. HRMS (ESI-pos): calcd for
C₄₇H₅₂OPFeZr [M-CH₃B(C₆F₅)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 C₆H₅Br (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 CH₂Cl₂,
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 hr. 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 ex-
change of 0.1 mmol of **11a** with 0.12 mmol of NaBAR₄^F in
CD₂Cl₂ (1.5 mL) and subsequent crystallization by diffusion
of pentane at -35 °C. Multinuclear 1D NMR (¹H, ³¹P {¹H}, ¹⁹F)
performed before crystallization indicated >90 % anion ex-
change. Analytical data follow for **11a**. Elemental Analysis:
calcd for C₇₀H₅₇BF₁₅OPZr(C₅H₁₂): C, 64.14; H, 4.95. Found:
C, 63.23; H, 5.66. HRMS (ESI-pos): calcd for C₅₁H₅₄OPZr
[M-CH₃B(C₆F₅)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 C₆D₅Br (0.8 mL) in an NMR tube

fitted with a pressure valve. The tube was evacuated and re-filled with 2 bar of CO₂. 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 °C for 4 hrs 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 B(C₆F₅)₃ in 1.0 mL C₆D₅Br) was prepared and a 0.2 mL aliquot was added to a solution of Cp₂Fe (standard ; 9.3 mg, 0.05 mmol) and the substrate (1.0 or 2.0 mmol) in C₆D₅Br (0.6 mL). The Schlenk vessel was frozen with liquid nitrogen and was evacuated. After thawing, it was refilled with 1.5 bar of H₂. The reaction mixture was stirred for the indicated time at room temperature. Product conversion was estimated by ¹H NMR after dilution with C₆D₅Br (integration of a suitable signal vs Cp₂Fe 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 B(C₆F₅)₃ in 1 mL C₆D₅Br) was prepared and this was added to a solution of styrene (10 mmol) in C₆D₅Br (3 mL). The Schlenk vessel was evacuated and refilled with 1.5 bar of H₂. The reaction mixture was stirred for 2 hours 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 CH₂Cl₂. After evaporation the residue was distilled at 60 °C/0.3 mBar and the residue was analyzed by ¹H NMR in CDCl₃ 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 (Mw = 314).

ASSOCIATED CONTENT

Details about the experimental procedures, characterization of all new compounds, and crystal structure data as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>

AUTHOR INFORMATION

Corresponding Authors

*E-mail: erker@uni-muenster.de.

*E-mail: pierre.le-gendre@u-bourgogne.fr.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

Financial support from Agence Nationale de la Recherche and Deutsche Forschungsgemeinschaft (MENOLEP programme) and Conseil Régional de Bourgogne (PARI CDEA program) is gratefully acknowledged.

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.; Frohlich, 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, 2013; Vol. 332; (b) *Frustrated Lewis Pair Chemistry II: expanding the scope*; Erker, G.; Stephan, D. W., Eds.; Springer, 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 Catalysis* **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.; Frohlich, 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) Podiyanachari, 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. Hultzsch has reported a Zr system for hydroamination which was claimed to involve an active catalyst of general formula $Cp_2Zr=NRR^+$: Gribkov, D. V.; Hultzsch, 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.; Reves, 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 phi 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) PR₂ 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 ($Cp^*_2YPPPh_2$) 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 Grützmaier, 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 Catalysis* **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 eq of THF yielded a labile adduct with a ^{31}P NMR signal of 340.5 ppm, see supporting information; this compound was never observed in THF solutions of **3a-I**.

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; and (b) Nakano, T.; Umamo, S.; Kino, Y.; Ishii, Y.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3752-3757.

39. Insertion of phenylacetylene into the Zr-P bond of $[Cp_2Zr(Cl)(P(SiMe_3)_2)]$ 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 $B(C_6F_5)_3$.

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 1H and ^{31}P NMR spectroscopy.

TOC

