Zinc-Catalyzed Hydrogenation

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H_2 Cleavage, Hydride Formation, and Catalytic Hydrogenation of Imines with Zinc Complexes of C_5Me_5 and N-Heterocyclic Carbenes**

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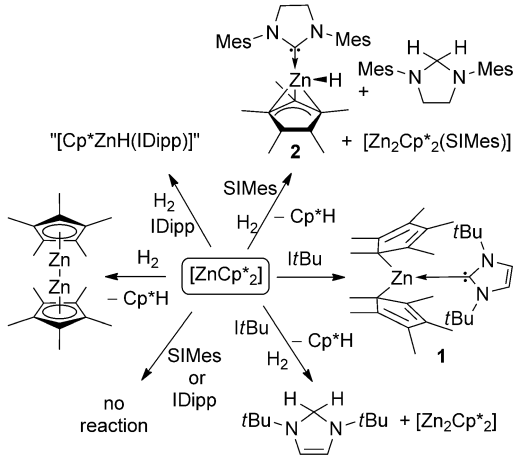
The catalytic hydrogenation of unsaturated organic substrates with H_2 is a process of great importance.[1] In the specific case of the production of amines, the development and optimization of catalytic procedures is of significant interest to the chemical industry.[2] In this context, the reduction of imines with H_2 to produce amines offers and an atom-efficient approach,[3] although expensive precious metals (Ir,[4] Ru,[5] Rh,[6] Pd[7]) are commonly employed for this task.[8] In recent years, we and others have described efficient metal-free hydrogenation utilizing frustrated Lewis pairs (FLPs).[7c,9] An alternative approach exploiting more abundant, but nonprecious metal complexes for the catalytic reduction of imines with H_2 has garnered much less attention. Recently, Cantat et al. reported NHC adducts of Zn salts to be catalytically active in deoxygenative C–N coupling reactions of CO_2 with methylanilines.[10] Blechert, Roesky, et al. successfully tested $[ZnCp^*_2]$ and $[Zn_2Cp^*_2]$ in catalytic hydroamination reactions.[11] Furthermore, Beller et al. have reported the first example of imine hydrogenation catalyzed by $Zn(OTf)_2$.[12] In the latter case, the reduction is proposed to involve coordination of an iminium ion to Zn, whereas in other catalytic and stoichiometric transformations zinc hydride species are believed to be key intermediates.[13] Although a number of hydride-bridged oligonuclear Zn compounds have been reported,[14] well-defined and structurally characterized terminal Zn hydride complexes are rare.[15] Parkin and Sattler obtained the first mononuclear alkyl-Zn-hydride complex, $[(\kappa^3\text{-Tptm})ZnH]$ (Tptm = tris(2-pyridylthio)methyl),[16] from reaction of the precursor with Ph_3SiH as a hydride source. This compound showed activity in the catalytic hydrosilylation of CO_2 and in methanolysis of silanes.[17] In a very recent report, Okuda, Maron, et al. described the dimeric species $[\{Zn(\mu\text{-}H)(H)(NHC)\}_2]$ from the reaction of solid $[ZnH_2]_n$ with NHCs or the conversion of $[Zn(OMe)_2(NHC)]$ with $PhMeSiH_2$ (NHC = IDipp: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; IMes: 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene).[18]

Herein, we report the reactivity of decamethylzincocene, $[ZnCp^*_2]$, with several N-heterocyclic carbenes, which yields either an adduct or a sterically frustrated Lewis pair. These combinations react with H_2 to generate Zn-hydride species, allowing the isolation of the mononuclear zinc hydride $[Zn(\eta^3\text{-}Cp^*)(H)(SIMes)]$ (SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene). Such species are also shown to effect the catalytic hydrogenation of imines.

In initial experiments, the coordination chemistry of $[ZnCp^*_2]$ with NHCs was probed. While the combination of $[ZnCp^*_2]$ with SIMes or IDipp resulted in no reactions, the addition of I*t*Bu (1,3-di-*tert*-butylimidazol-2-ylidene) to $[ZnCp^*_2]$ gave $[ZnCp^*_2(I\textit{t}Bu)]$ (**1**) in quantitative yield as a crystalline solid (Scheme 1). ^{13}C NMR spectra of **1** in C_6D_6 and CD_2Cl_2 showed resonances for $C_2^{I\textit{t}Bu}$ at $\delta = 179.7$ and 167.1 ppm, respectively. The Cp* ligands in **1** display solvent dependent coordination modes: In C_6D_6 and $[D_8]$toluene, a bis(η^5-Cp*) coupling pattern is observed. In contrast, **1** shows a (η^1-Cp*)(η^5-Cp*) coordination in CD_2Cl_2. Variable-temperature NMR spectroscopy revealed no (de)coalescence in the temperature range between 30 and −80 °C for any solvent. Species **1** decomposes in CD_2Cl_2 at 25 °C during the course of days to a mixture of degradation products due to activation of the solvent.[19]



Scheme 1. Reactions of $[ZnCp^*_2]$ with NHCs and/or H_2. [Cp*ZnH(IDipp)] is a proposed product and was not isolated.

The solid state molecular structure of **1** (Figure 1)[20] features a trigonal-planar coordination around Zn, with one I*t*Bu (Zn–C1 2.103(2) Å) and two σ-Cp* ligands (Zn–C12 2.146(2) Å, Zn–C22 2.146(2) Å). Ring slip results in pyramidalization of the Zn-bound carbon atoms C12 and C22. In

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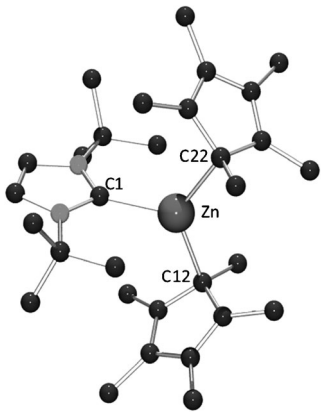


Figure 1. Pov-ray depiction of **1**. Hydrogen atoms omitted for clarity.

agreement with a localized charge, alternating bond lengths are observed in the Cp* ligands. The coordination geometry is similar to the only other isolated NHC adduct of decamethylzincocene, $[ZnCp^*_2(IMe_4)]$ (IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene).[21] However, the Zn–NHC distance is slightly longer for **1**, reflecting weaker donation from I*t*Bu compared to IMe_4. This notion is also consistent with the downfield $^{13}C_2^{NHC}$ chemical shifts: 179.7 ppm for **1** compared to the corresponding shift of 175.4 ppm for $[ZnCp^*_2(IMe_4)]$.[21]

Exposure of a solution of **1** in C_6D_6 to about 4 bar of H_2 results in the slow production of 1,3-di-*tert*-butyl-2,3-dihydroimidazole with concomitant formation of two equivalents of Cp*H and one equivalent of a new η^5-Cp* species (Scheme 1). The latter new species was identified as $[Zn_2Cp^*_2(I^tBu)]$ by NMR data ($^1H^{Cp*}$: 2.07 ppm, $^{13}C_2^{ItBu}$: 205.8 ppm) and confirmed by independent in situ synthesis of from $[Zn_2Cp^*_2]$ and I*t*Bu. The related adduct $[Zn_2Cp^*_2(DMAP)_2]$ (DMAP = 4-dimethylaminopyridine) has been reported and it showed a singlet for Cp* at 2.03 ppm in the ^1H NMR spectrum.[22] The reaction was driven to completion by application of H_2 (68 bar) at 25 °C for 24 h, resulting in full conversion into the aminal and $[Zn_2Cp^*_2]$ (Scheme 1). It is noteworthy that aminals can be produced by reaction of $LiAlH_4$ with NHCs.[23] Alternatively, Arduengo, Runyon, et al. have demonstrated an FLP-type activation of H_2 by 1-boraadamantane and I*t*Bu to generate an aminal via an imidazolium borohydride intermediate.[24] Furthermore, the direct reaction of alkylaminocarbenes with H_2 has been reported by Bertrand et al.[25] Nonetheless, the direct reaction of diaminocarbenes or NHCs with H_2 is not known. However, oxidation of $[Pd(I^tBu)_2]$ with H_2 has been shown by Cloke, Arnold, et al. to result in the formation of imidazolidine and Pd^0.[26] In both this and the present case, although no intermediate metal–H_2 and/or hydride complexes are observed, they are proposed as transient intermediates.

In the absence of carbene, a solution of $[ZnCp^*_2]$ in C_6D_6 pressurized with H_2 (ca. 4 bar) at 25 °C reacts slowly but cleanly to give $[Zn_2Cp^*_2]$ and a stoichiometric amount of Cp*H.[27] Whereas elevated temperatures led to complex mixtures and formation of Zn^0, quantitative reduction to yield $[Zn_2Cp^*_2]$ was achieved at elevated pressures of H_2 (68 bar, 25 °C, 24 h). Although previous routes to $[Zn_2Cp^*_2]$ have been reported employing a variety of reducing agents,[27b] the involved facile work-up and high yield of the present method offer considerable advantages. At low pressures (ca. 4 bar), the addition of IDipp to the above reaction had no influence on the formation of $[Zn_2Cp^*_2]$; however, at 68–100 bar H_2, the reaction with $[ZnCp^*_2]$ with IDipp resulted in colorless crystals of unknown composition. This product repeatedly deposited elemental zinc and other unknown compounds. Despite the lack of analytical data, the formation of [ZnCp*(H)(IDipp)] is suggested, which would explain the catalytic activity of $[ZnCp^*_2]$ and IDipp in hydrogenation at high H_2 pressures. Addition of H_2 (ca. 4 bar) to a solution of $[ZnCp^*_2]$ and SIMes resulted in the activation of H_2, affording colorless single crystals of **2** and a solution containing 1,3-dimesitylimidazolidine, Cp*H, and $[Zn_2Cp^*_2(SIMes)]$ (**3**; ratio ca. 1:3:1). The latter carbene adduct **3** was identified by NMR spectroscopic data ($^1H^{Cp*}$: 2.11 ppm, $^{13}C_2^{SIMes}$: 208.4 ppm) and confirmed by independent in situ synthesis of this adduct from $[Zn_2Cp^*_2]$ and SIMes.

Compound **2** did not dissolve in hydrocarbon solvents and was poorly soluble in THF; however, a hydride resonance was observed in the ^1H NMR spectrum at 3.73 ppm in $[D_8]$THF solution when cooled to −25 °C. This implies fluxional hydride coordination at ambient temperature. The Cp* ligand in **2** appears to adopt an η^5-coordination mode in solution. A Zn–H stretching frequency for **2** was recorded at $\tilde{\nu}_{Zn\text{-}H} = 1734\ cm^{-1}$, and the deuteride isotopomer [D_1]-**2** gave a corresponding band at $\tilde{\nu}_{Zn\text{-}D} = 1246\ cm^{-1}$. These IR bands for **2** are very similar to values reported for [(κ^3-Tptm)ZnH] ($\tilde{\nu}_{Zn\text{-}H} = 1729\ cm^{-1}$ and $\tilde{\nu}_{Zn\text{-}D} = 1242\ cm^{-1}$),[16] suggesting a terminal hydride. However, the ^1H hydride chemical shift is in better agreement with those reported for the dimeric species $[\{ZnH_2(NHC)\}_2]$ (3.57 and 3.97 ppm for NHC = IDipp and IMes, respectively).[18] Crystals of **2** were subjected to X-ray structure determination[20] and the formula [Zn(H)(Cp*)(SIMes)] for **2** was unequivocally established. The molecule sits on a crystallographically imposed twofold symmetry in the solid state and **2** features an η^3-Cp* ligand with Zn–C bond lengths between 2.139(2) and 2.460(1) Å (Figure 2). A slightly shorter bond is observed for the carbene–metal interaction (Zn–C 2.100(1) Å). The zinc hydride distance is 1.44(3) Å and compares well to findings for [(κ^3-Tptm)ZnH] (Zn–H 1.51(3) Å),[16] $[\{Zn(H)_2(IDipp)\}_2]$, and $[\{Zn(H)_2(IMes)\}_2]$ ($Zn–H_{terminal}$ 1.47(4)–1.56(4) Å).[18]

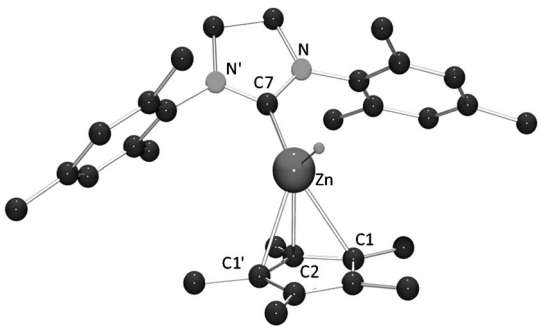


Figure 2. Pov-ray depiction of **2**. Hydrogen atoms except Zn–H omitted for clarity.

The above reactions of [$ZnCp^*_2$], NHC, and H_2 either suggest the intermediacy or allow for the isolation of a zinc hydride species. This prompted experiments probing the ability of such species to effect catalytic hydrogenation. Employing 10 mol% of compound **1** as the pre-catalyst at 50 °C and 100 bar H_2 for 72 h resulted in only 8% reduction of *t*BuN=CHPh, while the imine MeN=CHPh was reduced in 54% yield at 25 °C and 68 bar H_2 in just 24 h. In the former case, the competing hydrogenation of I*t*Bu resulted in 100% of the corresponding aminal, while in the latter case 43% of the aminal were formed. Compound **2** was not used as a pre-catalyst owing to its poor solubility. Nonetheless, 10 mol% of [$ZnCp^*_2$] and SIMes was used to generate **2** in situ under catalytic conditions. While this procedure led to reduction of a series of imines in varying yields, the precipitation of crystalline **2** from solution was frequently observed.

Interestingly, the most effective catalyst was generated from the combination of [$ZnCp^*_2$] and IDipp under H_2. This results in the reduction of a series of imines (Table 1) affording the corresponding amines in yields ranging from

Table 1: Catalytic hydrogenation of imines with H_2.[a]

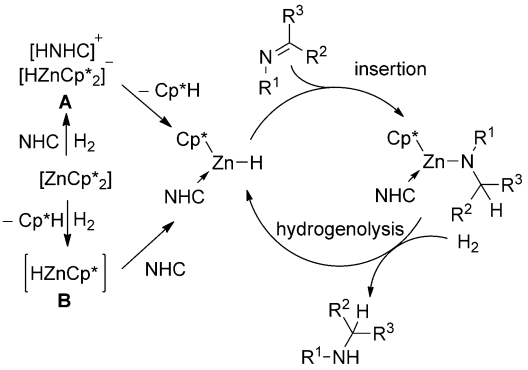
No.	Substrate	NHC	*T* [°C]	*P* [bar]	*t* [h]	Y [%][b]
1	MeN=CHPh	I*t*Bu	25	68	24	54
2	*t*BuN=CHPh	I*t*Bu	50	100	72	8
3	MeN=CHPh	SIMes	25	68	24	96
4	Me_3SiN=CHPh	SIMes	25	100	72	100
5	$PhCH_2N$=CHPh	SIMes	25	100	72	100
6	*t*BuN=CHPh	SIMes	50	100	72	18
7	*t*BuN=CH-*p*-BrC_6H_4	SIMes	50	100	72	84
8	*t*BuN=CH-*m*-BrC_6H_4	SIMes	50	100	72	67
9	*t*BuN=CH-*p*-$OMeC_6H_4$	SIMes	50	100	72	36
10	*t*BuN=CH-*p*-$NMe_2C_6H_4$	SIMes	50	100	72	21
11	*t*BuN=CH-*p*-*t*BuC_6H_4	SIMes	50	100	72	54
12	MeN=CHPh	IDipp	25	68	24	98
13	Me_3SiN=CHPh	IDipp	25	100	72	92
14	$PhCH_2N$=CHPh	IDipp	50	100	72	100
15	*t*BuN=CHPh	IDipp	50	100	72	60
16	*t*BuN=CH-*p*-Br-Ph	IDipp	50	100	72	100
17	*t*BuN=CH-*m*-BrC_6H_4	IDipp	50	100	72	60
18	*t*BuN=CH-*p*-$OMeC_6H_4$	IDipp	50	100	72	79
19	*t*BuN=CH-*p*-$NMe_2C_6H_4$	IDipp	50	100	72	10
20	*t*BuN=CH-*p*-*t*BuC_6H_4	IDipp	50	100	72	83

[a] All catalytic runs in C_6D_6 with [$ZnCp^*_2$]/NHC (10 mol%, $c = 4$ mM). [b] Y: yields based on ^1H NMR data.

60–100%. While the conditions were varied (see the Supporting Information), the best yields generally required 72 h at 100 bar H_2 and 50 °C. Increased steric bulk on N (imine) appears to decrease the reduction rate. While brominated substrates are tolerated, the introduction of a dimethylamino substituent appears to inhibit reduction, which is presumably a result of catalyst sequestration by amine–zinc interactions. Attempts to reduce bulky ketimines, pyridine, diphenylacetylene, 1,3,3-trimethyl-2-methyleneindoline, or N-cyclohexenylpiperidine proved unsuccessful, even under forcing conditions.

To probe the reaction mechanism of these reductions, control experiments in which [$ZnCp^*_2$] or [$Zn_2Cp^*_2$] alone were employed in attempted hydrogenation of *t*BuN=CHPh showed no evidence of reduction after 24 h at 25 °C and 68 bar of H_2. In either case, only [$Zn_2Cp^*_2$] was isolated. Furthermore, [$Zn_2Cp^*_2$] showed no activity in imine reduction even in the presence of I*t*Bu or IDipp. In the absence of zinc compounds, I*t*Bu, IDipp, and SIMes failed to produce amines from *t*BuN=CHPh or MeN=CHPh even after 72 h at 50 °C and 100 bar H_2. These data are consistent with the active species being derived from the combined action of [$ZnCp^*_2$] and an NHC.

In the case of the reaction using I*t*Bu, the generation of **1** and subsequent reaction with H_2 generating an analogue of **2** seems a reasonable route to a reactive zinc hydride. In a similar fashion, the catalyst derived from IDipp/[$ZnCp^*_2$] under H_2 is proposed be [Cp*ZnH(IDipp)], despite the fact that IDipp does not coordinate to [$ZnCp^*_2$]. Two possible mechanistic pathways for the initial reaction of [$ZnCp^*_2$], NHC, and H_2 are proposed. One possibility involves an FLP-like activation of H_2 in which the carbene and Zn^{II} act as a Lewis acid–base combination to generate a transient imidazolium hydridozincate ion pair (**A**; Scheme 2). This species could then prompt elimination of Cp*H affording a neutral, carbene stabilized zinc hydride. Alternatively, the



Scheme 2. Proposed mechanisms for the formation of NHC-supported zinc hydride and catalytic hydrogenation of imines.

direct reaction of H_2 with [$ZnCp^*_2$] could affect loss of Cp*H, generating [Cp*ZnH] (**B**), which could then be stabilized by the NHC. To probe these possibilities, the reaction of [$ZnCp^*_2$] and H_2 was carried out in the presence of 10 equiv of Ph_2CO as a hydride scavenger. The only products observed were [$Zn_2Cp^*_2$] and Cp*H, while the benzophenone remained unreacted. While this observation disfavors the latter proposed mechanism, it is possible that capture of the transient zinc hydride by ketone is kinetically slow. It is also noteworthy that a recent report documented the reductive elimination of Cp*H from [Cp^*_2AlH] affording AlCp*.[28] Thus, the data suggests an FLP type mechanism, yet the hydrogenolysis of Cp* cannot be ruled out. Regardless of the route to [Cp*ZnH(NHC)], this species is thought to undergo insertion of imine into the Zn–H bond, affording a zinc amide complex, which then undergoes hydrogenolysis affording the product amine and regenerating the catalyst [Cp*ZnH(NHC)]. This proposition is consistent with the observations of slowed

reaction rates with increased steric demands of the N-bound substituents on the imine.

Thus, the reason for this is believed to result from a non-coordinating and therefore unquenched combination of a Lewis acid and a Lewis base which at the same time supports the formation of a zinc hydride. The resulting IDipp supported hydrido complex has a much lower lattice energy, and as a consequence it remains in solution, that is, it is available for catalytic turnover.

In summary, the cleavage of dihydrogen can be effected by [ZnCp*$_2$] in the presence or absence of NHCs. Catalytic hydrogenation of imines is achieved in the presence of NHCs. The isolation of a monomeric zinc hydride from catalytic experiments strongly suggests substrate insertion into the Zn–H bond is the key step in the reduction of the C=N double bond. Subsequent hydrogenolysis of the proposed zinc amide is likely to close the catalytic cycle. Details of the mechanism of the initial H_2 splitting by [ZnCp*$_2$] and IDipp or SIMes may involve FLP-like or more classic organometallic characteristics and remain to be confirmed. This reactivity of [ZnCp*$_2$] towards H_2 opens the door to a broad variety of chemistry which is the subject of continuing efforts in our laboratories.

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[20] CCDC 937891 (**1**) and 937892 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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