Zirconocene Hydrido Complexes

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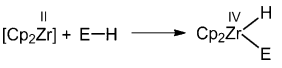
Facile Access to Tuneable Schwartz's Reagents: Oxidative Addition Products from the Reaction of Amide N–H Bonds with Reduced Zirconocene Complexes**

Martin Haehnel, Jacky C.-H. Yim, Laurel L. Schafer, and Uwe Rosenthal**

Dedicated to Professor Christoph Marschner on the occasion of his 50th birthday

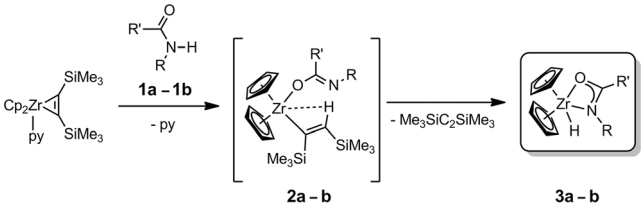
Since the development of Schwartz's reagent and its use in hydrozirconation reactions over the past decades,[1] the chemistry of modified zirconocene hydride complexes continues to be of key interest to both inorganic and organic chemists.[2] In contrast to the oligomeric structure of Schwartz's reagent, monomolecular terminal hydride complexes $[Cp'_2Zr(H)E]$ (Cp' = unsubstituted or substituted Cp ($Cp = \eta\text{-}C_5H_5$), E = alkoxide,[3] amide,[4] alkyl,[5] aryl,[6] silyl,[7] phosphanyl[8]) have been rarely reported and their syntheses are typically limited to examples with special substituents on the Cp rings and/or the E substituent. General approaches to such complexes often exploit salt metathesis (starting from $[Cp'_2Zr(H)Cl)]$[4,5d]) or protonolysis reactions (starting from $[Cp'_2ZrH_2)]$.[5c]) Herein we show that the formal oxidative addition of organic amides to a masked reduced zirconocene complex is an alternative and high yielding route to amidate-ligated terminal hydrido zirconocene complexes.

Oxidative addition of E–H bonds (E = OR, NR_2, PR_2, CR_3, SiR_3, Scheme 1) to transiently generated Zr^{II} species has been invoked in reactivity investigations of a variety of zirconocene complexes $[Cp'_2ZrX_2]$.[5a,e,6,7a] The oxidative addition of Si–H and C–H bonds to reduced zirconocene derivatives has yielded monomolecular terminal hydride complexes.[6a,b,7a] In the case of more polar E–H bonds, such as N–H bonds, there are few reported examples with Group 4 metals,[9] and the only structurally characterized product involves the oxidative addition of an N–H bond of aminoborane to yield zirconocene amidoborane complexes.[10] While late-transition-metal complexes promote N–H oxidative addition,[11] characterized examples of the oxidative addition of amides are restricted to Pt,[12] Ru,[13] and Ir.[11c,14] To our knowledge, the oxidative addition of N–H bonds of amides at early transition metals has not yet been reported.



Scheme 1. Oxidative addition of E–H bonds to $[Cp_2Zr]$ fragments (E = OR, NR_2, PR_2, CR_3, SiR_3).

It has been shown recently that 4-membered heterometallacycles can stabilize zirconocene hydrido complexes,[8] although these complexes are limited to those with special substituents on the cyclic unit. By comparison, amidates are readily modified 4-membered heterometallacycles with tunable electronic and steric properties by simply changing the N and carbonyl substituents.[15] Moreover, their coordination modes are not limited to cyclic κ^2-binding modes, but can also exist as κ^1-bound amidate ligands, resulting in a highly flexible coordination sphere about the metal center. Furthermore, the synthesis of such zirconocene hydrido amidate complexes is easily accomplished by reaction of the established zirconocene source $[Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)]$[16] with various amides according to Scheme 2. This high-yielding route



Scheme 2. Key steps in the formal oxidative addition of amides to $[Cp_2Zr^{II}]$.

results in the preparation of mononuclear and tunable alternatives to Schwartz's reagent, that take advantage of the stabilizing effect of heterometallacycles.[17] Herein we show that the facile accessibility and variability of the amidate ligands afford halogen-free, mononuclear versions of Schwartz's reagent that can afford branched insertion products selectively.

Two amides with different electronic and steric properties were selected to evaluate the generality of this approach for accessing oxidative-addition products. Amide **1a** has alkyl

[*] Dipl.-Chem. M. Haehnel, Prof. Dr. U. Rosenthal
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
E-mail: uwe.rosenthal@catalysis.de
B. Sc. J. C.-H. Yim, Prof. Dr. L. L. Schafer
Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, BC, V6T 1Z1 (Canada)
E-mail: schafer@chem.ubc.ca

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substituents with a small isopropyl group on the N atom, while amide **1b** has aryl substituents and is substantially more sterically demanding with a *N*-2,6-diisopropylphenyl (Dipp) group. The initial step in accessing the oxidative-addition products is the substitution of the stabilizing pyridine ligand with coordinated amide, as suggested by similar reactions with N-alkylated lactams (cyclic amides).[18] The subsequent formation of intermediates **2a** and **b** would then take place by a proton transfer from the Lewis acid activated amide to the bis(trimethylsilyl)acetylene ligand to give amidate ligated σ-alkenyl complexes. Such metal vinyl species have been characterized as products of reactions of polar, protic E–H bonds of lactams, amines, water, or acetylene with $[Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (L = pyridine, THF).[18–21]

In the case of **1a**, this proton-transfer reaction could be monitored by ^{1}H NMR spectroscopy because the sterically less-demanding *N*-(isopropyl)*tert*-butylamide (**1a**) allowed for the spectroscopic characterization of **2a** within the first hour of the experiment at room temperature. Complex **2a** features the previously observed agostic interaction of the β-hydrogen, as indicated by the downfield shift in the ^{1}H NMR spectrum ($\delta = 8.08$ ppm).[18] In the ^{13}C NMR spectrum, characteristic resonance signals of the σ-alkenyl unit appear at $\delta =$ 234.5 (C^α) and $\delta = 113.8$ ppm (C^β). This agostic interaction is anticipated to be critical for the subsequent formation of the terminal hydrido complex **3a**. The characteristic resonance signal of the amidate ligand in **2a** appears at $\delta = 168.1$ ppm, indicating a κ^1-binding mode. Additionally, complex **2a** could be characterized by mass spectrometry, in which a [*M*+H] peak was observed at *m*/*z* 534.[22] However, isolation of pure **2a** was not possible and the formal oxidative-addition product **3a** was obtained exclusively.

In contrast to previous results with lactams or amines,[19] it was found that complexes **2** liberate bis(trimethylsilyl)acetylene by a hydride transfer to the Zr center, to give the desired zirconocene hydrido amidate complexes **3** (Figure 1). Presumably relief of steric strain upon bis(trimethylsilyl)acetylene elimination is the driving force for the reaction. This notion is further supported by the observation that the reaction proceeds only at elevated temperature (65 °C) with **1a**, while the use of sterically demanding **1b** results in product **3b** at room temperature. With **1b** the intermediate complex **2b** could not be detected spectroscopically.

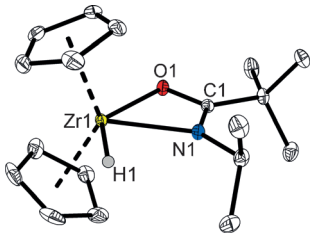
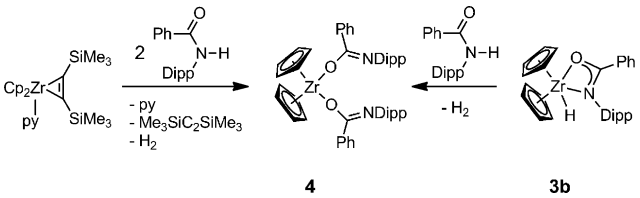


Figure 1. Crystal structure of **3a**. Hydrogen atoms except for H1 are omitted for clarity. The thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°], C1-O1 1.2984(12), C1-N1 1.3096(13), Zr1-O1 2.2595(8), Zr1-N1 2.2784(9), Zr1-H1 1.768(17); O1-C1-N1 113.51(9), O1-Zr1-N1 57.45(3).

Complexes **3a** and **3b** have been fully characterized, with the solid-state molecular structure of **3a** being provided as a representative example (Figure 1). In complex **3a**, the zirconium center is surrounded by two Cp units, the chelating amidate, and the hydrido ligand (H1). As known for zirconium amidate complexes, the central metallacyclic unit is almost planar (torsion angle 1.3°).[15,23] The hydrogen atom H1 is only slightly out of this plane. The Zr1–O1 (2.2595(8) Å) and Zr1–N1 (2.2784(9) Å) bond lengths are typical for Zr amidate complexes,[15,23,24] and C1–O1 (1.2984(12) Å) and C1–N1 (1.3096(13) Å) bond lengths are consistent with partial multiple bond character.[25] Spectroscopically, the resonance signals of the hydrido signals in the ^{1}H NMR spectra appear at $\delta = 5.01$ (**3a**) and $\delta = 5.72$ ppm (**3b**), respectively. Using ^{13}C NMR spectroscopy the resonance signals of C1 appear at $\delta = 185.8$ ppm (**3a**) and $\delta =$ 176.9 ppm (**3b**), which are characteristic for the κ^2-metallacyclic binding mode of the amidate ligand.[15,23,24]

Not surprisingly, the reaction of $[Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ with two equivalents of amide **1b** results in the formation of the bis(amidate) complex **4** (Scheme 3), analogous to that observed for reactions with amines.[19] Interestingly, the evolution of H_2 gas was detected by ^{1}H NMR spectroscopy ($\delta = 4.47$) along with free bis(trimethylsilyl)-acetylene ($\delta = 0.16$). Notably, there was no evidence for bis(trimethylsilyl)ethylene ($Me_3SiCH{=}CHSiMe_3$) reduction product. This result suggests that the formation of the zirconocene hydrido complex **3b** is an intermediate on the path to the bis(amidate) complex. Indeed, the reaction of **3b** with one equivalent of **1b** cleanly affords complex **4** together with H_2 gas.



Scheme 3. Formation of complex **4**.

The molecular structure of complex **4** is depicted in Figure 2. The Zr center is surrounded by two Cp ligands and two κ^1-*O* amidate bound ligands are coordinated to Zr in a distorted tetrahedral coordination geometry. In the κ^1-*O* amidate binding mode, the C–O bond lengths (av. 1.336 Å) correspond more closely to a typical single bond while the C–N bond lengths (av. 1.276 Å) are closer to that of C–N double bonds.[18]

All the resonance signals in the room-temperature ^{1}H NMR spectrum of complex **4** appear broad, most likely a result of equilibria between κ^2-metallacycles and κ^1-*O* bound amidate isomers in solution (Scheme 4). Low-temperature NMR studies (−75 °C) confirmed such fluxionality and resonance signals for the κ^1-*O* bound and κ^2-*N*,*O* bound ligand could be observed.[26] This situation is most clearly seen in the ^{13}C NMR spectrum, in which the resonance signals for the central carbon atom C1 of metallacyclic amidate ligand

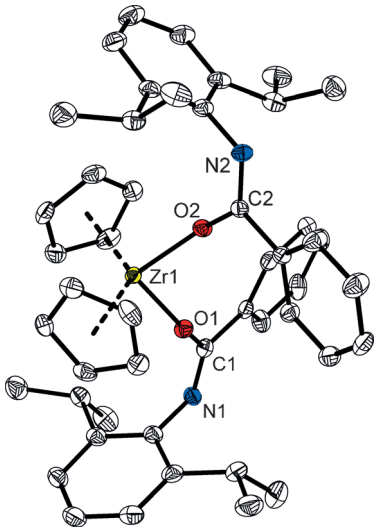
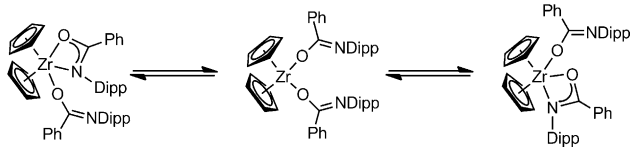


Figure 2. Crystal structure of **4**. Hydrogen atoms and the second independent molecule of the unit cell are omitted for clarity. The thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°], corresponding values of the second molecule in the asymmetric unit are given in square brackets: C1-O1 1.334(3) [1.336(3)], C2-O2 1.333(3) [1.339(3)], C–N1 1.275(3) [1.277(3)], C2-N2 1.276(3) [1.275(3)], Zr1-O1 2.0073(16) [2.0191(15)], Zr1-O2 2.0096(15) [2.0145(15)]; O1-C1-N1 124.4(2) [125.1(2)], O2-C2-N2 124.5(2) [124.8(2)], O1-Zr1-O2 95.71(6) [97.69(6)]



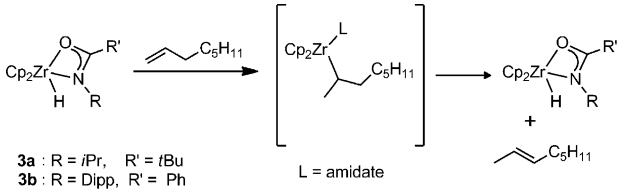
Scheme 4. Possible isomers of complex **4** in the solution phase.

($\delta = 172.1$ ppm) differ significantly from the resonance of the κ^1-*O* bound amidate ligand ($\delta = 163.3$ ppm). Also, in the ^{1}H NMR spectrum two distinct ligand environments are observed whereby the chemical shifts of the methine signals of the isopropyl groups of one ligand appear as one septet at $\delta = 3.27$ ppm (2H), while the other ligand has two independent septets at $\delta = 3.63$ (1H) and $\delta = 3.54$ ppm (1H) respectively.

Hydrozirconation is an important reaction in synthetic chemistry as it offers a direct route for the functionalization of unactivated olefins.[1b,c] Hydrozirconation of terminal alkenes gives the less sterically hindered primary zirconocene alkyl complexes.[27] Such linear products are even observed when internal alkenes are used as starting materials, because facile β-hydride eliminations/reinsertions allow the Cp_2Zr moiety to "chain-walk" to the terminal position.[27] This regioselectivity can be perturbed by the use of arylalkenes to give mixtures of the branched and linear products.[28]

While Schwartz's reagent typically provides excellent regioselectivity for the linear product, it excludes the possibility of accessing the branched hydrozirconation product selectively. By using a half-sandwich Zr complex, Sita and co-workers have shown that asymmetric hydrozirconation of an alkene is possible and the alternative branched product can be prepared.[29] Efforts to access the branched product selectively with traditional zirconocene type complexes have been unsuccessful to date.[2b] Herein we show that by modifying the Cl^- ligand of Schwartz's reagent with an amidate, variable reactivity can be targeted and most importantly, rarely observed branched products can be selectively obtained.

In contrast to Schwartz's reagent, the reaction of excess 1-octene with both complexes **3a** and **3b** at elevated temperatures results in the clean formation of 2-octene (Scheme 5).



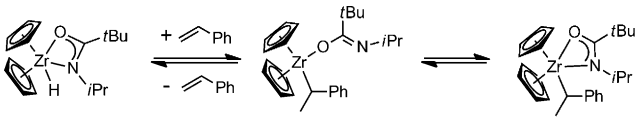
3a : R = *i*Pr, R' = *t*Bu
3b : R = Dipp, R' = Ph

L = amidate

Scheme 5. Selective isomerization of 1-octene to 2-octene by 2,1-insertion.

Such isomerization reactions using zirconium complexes are known,[30] however, the proposed hydrido intermediates have not been observed to date. The hydrido complexes **3a** and **3b** act as catalysts for this reaction. In contrast to the reactivity of Schwartz's reagent, the initial key step is presumably the formation of the branched insertion product as an intermediate, and subsequent β-hydride elimination to give 2-octene.

In an attempt to obtain the branched product selectively, the reaction of **3a** and **3b** with styrene (having no allylic hydrogen atoms) was monitored by ^{1}H NMR spectroscopy. Schwartz's reagent typically furnishes a mixture of branched and linear products with this substrate.[28] At room temperature using complex **3a** an equilibrium between the branched insertion product **5a** and the starting terminal hydrido complex **3a** was observed (Scheme 6). Well resolved room-

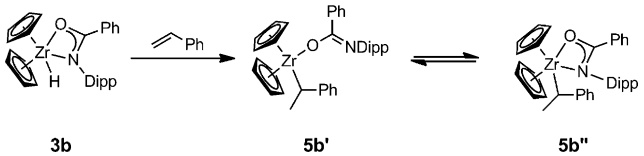


3a **5a'** **5a"**

Scheme 6. Equilibrium between the two isomers of **5a** and **3a**/styrene.

temperature spectra showed that over 4 days a reaction equilibrium can be reached: 42:58 ratio of free styrene:**5a**. The ^{13}C NMR spectrum is consistent with a κ^1-bound amidate ligand for **5a'** ($\delta = 166.4$ ppm). However, at 70 °C this equilibrium is shifted and only **3a** and free styrene are detected. Consequently, complex **5a** could not be purified and isolated for complete characterization.

In contrast, at room temperature styrene reacts with the more sterically demanding **3b** to give the branched insertion product **5b** (Scheme 7). In this case, by increasing the reaction temperature to 70 °C, completion of the regioselective



3b 5b' 5b''

Scheme 7. Insertion reaction of styrene with complex **3b** to give **5b**, observed as an equilibrium.

reaction can be achieved within 4 h and polymerization of styrene is not observed.

Similar to the ^{1}H NMR spectrum of complex **4**, the signals of complex **5b** appear broad at room temperature. This broadening can be attributed to a similar equilibrium in solution between the κ^1- and the κ^2-amidate isomers (**5b′**/**5b″**). Low-temperature NMR spectroscopic analysis (−35 °C) revealed the existence of only the κ^1-*O* bound amidate isomer. In the ^{13}C NMR spectrum, the resonance of the central carbon atom of the amidate ligand appears at $\delta =$ 156.1 ppm. In the ^{1}H NMR spectrum, the methine signals of the *i*Pr groups of the ligand appear as independent septets at $\delta = 3.07$ and $\delta = 3.00$ ppm. Most importantly, the diagnostic doublet of the methyl group appears at $\delta = 1.55$ ppm ($^3J =$ 7.0 Hz) as a result of coupling with the methine proton of the branched insertion product ($\delta = 3.17$ ppm). This low-temperature solution-phase data matches the solid-state molecular structure obtained by X-ray crystallography (Figure 3). The

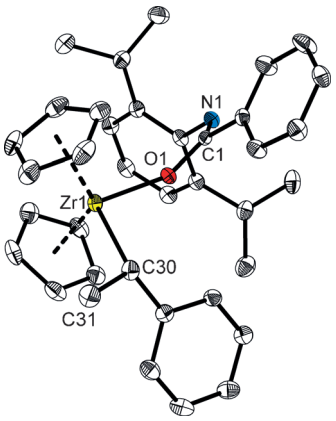


Figure 3. Crystal structure of **5b**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: C1-O1 1.336(2), C1-N1 1.276(2), Zr1-O1 2.0173(12), Zr1-C30 2.3613(19); O1-C1-N1 124.95(16), Zr1-C30-C31 118.10(13).

Zr center is surrounded by two Cp ligands, the branched insertion product, and the amidate ligand in a distorted tetrahedral coordination geometry. The molecular structure of **5b** is a rare example of a branched insertion product with zirconocene complexes and there is no spectroscopic evidence for the formation of the linear regioisomer.

The amidate ligand results in increased steric bulk about the metal center, thereby influencing both regioselective insertions and differences in reactivity between complexes **3a** and **3b** with styrene. Most importantly, the incorporation of the amidate ligand into a modified Schwartz's reagent favors the formation of the branched insertion products, either as isolable or proposed intermediates, with both aryl- and alkyl-substituted alkenes. The mechanistic rationalization for the preference for branched insertion products is being investigated and will be reported in due course. Notably, the increased steric bulk of **3b** specifically enhances the hemilability of this ligand, thereby facilitating the high-yielding preparation of the branched insertion product **5b** exclusively. Thus, the κ^1-bound amidate species, with its alkoxyimine binding mode, is postulated as a key reactive intermediate.

In conclusion, we present a facile synthetic pathway to an alternative and tunable Schwartz's reagent by direct amide N–H bond activation, to furnish the first examples of the formal oxidative addition products of amides with reduced early transition metals. In the case of **1a**, we were able to characterize the metal–vinyl intermediate by NMR spectroscopy and the resulting mononuclear zirconocene hydrido complex **3a** in both the solution phase and by X-ray analysis. Preliminary reactivity studies showed that **3a** and **3b** undergo regioselective insertion reactions with 1-octene and styrene, resulting in the preferential formation of the branched insertion products. In the case of **5b**, this product could be structurally characterized by X-ray analysis. The variable reactivity achieved between these easily prepared amidate ligated terminal-hydride zirconocene complexes points toward the tunable reactivity achievable with these systems. Work in progress focuses on mechanistic investigations to guide the development of new tunable Schwartz's reagents with easily installed amidate ligands for novel synthetic applications in organic and organometallic chemistry.

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