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Catalytic Hydrogenation of Sensitive Organometallic Compounds by Antagonistic N/B Lewis Pair Catalyst Systems

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Carrying out typical organic functional group chemistry on many organometallic frameworks is difficult due to the often high sensitivity of such systems. This is especially true for air and moisture sensitive early d-block metals and the f-elements.[1] It is highly desirable to develop new reagents and viable preparative protocols to overcome these problems. Recently, a new class of dihydrogen activating systems was developed[2] that may turn out to be useful in that sense. "Frustrated"[3] (or "antagonistic"[4]) pairs of bulky Lewis acids and bases were shown to split dihydrogen heterolytically. Some of the resulting zwitterionic products were shown to serve as catalysts for the hydrogenation of a series of specific substrates, namely of bulky imines,[3,5] enamines,[6] and silyl enol ethers.[7] We have now used unique active antagonistic imine (respectively amine)/borane pairs for the selective catalytic hydrogenation of sensitive imino-functionalized zirconocene complexes in a quasi-autocatalytic way. This represents an interesting application of this novel catalyst type in synthetic organometallic chemistry.

Our synthesis of bis(arylimino-Cp)zirconium complexes started from 6-dimethylaminofulvene (**1**) that was converted to the "imino-Cp" lithium compound **3** by treatment with lithium 2,6-diisopropylanilide (**2**) in ether or THF, as previously described by us.[8] Selective protonation of **3** was rather difficult to achieve. Eventually, treatment of the THF-free variant of **3** in ether with the Brønsted acid acetylacetone gave the *N*-aryl-substituted 6-aminofulvene **4**. In solution, we found two isomers (syn, anti) in a 1:2 ratio. Samples of **4** always contained some amount of 2,6-diisopropylaniline. Single crystals of **4** were obtained from heptane at −33 °C. In the crystal we have observed only the minor syn-**4** isomer (see Supporting Information).

We then reacted **4** with the $Cl_2Zr(NMe_2)_2(THF)_2$ reagent **5**[9] in toluene at reflux temperature for 3 h. Deprotonation of **4** by the [Zr]-NMe_2 base proceeded smoothly under these forcing conditions. We isolated the bis(arylimino-Cp)$ZrCl_2$ product **6** from the reaction mixture in >60% yield. Complex **6** features a ^{1}H NMR imino −C*H*=N singlet of 2H intensity at δ 7.99 in d_6-benzene (corresponding ^{13}C −*C*H=N signal at δ 156.2). It shows an AA′BB′ ^{1}H NMR η^5-C_5H_4 spin system at δ 6.72 and 5.89.

A catalytic amount of an antagonistic imine/borane pair[10] was generated in situ by the addition of a substoichiometric quantity of $B(C_6F_5)_3$ (between 0.5 to 0.25 mol equiv) to a solution of the (arylimino-Cp)$_2$$ZrCl_2$ system **6** in benzene. The mixture was purged with H_2 and then kept in an atmosphere of dihydrogen (2 bar) with stirring at room temperature overnight. In a typical experiment that was carried out by using 0.5 molar equiv of the boron Lewis acid, we obtained a mixture of the bis(*N*-aryl-aminomethyl-Cp)$ZrCl_2$ hydrogenation product (**7**)[11] (ca. 75%) and the ammonium salt (**8**) (ca. 25%).[12] We could not separate these two compounds on a preparative scale, but we obtained single crystals of the imine-hydrogenation product **7** from a pentane solution at −33 °C. The X-ray crystal structure analysis of **7** (see Figure 1) features a bent metallocene framework that has a pair of saturated $-CH_2-NH-$aryl substituents attached at its Cp-rings. The corresponding C6−N7 bond lengths [1.466(3) Å, 1.471(3) Å] are in the typical C(sp^3)-NHR σ-bond range. In the crystal compound **7** adopts a close to C_2-symmetric metallocene conformation with both bulky substituents being oriented toward the open front side of the bent metallocene wedge. In solution (d_8-THF, 198 K) a ^{1}H NMR singlet at δ 4.04 with a relative intensity of 4H was observed for the $-CH_2-$N groups of complex **7** (corresponding ^{13}C resonance at δ 50.4; NH signal at δ 4.00).

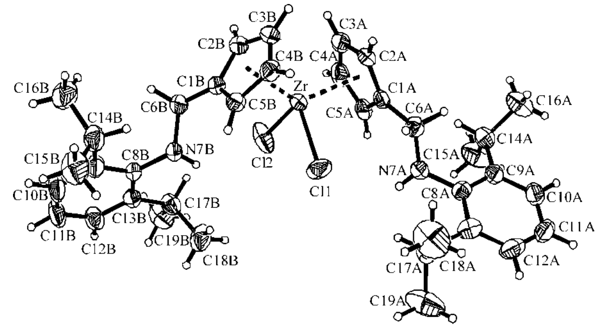

Figure 1. Molecular structure of the imine-hydrogenation product **7**. Selected bond lengths (Å) and angles (deg): Zr−Cl1 = 2.4469(6), Zr−Cl2 = 2.4264(7), C6A−N7A = 1.466(3), C1A−C6A = 1.502(3), N7A−C8A = 1.426(3); Cl1−Zr1−Cl2 = 98.02(3), C6A−N7A−C8A = 116.4(2), C1A−C6A−N7A = 111.9(2), C6B−N7B = 1.471(3), C1B−C6B = 1.494(3), N7B−C8B = 1.431(3), C6B−N7B−C8B = 117.8(2), C1B−C6B−N7B = 110.8(2).

The organometallic bis-amine **7** itself forms an antagonistic Lewis pair with $B(C_6F_5)_3$ which is very effective in heterolytic splitting of dihydrogen.[13] Treatment of a 1:1 mixture of **6** with $B(C_6F_5)_3$ with H_2 (2 bar) in benzene at room temperature results in the formation of the salt **8** (mixed with some **7** and **9**; see Scheme 1). Consequently, exposure of a ca. 1:2 mixture of **6** with $B(C_6F_5)_3$ to H_2 at room temperature in benzene (2 bar, overnight or 60 bar, 2 h) led to the predominant formation of the bis(ammonium) salt **9**[12] (isolated after workup in ca. 80% yield, containing a small amount of **8**).

The ammonium salt **9** itself is an active hydrogenation catalyst. The aldimine **10a** was cleanly hydrogenated with 2 bar of dihydrogen pressure using 5.6 mol% of the N/B catalyst **9** to give a quantitative yield of the secondary amine product **11a**. A similar result was obtained with the more bulky imine **10b**. Here only 2.3 mol% of the catalyst **9** was sufficient to achieve complete hydrogenation to **11b**. Hydrogenation of the silyl enol ether **12** with 4.8 mol% of **9** gave an 85% yield of the product **13** (see Scheme 2).

Our study demonstrates that the novel method of catalytic hydrogenation using "frustrated" (or "antagonistic") Lewis pairs, of which an increasing number of examples are currently emerging from the literature,[14] is beginning to find synthetic applications.

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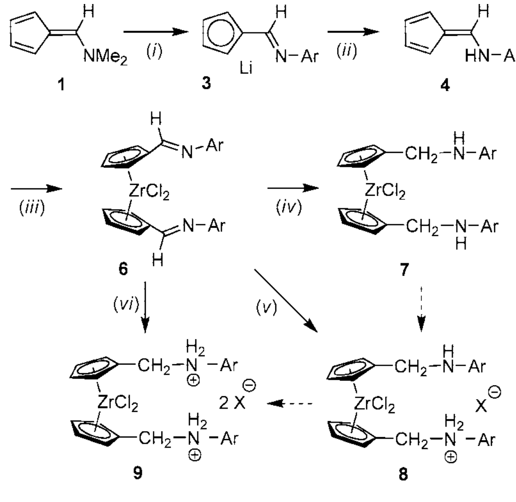
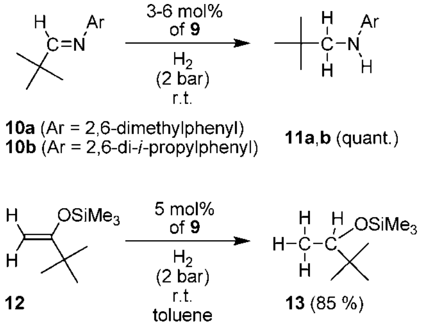
Scheme 1 [a]



Ar = 2,6-di-*i*-propylphenyl; $X^{\ominus} = [HB(C_6F_5)_3]^{\ominus}$

[a] (*i*) + LiN(H)Ar (**2**), − $HNMe_2$; (*ii*) acacH; (*iii*) $Cl_2Zr(NMe_2)_2(THF)_2$ (**5**), toluene, reflux; (*iv*) catalytic $B(C_6F_5)_3$, H_2 (2 bar), rt; (*v*) ca. 1 equiv of $B(C_6F_5)_3$, H_2 (2 bar), rt; (*vi*) ca. 2 equiv of $B(C_6F_5)_3$, H_2 (2 bar), rt, overnight or H_2 (60 bar), 2 h.

Scheme 2



The use of the N/B catalyst pair of our study is such an example in synthetic organometallic chemistry. We expect that many applications of this new technique of heterolytic dihydrogen splitting and activation will follow.

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Supporting Information Available: Experimental details and information about the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The corresponding product obtained from the analogous reaction of **6**/$B(C_6F_5)_3$ with dideuterium showed a ^2H NMR (d_8-toluene, 298 K) feature at δ 4.04 and a ^{13}C NMR (d_8-toluene, 298 K) 1:1:1 triplet at δ 50.4 ($^1J_{CD}$ = 21.5 Hz).

(12) Solutions containing cations **8** and/or **9** exhibit broad averaged NMR features at ambient temperature due to rapid proton transfer. However, the H-exchange was sufficiently slow on the NMR time scale at low temperature in d_8-THF solution to allow clear spectroscopic identification and characterization of the individual products **7**−**9**. Selected data of **7**: ^1H NMR (600 MHz, d_8-THF, 198 K, from a 2:1 **7/8** mixture): δ 7.06 (m, 4 H, Ar), 7.00 (m, 2 H, Ar), 6.00, 6.37 (each 4 H, Cp), 4.04 (br., 4 H, CH_2), 4.00 (br.,2 H, NH), 3.29 (sept., 4 H, C*H*Me_2); **8**: (from a **7/8/9** mixture of 5:20: 3), ^1H: δ 9.65 (br., 2 H, NH_2^+), 7.56 (m, 2 H, Ar), 7.48 (m, 1H, Ar), 7.05 (m, 2 H, Ar), 6.99 (m, 1H, Ar), 6.75, 6.60, 6.33, 6.14 (each 2 H, Cp), 4.62 (br., 2 H, CH_2NH_2), 4.01 (br., 3 H, CH_2NH), 3.19, 2.77 (each 2 H, C*H*Me_2); $[HB(C_6F_5)_3^-]$: ^{19}F (564 MHz, d_8-THF, 298 K): δ−133.4,−166.4,−168.8 (*o*-, *p*-, *m*-C_6F_5); ^{11}B (192 MHz, d_8-THF, 298 K): δ−25.5 (br. d, $^1J_{BH} \approx 94$ Hz); **9** (from a 1:5 **8/9** mixture), ^1H: δ 9.65 (br. 4 H, NH_2^+), 7.55 (m, 2 H, Ar), 7.48 (m, 4 H, Ar), 6.76, 6.19 (each 4 H, Cp), 4.59 (br. 4 H, CH_2), 3.70 (br., 2 H, BH), 2.72 (br., 4 H, C*H*Me_2). For further details see the Supporting Information.

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