

## Metal-Free Frustrated Lewis Pair Catalyzed 1,4-Hydrogenation of Conjugated Metallocene Dienamines

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Summary: Frustrated Lewis pairs, highly active in heterolytic dihydrogen splitting, were used as active and very selective hydrogenation catalysts for organometallic substrates. Conjugated dienamines fixed at the ferrocene framework and at the zirconocene nucleus were selectively 1,4-hydrogenated under catalytic conditions at ambient temperature.

Heterolytic cleavage and activation of dihydrogen by frustrated Lewis pairs is receiving quite some attention lately.<sup>1</sup> An increasing number of examples is emerging from the literature, where such systems are used for metal-free catalytic hydrogenation.<sup>2-6</sup> It seems that catalysts derived from frustrated Lewis pairs are especially suited for carrying out selective catalytic hydrogenation reactions of sensitive organometallic substrates.<sup>6</sup> We here wish to describe examples of such an application of these novel catalyst systems in metallocene chemistry.

The [3]ferrocenophane systems **1** are readily obtained by Mannich coupling of 1,1'-diacetylferrocene.<sup>7</sup> We had used these compounds extensively as starting materials for the preparation of ferrocenophane-based ligands:<sup>8</sup> e.g. in asymmetric catalysis.<sup>9</sup> These syntheses were usually initiated by catalytic hydrogenation of both C=C double bonds of the 1,3-connected dienamine bridge by conventional means (i.e. Pd/C, H<sub>2</sub>) to yield the corresponding fully saturated [3]ferrocenophanes **2**. It would be desirable to have a method at hand that allows for a stepwise, selective catalytic hydrogenation of the conformationally restricted bridging dienamine to yield derivatives (such as **3**, for example) of these useful frameworks of a higher functionality.

We recently showed that the intramolecular frustrated Lewis pair  $Mes_2P-CH_2CH_2-B(C_6F_5)_2$  (4) readily activates dihydrogen heterolytically to yield the zwitterion 5.<sup>3,4</sup> The 4/5 system turned out to be an active catalyst for enamine hydrogenation under mild conditions.<sup>4</sup> We have now used the catalyst system 4/5 for a rather selective 1,4-hydrogenation of the dienamine unit of the [3]ferrocenophane systems 1 and even of the related *ansa*-zirconocene derivative 6.

Treatment of **1a** ( $-NR_2 = -NMe_2$ ) with dihydrogen (2.5 bar) in toluene solution in the presence of 5 mol % of the prehydrogenated metal-free catalyst system **5** at ambient temperature resulted in the rapid formation of the hydrogenation products **3a** and **2a** in a 77:23 ratio (Scheme 1).<sup>10</sup> We isolated the mixture **2a/3a** in a combined yield of about 86%. Compound **3a** was characterized by X-ray diffraction (see Figure 1). It features the newly formed methyl substituent at the sp<sup>2</sup>-carbon atom of the C<sub>3</sub> bridge (values from molecule A: C6–C8 = 1.338(3) Å, C1– C6–C7 = 114.7(2)°, C1–C6–C8 = 124.0(2)°, C6–C8–C9 = 128.8(2)°). The saturated carbon atom C9 now bears a hydrogen in addition to the amino substituent (C10–C9–C8 = 116.6(2)°, C8–C9–N1 = 108.9(2)°, C8–C9 = 1.514(3) Å). Compound **3a** features a typical set of eight <sup>1</sup>H NMR signals of the pair of Cp

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<sup>(10)</sup> It is likely that the small amount of the fully saturated hydrogenation product 2 is a slowly formed follow-up product of 3 and is potentially formed from 3 via an isomerization pathway. For details see the Supporting Information.



**Figure 1.** Molecular structure of compound **3a** (atoms are shown at the 50% probability level).



ligands, the 6-CH<sub>3</sub> resonance at  $\delta$  1.99, the signal of the single olefinic 8-H proton at  $\delta$  5.82, and the 9-H resonance at  $\delta$  4.09 (1H). The NMe<sub>2</sub> signal was found at  $\delta$  2.24 (s, 6H). We carried out the catalytic hydrogenation of the derivatives **1b** ( $-NR_2 = -NC_5H_{10}$ ) and **1c** ( $-NR_2 = -NC_4H_8O$ ) analogously using the metal-free frustrated Lewis pair derived catalyst **5**. The hydrogenation reactions of the more bulky dienamines (**1b**,**c**) with the frustrated Lewis pair catalyst **5** are more selective. Under the applied reaction conditions we observed practically only the formation of the 1,4-hydrogenation products **3b**,**c**. Both were isolated in ca. 90% yield.

The metal-free Mes<sub>2</sub>PH<sup>+</sup>(CH<sub>2</sub>CH<sub>2</sub>)BH<sup>-</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> catalyst **5** can even be used for the selective hydrogenation of the conjugated dienamine moiety at the *ansa-zi*rconocene complex **6**, which was prepared by a related Mannich condensation route as previously described.<sup>11</sup> Treatment of **6** with H<sub>2</sub> under our typical nearly ambient conditions in the presence of 20 mol % of the catalyst **5** resulted in selective 1,4-hydrogenation of the bridging unit to yield the product **7** (Scheme 2) (isolated in 27% yield by crystallization; <sup>1</sup>H NMR  $\delta$  1.58 (s, 3H, 6-CH<sub>3</sub>),  $\delta$  5.75 (=CH–),  $\delta$  4.26 (9-H),  $\delta$  1.78 (s, 6H, 9-NMe<sub>2</sub>); for further details see the Supporting Information).

![](_page_1_Figure_7.jpeg)

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**Figure 2.** Molecular structure of the salt 8-[HB( $C_6F_5$ )<sub>3</sub>] (atoms are shown at the 50% probability level).

![](_page_1_Figure_10.jpeg)

It may be assumed that these catalytic 1,4-hydrogenation reactions proceed by proton transfer from **5** followed by hydride attack on the resulting in situ generated iminium ion. We have generated the iminium ion **8** by an alternative protonation route. Treatment of the dienamine **1a** with a stoichiometric amount of HCl in ether gave the conjugated iminium ion system **8**-[Cl] with a Cl<sup>-</sup> counteranion (Scheme 3). The anion could be exchanged by treatment with AgBF<sub>4</sub> to give **8**-[BF<sub>4</sub>]. Treatment of **1a** with the organometallic ammonium/ hydridoborate system {[(CpCH<sub>2</sub>NH<sub>2</sub>Ar)<sub>2</sub>ZrCl<sub>2</sub>]<sup>2+</sup>/2[HB-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup>} (**9**) gave the salt **8**-[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>], which was characterized by X-ray diffraction (see Figure 2 and the Supporting Information).

The salt **8**-[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] is stable at room temperature.<sup>12</sup> Upon heating (80 °C, C<sub>6</sub>D<sub>6</sub>) it is converted to a ca. 1:1 mixture of the products  $10^{13}$  and 11,<sup>14</sup> which are potentially follow-up products derived from **2a** and **1a**, respectively. We then treated the related **8**-[BF<sub>4</sub>] salt with a stoichiometric

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<sup>(14)</sup> Compound 11 was independently prepared by treatment of 1a with  $B(C_6F_5)_3$ ; for details see the Supporting Information.

![](_page_2_Figure_2.jpeg)

<sup>*a*</sup> Legend: (i) 2M HCl in Et<sub>2</sub>O; (ii) Ag[BF<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub>; (iii) 0.5 equiv of {(Cp-CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>Ar)<sub>2</sub>ZrCl<sub>2</sub>/2[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup>]} (9) [Ar = 2,6-(iPr)2C<sub>6</sub>H<sub>3</sub>] in CH<sub>2</sub>Cl<sub>2</sub>; (iv) 8-[BF<sub>4</sub>], 5 in C<sub>6</sub>D<sub>6</sub>, 70 °C; (v) 8-[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] in C<sub>6</sub>D<sub>6</sub>, 80 °C.

amount of the compound Mes<sub>2</sub>PH<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>BH<sup>-</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (5) in C<sub>6</sub>D<sub>6</sub> solution. At ambient temperature no reaction was observed, probably due to low solubility of **8**-[BF<sub>4</sub>] in C<sub>6</sub>D<sub>6</sub>. At 70 °C within 20 min this resulted in clean formation of the neutral 1,4-hydrogenation product **3a**, admixed with **2a**,<sup>10</sup> in a similar ratio (**3a**:**2a**  $\approx$  71:29 in a typical experiment), as observed in the catalytic hydrogenation reaction (see above). These experiments may indicate that the actual catalytic hydrogenation reaction of the substrates **1** proceeds by means of a sequential pathway initiated by proton transfer followed by hydride reduction of an in situ generated iminium ion intermediate. Our study shows that metal-free hydrogenation catalysts based on specific frustrated Lewis pairs can in special cases effect remarkable activities and selectivities. This indicates an increasing potential of this novel catalyst type for synthetic applications.

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**Supporting Information Available:** Text and figures giving further experimental and spectroscopic details and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.