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Stoichiometric Reactions and Catalytic Hydrogenation with a Reactive Intramolecular Zr^+/Amine Frustrated Lewis Pair

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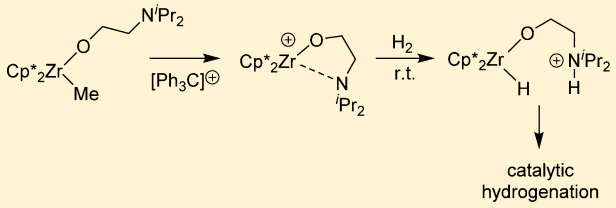
Supporting Information

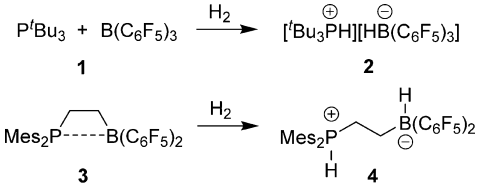
ABSTRACT: Methyl anion abstraction from $Cp^*_2Zr(CH_3)$-$OCH_2CH_2N^iPr_2$ (**13**) with trityl cation generates $[Cp^*_2Zr$-$(OCH_2CH_2N^iPr_2)]^+$ (**14**). Complex **14** behaves as a reactive Zr^+/amine frustrated Lewis pair (FLP). It reacts with dichloromethane to give the $[Zr]Cl[OCH_2CH_2N(CH_2Cl)^iPr_2]^+$ cation (**15**), it slowly loses H_2 upon standing at 60 °C to give a metallacyclic iminium cation product **18**, and it reacts with terminal alkynes to give the [Zr]-alkynyl/ammonium systems **19**. The organometallic FLP **14** cleaves dihydrogen heterolytically at near to ambient conditions to give the $[Zr]H$-$[OCH_2CH_2NH^iPr_2]^+$ complex **20**, which reduces benzaldehyde to the respective $[Zr]OCH_2Ph$ product **21** and is able to transfer the H^+/H^- pair to styrene to give ethylbenzene. Consequently, the Zr^+/amine FLP **14** was used as an active hydrogenation catalyst for a series of alkenes and internal alkynes. The catalytic hydrogenation reactions were carried out under mild conditions (r.t., 1.5 bar of H_2) using between 1 and 4 mol % FLP catalyst **14**.



INTRODUCTION

Frustrated Lewis pairs (FLPs) are comprised of Lewis acids and bases that are hindered from effective neutralizing adduct formation by steric bulk or (less often) special electronic features.[1] These often weakly interacting Lewis pairs have been used for binding and/or activation of a variety of small molecules,[2] including the heterolytic cleavage of dihydrogen.[3,4] This has led to the development of metal-free catalytic hydrogenation processes[5] of a variety of organic (and to a lesser extent organometallic[6]) substrates. The systems **1** (intermolecular)[3] and **3** (intramolecular)[4] are typical examples (see Scheme 1).

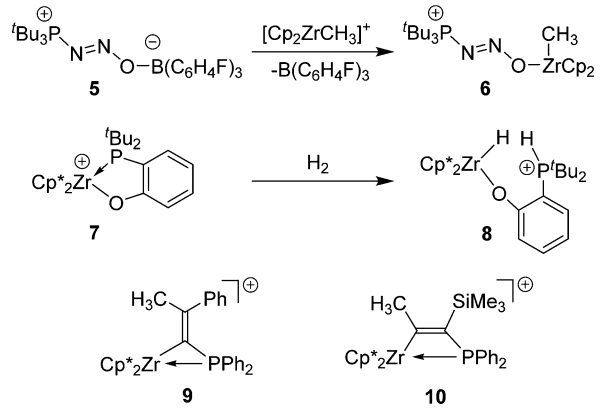
Scheme 1



Frustrated Lewis pairs can add to alkenes and alkynes,[7] to carbonyl compounds,[8] including CO_2,[9] to SO_2,[10] to nitrogen oxides,[11,12] etc. They have been used for inducing CO or CO_2 reduction processes[13−15] and for developing new ways to methylene phosphonium[16] or borata-alkene chemistry.[17] Most of this chemistry involves purely main group element containing FLPs. The majority of these systems make use of strongly electrophilic boron Lewis acids,[18] but there has been a desire to develop other Lewis acid containing systems by, e.g., using aluminum-based[19] or phosphorus-based[20] systems. Even electrophilic carbon containing systems have been considered.[21] There is a recent trend to revert in some cases to transition metal containing systems, especially to make use of the strongly Lewis acidic character of the group 4 metallocene derived $[^RCp_2ZrX]^+$ cations (or their Ti or Hf analogues).[22] Stephan et al. first introduced the $[Cp_2ZrMe]^+$ unit into an FLP product by Lewis acid exchange (see Scheme 2).[23] Wass et al. described system **7** (and related complexes), which showed a remarkable FLP chemistry, including H_2 activation.[24] We prepared the [Zr]-alkenyl/phosphane FLPs **9** and **10** and investigated their distinct small-molecule chemistry.[25,26]

We have now prepared the intramolecular Zr^+/amine FLP **14** by a simple route starting from $Cp^*_2ZrMe_2$ and the 2-

Scheme 2



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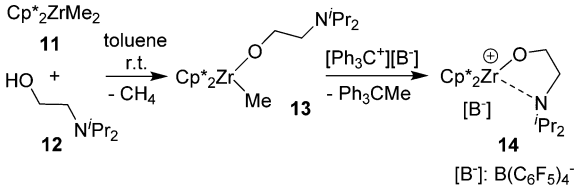
aminoethanol system $HOCH_2CH_2N^iPr_2$. The resulting FLP, in situ generated, turned out to provide a simple and rather robust entry to a variety of typical frustrated Lewis pair reactions, including rather effective catalytic hydrogenation of a variety of olefinic and acetylenic substrates. This development will be described in this paper.

RESULTS AND DISCUSSION

Generation of the Intramolecular Zr^+/Amine System and Its Stoichiometric FLP Reactions. The starting material of our study was prepared by treatment of $Cp^*_2ZrMe_2$ (**11**) with 1 molar equiv of the aminoalcohol derivative **12** in toluene at r.t. The reaction took place with liberation of methane, and the organometallic product **13** was isolated as a white solid in 81% yield (see Scheme 3).

Scheme 3



It was characterized by C,H-elemental analysis, by NMR spectroscopy (^1H, δ −0.07 (Zr−CH_3), δ 4.11 and 2.53 (−O−CH_2−CH_2−[N]), δ 1.85 (ZrCp*$_2$); ^{13}C, δ 117.2, 11.3 Cp*), and by X-ray diffraction (see Figure 1). It shows a bent

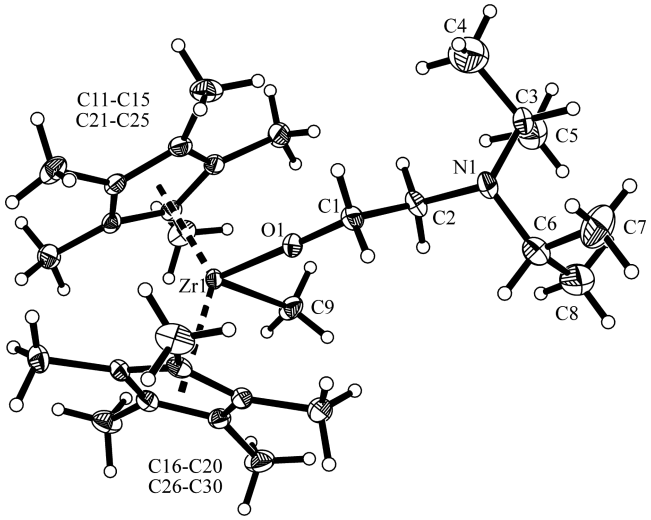


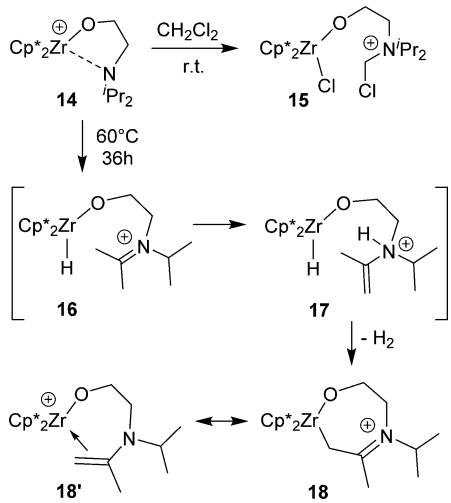
Figure 1. View of the molecular structure of complex **13** (thermal ellipsoids are shown with 15% probability).

metallocene unit with a σ-CH_3 ligand bonded in the σ-ligand plane (Zr1−C9 = 2.280(4) Å) and a σ-O−CH_2− group [disordered over two positions; Zr1−O1 = 1.928(9) Å, Zr1−O1A = 1.946(10) Å; angles Zr1−O1−C1 = 179(2)° and O1−Zr1−C9 = 90.9(7)°]. The −O−CH_2−CH_2−N unit shows an extended antiperiplanar arrangement (dihedral angle O1−C1−C2−N1 = 171.0(2)°). The terminal nitrogen atom bears a pair of isopropyl substituents. It shows a distorted trigonal pyramidal coordination geometry ($\sum N1^{CCC}$ = 343.4°).

The selective removal of the methyl anion ligand of **13** was achieved by treatment with trityl tetrakis(pentafluorophenyl)-borate in bromobenzene (see Scheme 3).[22] The cationic complex **14** is very reactive (see below); therefore, it was not isolated but characterized spectroscopically in situ generated from the reaction mixture in d_5-bromobenzene. Cation **14** showed NMR features of the Cp^*_2Zr moiety at δ 1.70 (^1H) and δ 125.6/11.3 (^{13}C). It showed a ^1H NMR AA′XX′ pattern of the −OCH_2CH_2N unit at δ 4.10 and 2.42 (^{13}C, δ 75.1, 47.5) and the ^1H NMR signals of the pair of symmetry-equivalent isopropyl substituents at nitrogen at δ 2.87 (sept, CH) and δ 0.96 (d, $^3J_{HH}$ = 6.6 Hz, 12H) (^{13}C, δ 49.6, 21.1). The structural details of this complex are not completely worked out at present. It might be that there is a weak internal interaction between the amine and the strong Zr^+ Lewis acid.

The Zr^+/amine FLP **14** is so reactive that it cannot be handled as such in dichloromethane. Compound **14** was in situ generated in the usual way in bromobenzene solution, and then we added a small amount of dichloromethane. Workup eventually gave the CH_2Cl_2 addition product **15** (see Scheme 4), which was isolated as a white solid in 62% yield. The X-ray

Scheme 4



crystal structure analysis showed that the $[Cp^*_2Zr]^+$ Lewis acid had effected a net chloride abstraction from the dichloromethane reagent and the remaining CH_2Cl residue was attached to the nitrogen Lewis base (see Figure 2).[27] The ^1H NMR spectrum of compound **15** showed the resonance of the newly formed Cl−CH_2−$[N]^+$ unit at δ 4.90 (s, 2H) (^{13}C, δ 63.2).

Even in the absence of added suitable reagents, the reactive Zr^+/amine FLP **14** turned out not to be stable for prolonged periods of time. We kept compound **14**, in situ generated at r.t. in bromobenzene solution, for 36 h at 60 °C and then isolated the pale yellow solid compound **18** in 41% yield from the reaction mixture (see Scheme 4). Compound **18** was apparently formed from **14** by loss of dihydrogen. We assume a reaction pathway that involves a typical hydride abstraction reaction from the isopropyl α-CH position of the amino group in **14** by the adjacent $[Cp^*_2Zr]^+$ Lewis acid.[28] This would generate the reactive bifunctional zirconium hydride/iminium intermediate **16** (see Scheme 4). Subsequent iminium/enaminium tautomerization followed by H_2 elimination would then provide a reasonable direct route to the observed product **18**.

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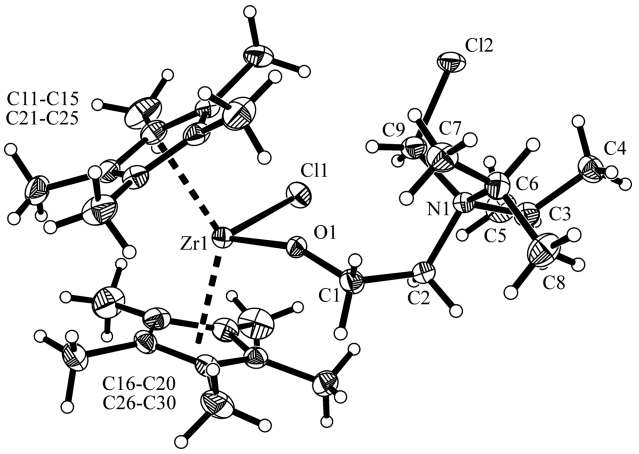


Figure 2. Projection of the molecular structure of the FLP dichloromethane addition product **15** (only the cation is depicted; thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): Zr1−O1, 1.991(4); Zr1−Cl1, 2.454(2); N1−C2, 1.530(7); N1−C3, 1.585(7); N1−C6, 1.570(7); N1−C9, 1.486(7); C9−Cl2, 1.784(8); O1−Zr1−Cl1, 93.6(1); C2−N1−C3, 104.0(5); C3−N1−C6, 108.6(5); C6−N1−C9, 111.9(6); C2−N1−C9, 106.2(5); O1−C1−C2−N1, 78.8(10); C2−N1−C9−Cl2, 179.3(8).

The X-ray crystal structure analysis of compound **18** has confirmed the formation of the metallacyclic $[Cp^*_2Zr]^+$ addition product to the incipient pendant enamine (see Figure 3).[29] The resulting Zr1−C7 linkage (2.443(5) Å) corresponds

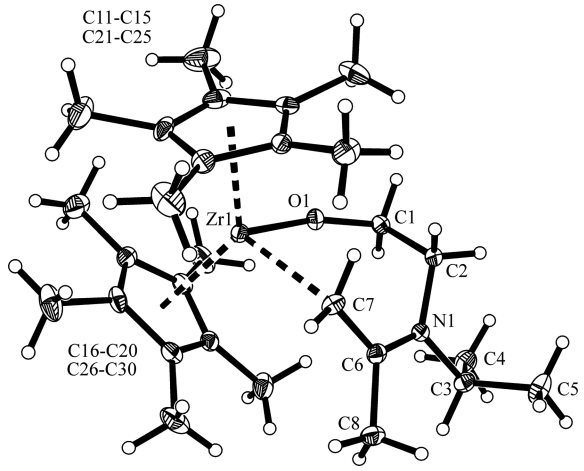


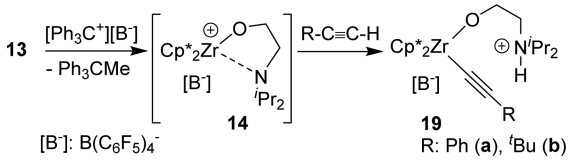
Figure 3. Molecular structure of compound **18** (only the cation is depicted; thermal ellipsoids are shown with 15% probability).

to a value located between typical Zr−carbon σ- and π-bonds. The C7−C6 bond (1.418(6) Å) is also at an intermediate value between carbon−carbon single and double bonds. The adjacent C6−N1 bond length amounts to 1.335(6) Å. Zr1−C7−C6 was found at 119.7(3)°. The coordination geometries at both C6 ($\sum C6^{NCC}$ = 360°) and N1 ($\sum N1^{CCC}$ = 359.4°) are planar tricoordinate. The Zr···C6 distance in complex **18** is large (3.378 Å). Compound **18** contains a Zr1−O1 bond at 1.935(3) Å with a Zr1−O1−C1 angle of 155.8(3)° (O1−Zr1−C7 = 83.5(2)°). We conclude that the structure of the thermolysis product of the Zr^+/amine FLP **14** can probably be described as a resonance hybrid of the structures **18** and **18′** (see Scheme 4).

Complex **18** shows very characteristic NMR spectra. It shows a pair of Cp^*_2Zr ^1H NMR methyl signals at δ 1.64/1.63 (^{13}C, δ 11.2, 11.0) which indicate a nonplanar chiral metallacyclic ring structure also in solution. Consequently, the methyl substituents of the *N*-isopropyl substituent are diastereotopic (^1H NMR, δ 0.88, 0.83; ^{13}C NMR, δ 19.5, 19.3). The Zr−CH_2 hydrogens are diastereotopic (δ 2.48, 1.08; ^{13}C, δ 51.1) with a negligible geminal coupling constant. The methylene hydrogens of the −O−CH_2−CH_2−N− moiety of **18** are also pairwise diastereotopic [OCH_2, δ 4.16/3.91 (^{13}C, 68.3); CH_2N, δ 3.03/2.78 (^{13}C, 47.5)]. The $^1H/^{13}C$ NMR signals of the methyl substituent attached at the sp^2-carbon center C6 (^{13}C, 191.5) occur at δ 2.06/26.2.

Phenylacetylene was added to complex **14**, generated in bromobenzene solution. The mixture was kept for 2 h at r.t. and then worked up to give the product **19a** as a white solid in 76% yield (see Scheme 5). The X-ray crystal structure analysis

Scheme 5



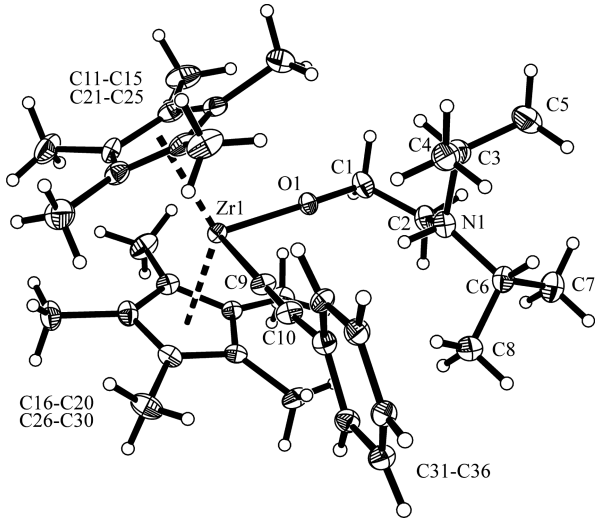


Figure 4. Molecular structure of complex **19a** (only the cation is shown; thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): Zr1−O1, 1.977(4); Zr1−C9, 2.255(6); C9−C10, 1.192(8); C1−C2, 1.443(13); C2−N1, 1.514(11); N1−C3, 1.536(11); N1−C6, 1.555(10); Zr1−C9−C10, 179.1(6); Zr1−O1−C1, 169.2(7); O1−Zr1−C9, 92.5(2); C2−N1−C3, 113.1(9); C2−N1−C6, 115.2(8); C3−N1−C6, 112.7(8).

(see Figure 4) showed that a typical frustrated Lewis pair reaction had taken place:[30] the pendant amino group had served to deprotonate the added terminal alkyne, and the resulting alkynyl unit was found σ-bonded to zirconium. The ^1H NMR NH resonance was located at δ 5.73 (for further details, see the Supporting Information).

We have also trapped the in situ generated Zr^+/amine FLP system **14** with *tert*-butylacetylene and isolated the corresponding alkynylzirconocene/ammonium product **19b** in 76% yield

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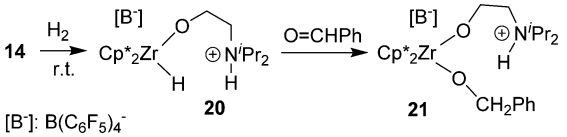
J. Am. Chem. Soc. 2015, 137, 4550−4557

(see Scheme 5). It was characterized by C,H elemental analysis and NMR spectroscopy [^{1}H, δ 5.25 (NH), 3.95, 2.62 ($OCH_2CH_2[NH]^+$); ^{13}C, δ 59.5, 48.5]. The isopropyl methyl groups of the ammonium unit are pairwise diastereotopic (for details, see the Supporting Information). Complex **19b** was also characterized by X-ray diffraction. Its structure is similar to that of **19a**. It is depicted in the Supporting Information.

Reactions with H_2 and Catalytic Hydrogenation. Not unexpectedly, the reactive Zr^+/amine FLP **14** reacts readily with H_2 under mild conditions. The in situ (in C_6D_5Br) generated organometallic FLP reacts within minutes at close to ambient conditions (1.5 bar of H_2, r.t.) with dihydrogen to give the product **20** of heterolytic dihydrogen splitting (see Scheme 6). During this process, the hydride anion was added to the

Scheme 6



zirconium cation of **14** and the nitrogen atom of the pendant amine base was protonated. Complex **20** was not isolated since it tended to lose some dihydrogen during the attempted workup process, but the reactive compound **20** was amply characterized spectroscopically and by subsequent chemical reactions.

The [Zr]H/NH^+ complex **20** shows a single sharp Cp^*_2Zr ^{1}H NMR resonance at δ 1.79 (^{13}C, δ 118.3/11.5) and a single ^{1}H NMR set of N^iPr_2 resonances [δ 3.20 (2H, CH), δ 0.93 (br d, 12H, CH_3); ^{13}C, δ 53.9 (CH), δ 18.1, 18.0 (CH_3)]. The NMR signals of the bridging $O-CH_2-CH_2-N$ unit were located at δ 3.92/2.57 (^{1}H) and δ 60.2/49.7 (^{13}C). Most importantly, the [Zr]H resonance and the NH signal of complex **20** were positively identified by means of the reaction of the FLP **14** with D_2, which generated the corresponding product **20**-*D* in C_6D_5Br solution. The [Zr]D (^{2}H, δ 5.48)[31] and [N]D (^{2}H, δ 4.60) resonances were monitored at their respective positions by ^{2}H NMR spectroscopy (the spectra are depicted in the Supporting Information).

The formation of the zirconium hydride product **20** by heterolytic splitting of dihydrogen by the Zr^+/amine FLP **14** was confirmed by its subsequent reaction with benzaldehyde. Hydridozirconocene complexes are known to reduce organic carbonyl compounds to alkoxyzirconocene complexes.[32] Therefore, we added benzaldehyde (1 molar equiv) to a solution of the in situ generated zirconocene hydride complex **20**. This resulted in an instantaneous reaction. From the reaction mixture, we isolated the alkoxyzirconocene product **21** as a yellow-orange solid in 50% yield (see Scheme 6). The composition of **21** was confirmed by an X-ray crystal structure analysis (which contained a 5% [Zr]Br contamination). It showed the presence of the $-OCH_2CH_2-NH^iPr_2^+$ ligand in a gauche-like confirmation (θ(O1−C1−C2−N1) = 47.4(4)°) σ-bonded at the Cp^*_2Zr bent metallocene wedge. The added aldehyde reagent was reduced to the benzyl alcohol stage. The alcoholate is bonded to the zirconocene unit in the σ-ligand plane (see Figure 5).

In solution compound **21** shows the NMR signals of the newly introduced [Zr]OCH_2Ph moiety. It shows the ^{1}H NMR singlet of the OCH_2Ph group at δ 5.05 [^{13}C, δ 71.4] in addition

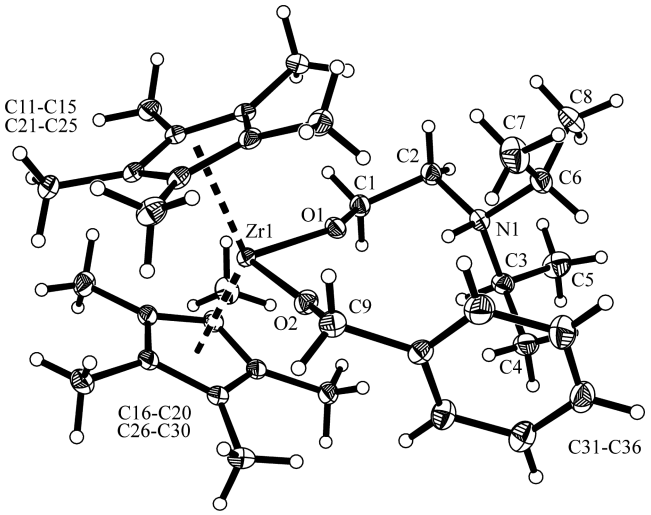
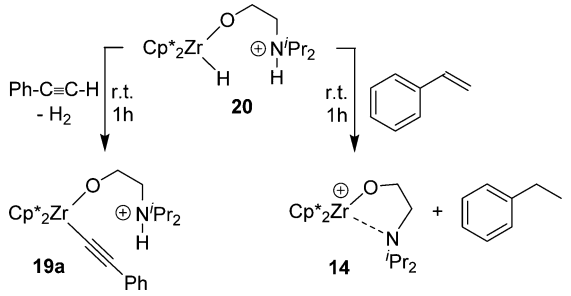


Figure 5. Molecular structure of complex **21** (only the cation is shown; thermal ellipsoids are shown with 15% probability).

to the typical resonances of the adjacent phenyl substituent. The nitrogen atom of the $-OCH_2CH_2NH^iPr_2^+$ ligand is protonated [^{1}H, δ 5.43 (br, NH)]; consequently, the methyl groups of the attached isopropyl substituents are pairwise diastereotopic. The ^{1}H/^{13}C NMR features of the $-CH_2-CH_2-$ group were found at δ 3.46/2.43 (^{1}H) and δ 60.7/50.2 (^{13}C). Complex **21** shows a single sharp Cp^*_2Zr moiety ^{1}H NMR singlet (δ 1.74) (^{13}C, δ 120.4/11.3).

We then treated the ZrH/NH^+ hydrogen activation product **20** with an alkyne and an olefin, respectively (see Scheme 7).

Scheme 7



The H_2-splitting product **20** was first treated with 1 molar equiv of phenylacetylene in C_6D_5Br solution. After addition the mixture was kept for 1 h at r.t., and then the solution was directly analyzed by NMR spectroscopy. It turned out that a near-quantitative formation of the [Zr]-acetylide/NH^+ product **19a** had occurred, the product that we had previously prepared directly by treatment of the Zr^+/amine FLP **14** with this terminal acetylene (see Scheme 5). Apparently, in the case of **20**, the HC≡CPh reagent was CH acidic enough to attack the [Zr]H unit forming **19a** with liberation of dihydrogen (see Scheme 7). The reaction of compound **20** with the olefin styrene took a markedly different course. In this case we observed a clean transfer of the H^+/H^- pair from the Zr/H_2 activation product to the olefin with formation of ethylbenzene and the free Zr^+/amine FLP **14** (see Scheme 7). Both compounds were unambiguously identified by NMR spectroscopy from the reaction mixture in d_5-bromobenzene solution.

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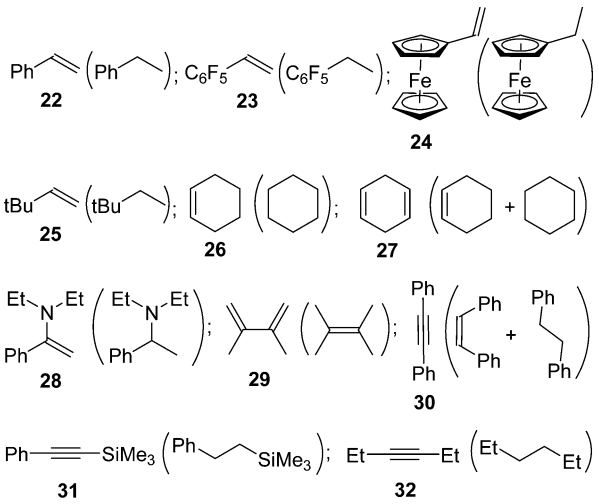
This reaction indicated the possibility of using the hydrogen activation product **20** (respectively the FLP **14** + dihydrogen) as an active hydrogenation catalyst. This turned out to be the case. We have catalytically hydrogenated a series of 11 alkenes or alkynes (compounds **22**–**32**; see Scheme 8) under mild conditions (1.5 bar of H_2, r.t., 1–4 h reaction time) using between 1 and 4 mol % in situ generated Zr^+/amine FLP **14** as the catalyst.

Scheme 8



The respective reactions were performed in C_6D_5Br solution, and the progress of the reaction was determined by ^1H NMR spectroscopy using the inert molecule ferrocene as an internal standard. In one case, namely, the reduction of vinylferrocene, we isolated the hydrogenation product ethylferrocene. In the other cases, the characterization of the hydrogenation products was carried out directly from the reaction mixtures. Scheme 8 shows the alkenes and alkynes that were subjected to catalytic FLP hydrogenation reactions; the structures of the resulting hydrogenation products are shown in parentheses. The monoolefinic substrates were usually readily hydrogenated, giving the respective alkane products. The nonconjugated substrate 1,4-cyclohexadiene gave a mixture of singly and doubly hydrogenated products. The conjugated diene **29** underwent a catalytic 1,4-hydrogenation, yielding tetramethylethylene. The internal alkynes **31** and **32** were hydrogenated to yield the respective alkane products. Tolane (**30**) was hydrogenated to give a mixture of *cis*-stilbene and 1,2-diphenylethane (see Scheme 8). Details of the catalytic hydrogenation reactions that were carried out within the scope of this study are listed in Table 1. We have also carried out a control experiment (entry 12 in Table 1) that showed that the neutral Zr containing material (**13**) was catalytically inactive, as expected. Further details of the catalytic hydrogenation reactions are provided in the Supporting Information.

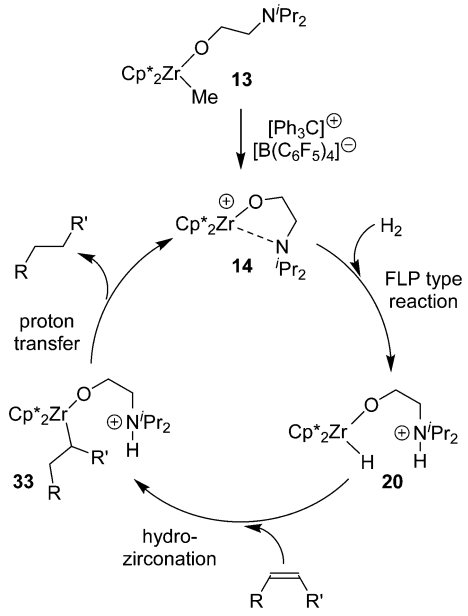
We assume a reaction pathway of these catalytic hydrogenation reactions as it is schematically depicted in Scheme 9. It is reasonable to assume that the in situ generated organometallic Zr^+/amine FLP **14** activates the dihydrogen molecule by heterolytic splitting to give the ZrH/ammonium system **20**. This then may undergo a hydrozirconation reaction[33,34] with the added olefin (or internal acetylene) substrate to give an alkylzirconocene complex (**33**) with an attached pendant $-OCH_2CH_2NH^iPr_2^+$ ammonium functionality. We assume

Table 1. Catalytic Hydrogenation of Alkenes and Alkynes with the Zr^+/Amine FLP Catalyst 14[a]

entry	substrate	complex loading (mol %)	reaction time (h)	conversion (%)
1[d]	**22**	1	2	93[b]
2	**23**	2	1	87[c]
3	**24**	2	1	77[e]
4	**25**	2	2	92[b]
5	**26**	4	4	79[c]
6	**27**	4	3	97[c] (5:1)[f]
7	**28**	4	2	>99[b]
8	**29**	4	4	77[b]
9	**30**	2	3	>99 (4:5)[g]
10	**31**	4	3	>99[b]
11	**32**	4	3	86[c,h]
12[i]	**32**	10	1	0

[a]Reaction conditions: 1.5 bar of H_2, r.t., C_6D_5Br as the solvent (0.8 mL), **14** (0.02 mmol). [b]Conversion determined by ^1H NMR relative to ferrocene as the internal standard. [c]Conversion determined by ^1H NMR relative to the respective starting material. [d]**14** (0.01 mmol). [e]Isolated yield. [f]Mole ratio of cyclohexene to cyclohexane. [g]Mole ratio of *cis*-stilbene to 1,2-diphenylethane. [h]*cis*/*trans*-3-hexene (6 mol %, 1:2). [i]Control experiment: reaction of complex **13** (0.02 mmol) with compound **32** and H_2 (1.5 bar).

Scheme 9



that the internal ammonium Brønsted acid is sufficiently acidic to cleave the adjacent Zr–C(alkyl) σ-bond.[25,26,35] This then liberates the hydrogenated product plus regenerates the active Zr^+/amine FLP to propagate the catalytic cycle (see Scheme 9).

CONCLUSIONS

Frustrated Lewis pair chemistry is usually associated with main group element Lewis acid/Lewis base combinations.[1,2,36] Some of these systems have indeed shown very remarkable reactions. There is indication that some transition metal containing systems show very similar reactions.[23–26] In the case studied here, it is the $Cp^*_2Zr-X^+$ bent metallocene moiety that shows a function very similar to that of, e.g., the $-B(C_6F_5)_2$ group in many B/P or B/N frustrated Lewis pairs. The zirconium Lewis

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acid reacts cooperatively with the bulky internal amine Lewis base in a variety of reactions that are quite analogous to the reactions of, e.g., typical main group element Lewis acid/Lewis base combination. This regards, e.g., the typical FLP reaction with a terminal alkyne but especially the heterolytic cleavage of dihydrogen that is done cooperatively by the internal Zr^+/amine Lewis pair. The Zr^+ Lewis acid has turned out to be a very reactive Lewis acid system. It undergoes a set of reactions similar to those known for, e.g., the $B(C_6F_5)_3$ Lewis acid, namely, hydride abstraction from an amine α-CH position. In the case of FLP **14**, this eventually resulted in the formation of the unusual reaction product **18**. In addition, the zirconium cation in complex **14** is so reactive that it even abstracts chloride from dichloromethane, but again this reaction is supported by concomitant trapping of the CH_2Cl moiety by the adjacent Lewis base. Hydrogen activation remains a most promising chemical feature of complex **14**. We have used this cooperative FLP property for developing a series of efficient Zr^+/amine-catalyzed hydrogenation reactions of alkenes and internal alkynes. Terminal alkynes can apparently not easily undergo this process because of the observed favored stoichiometric formation of the stable alkyne CH activation product **19**.[35] We are hopeful that the observations made with the reactive Zr^+/amine FLP **14** will help us develop some advanced FLP chemistry and catalysis based on very reactive transition metal Lewis acid/main group element Lewis base combinations.

EXPERIMENTAL SECTION

For general information and details of the characterization of the compounds, see the Supporting Information.

Preparation of Complex 13. A solution of $^iPr_2NCH_2CH_2OH$ (73 mg, 0.5 mmol) in toluene (1 mL) was added dropwise to a solution of $(C_5Me_5)_2ZrMe_2$ (196 mg, 0.5 mmol) in toluene (1 mL). After being allowed to stand at room temperature overnight, the reaction mixture was dried in vacuo to give complex **13** as a white solid (210 mg, 81%). Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated solution of **13** in toluene at −35 °C. Anal. Calcd for $C_{29}H_{51}NOZr$: C, 66.86; H, 9.87; N, 2.69. Found: C, 67.09; H, 9.89; N, 2.68.

In Situ Generation of Complex 14. A solution of $[Ph_3C][B(C_6F_5)_4]$ (27.7 mg, 0.03 mmol) in C_6D_5Br (0.5 mL) was added to a solution of compound **13** (15.6 mg, 0.03 mmol) in C_6D_5Br (0.3 mL). After being allowed to stand at room temperature for 30 min, the reaction mixture was transferred to an NMR tube and then characterized by NMR experiments.

Preparation of Complex 15. Complex **13** (42 mg, 0.08 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (74 mg, 0.08 mmol) were mixed in C_6H_5Br (2 mL), and then five drops of CH_2Cl_2 (excess) was added. After being allowed to stand at room temperature for 24 h, the reaction mixture was layered with cyclopentane (4 mL). After several days, complex **15** was obtained as a colorless crystalline solid (63 mg, 62%). Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **15** in CH_2Cl_2 covered with cyclopentane at room temperature. Anal. Calcd for $C_{53}H_{50}BCl_2F_{20}NOZr$: C, 50.13; H, 3.97; N, 1.10. Found: C, 50.52; H, 3.78; N, 1.05.

Preparation of Complex 18. Complex **13** (52 mg, 0.1 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.1 mmol) were mixed in C_6D_5Br (2 mL). After the reaction mixture was transferred to a Schlenk tube, it was heated at 60 °C for 36 h. The yellow-orange reaction mixture was then layered with cyclopentane (4 mL) to finally give complex **18** as a pale yellow crystalline solid (48 mg, 41%). Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **18** in C_6D_5Br covered with cyclopentane at room temperature. Anal. Calcd for $C_{52}H_{46}BF_{20}NOZr$: C, 52.80; H, 3.92; N, 1.18. Found: C, 51.64; H, 3.70; N, 1.14.

Preparation of Complex 19a. C_6H_5Br (2 mL) was added to a mixture of complex **13** (42 mg, 0.08 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (74 mg, 0.08 mmol). After 5 min, phenylacetylene (8 mg, 0.08 mmol) was added to the reaction mixture. After being allowed to stand at room temperature for 2 h, the reaction mixture was covered with cyclopentane (4 mL) to eventually give complex **19a** as a colorless solid (78 mg, 76%). Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **19a** in C_6H_5Br covered with cyclopentane at −35 °C. Anal. Calcd for $C_{60}H_{54}BF_{20}NOZr$: C, 55.99; H, 4.23; N, 1.09. Found: C, 55.72; H, 3.97; N, 1.19.

Preparation of Complex 19b. Following the procedure described for the preparation of compound **19a**, reaction of complex **13** (42 mg, 0.08 mmol), $[Ph_3C][B(C_6F_5)_4]$ (74 mg, 0.08 mmol), and *tert*-butylacetylene (7 mg, 0.08 mmol) gave **19b** as a pale yellow solid (77 mg, 76%). Crystals suitable for the X-ray crystal structure analysis were obtained by diffusion of cyclopentane into a solution of compound **19b** in C_6H_5Br at room temperature. Anal. Calcd for $C_{58}H_{58}BF_{20}NOZr$: C, 54.98; H, 4.61; N, 1.11. Found: C, 54.67; H, 4.38; N, 1.13.

Reaction of Complex 14 with H_2: Generation of Compound 20. A solution of complex **14** (in situ generation from the reaction of complex **13** (15.6 mg, 0.03 mmol) with $[Ph_3C][B(C_6F_5)_4]$ (27.7 mg, 0.03 mmol)) in C_6D_5Br (0.8 mL) was degassed, and H_2 (1.5 bar) was introduced to the evacuated reaction flask. After 30 min, the reaction mixture was transferred to an NMR tube, and the reaction mixture was characterized by NMR experiments. [Comment: it was not possible to isolate complex **20**; compound **20** partially releases H_2 in vacuum at r.t. or −20 °C.]

Reaction of Complex 14 with D_2: Generation of Compound 20-*D*. Following the procedure for the generation of complex **20**, complex **13** (10.4 mg, 0.02 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (18.4 mg, 0.02 mmol) in C_6D_5Br or C_6H_5Br (0.8 mL) were reacted with D_2 (1.5 bar, 30 min) to give complex **20**-*D*.

Preparation of Complex 21. Benzaldehyde (11 mg, 0.1 mmol) was added to a yellow solution of complex **20** which was in situ generated by the reaction of complex **13** (52 mg, 0.1 mmol), $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.1 mmol), and H_2 (1.5 bar, 30 min) in C_6H_5Br (2 mL). The color of the reaction mixture changed to red immediately. After being allowed to stand at r.t. for 1 h, cyclopentane (4 mL) was layered with the reaction mixture to finally give complex **21** as a yellow-orange solid (65 mg, 50%) after 2 days at room temperature. Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **21** in C_6H_5Br covered with cyclopentane at room temperature. Anal. Calcd for $C_{59}H_{56}BF_{20}NO_2Zr$: C, 54.80; H, 4.37; N, 1.08. Found: C, 54.35; H, 4.04; N, 1.03.

General Procedure for the Stoichiometric Reactions of Complex 20 with Styrene and Phenylacetylene (NMR Scale). The substrate (0.03 mmol, styrene (a) (3.1 mg) or phenylacetylene (b) (2.9 mg)) was added to a solution of complex **20** (0.03 mmol, in situ preparation following the standard procedure described above for the generation of complex **20**, in which complex **13** (15.6 mg, 0.03 mmol), $[Ph_3C][B(C_6F_5)_4]$ (27.7 mg, 0.03 mmol), and H_2 (1.5 bar, 30 min) were reacted in C_6D_5Br (0.8 mL)). After being allowed to stand at room temperature for 1 h, the reaction mixture was transferred to an NMR tube and then characterized by NMR experiments.

General Procedure of the Hydrogenation of Alkenes and Alkynes. Complex **14** (0.02 mmol, in situ preparation by the reaction of complex **13** (10.4 mg) with $[Ph_3C][B(C_6F_5)_4]$ (18.4 mg)), unsaturated substrate, and ferrocene (9.3 mg, 0.05 mmol) as the internal standard were mixed in C_6D_5Br (0.8 mL). Then the reaction flask was evacuated (−196 °C), H_2 (1.5 bar, r.t.) was introduced, and the reaction solution was stirred for the respective reaction time at room temperature. Subsequently, the reaction solution was transferred to an NMR tube and monitored by ^1H NMR. The conversion was determined by integration of a suitable ^1H resonance relative to ferrocene or the starting material.

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■ ASSOCIATED CONTENT

Supporting Information

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.

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Notes

The authors declare no competing financial interest.

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