Reactions of Imines with Azazirconacyclobutenes and Generation of Electron-Deficient Imidozirconocene Complexes

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Summary: Electron-deficient imines are shown to insert into the zirconium−carbon bond of azazirconacyclobutenes to generate new six-membered ring metallacycles. On heating, these expanded zirconacycles undergo a retro-[4 + 2] cycloaddition to generate α,β-unsaturated imines in excellent yields and novel, fully characterized electron-deficient imidozirconocene complexes.

Imidozirconocene complexes react with alkynes via a [2 + 2] cycloaddition to generate highly colored azazirconacyclobutenes (**1**).[1] We previously reported that compound **1a** can then react with benzaldehyde to generate the new six-membered ring zirconacycle **2**. Upon heating, this complex undergoes a retro-[4 + 2] cycloaddition to afford the α,β-unsaturated imine **3a**[2] and the (Cp₂ZrO)ₙ oligomer (Scheme 1).[3] Recently, we became interested in related chemistry employing an imine for the metallacycle insertion reaction. A similar retro-[4 + 2] cycloaddition from the resulting zirconacycle would afford an α,β-unsaturated imine and generate a new imidozirconocene species. We present herein our efforts to develop this imine insertion chemistry and its utility in synthesizing α,β-unsaturated imines and several new zirconium imido complexes. The imido complexes are unusual in that they bear strongly electron withdrawing groups at the nitrogen atom.

Azazirconacyclobutene **1a** was chosen for screening purposes, because it demonstrated the fastest and cleanest aldehyde insertion reactions. Further, the resultant α,β-unsaturated imine **3a** is a known compound, identified easily by ¹H NMR spectroscopy.[1] No reaction was observed between **1a** and a series of *N*-arylbenzaldimine derivatives, independent of the steric and electronic properties of the *N*-aryl group. Upon encountering these initial difficulties, we reasoned that several fundamental differences between aldehydes and imines could be preventing the desired analogous reactivity. This observation motivated us to attempt the insertion of *N*-sulfonylimines **4a**−**c** into the zirconium−carbon bond in **1a**. These electron-deficient imines display less steric hindrance about nitrogen, exhibit far greater electrophilicity at the C=N carbon, and feature two oxygen atoms in the N-protective group that could

Table 1. Temperatures and Yields for Insertion and Extrusion Reactions

Zr cycle	imine	$T_{insertion}$ (°C)[a]	$T_{extrusion}$ (°C)[b]	α,β-unsaturated imine	yield (%)[c]
1a	**4a**	45	105	**3a**	100
1a	**4b**	45	115	**7**	99
1a	**4c**	45	105	**8**	98
1a	**10**	45	105	**3a**	100
1a	**12**	105	135	**3a**	56[d]
1a	**14**	10	135	**3a**	96
1b	**14**	10	145	**3b**	95
1c	**14**	40	135	**3c**	96

[a] Temperature at which the starting imine inserts into the azazirconacyclobutene Zr−C bond. [b] Temperature at which the α,β-unsaturated imine is extruded from the expanded zirconacycle. [c] Isolated yield after chromatography. [d] The reaction was run in the presence of 10 equiv of 1-phenylpropyne relative to the zirconacycle.

themselves coordinate to zirconium. This hypothesis was confirmed on observing that the *N*-tosyl benzaldimine **4a**[4] reacted with zirconacycle **1a** at 45 °C to afford the expanded metallacycle **5**; a color change from dark blue to yellow accompanied this transformation. The structural assignment of **5** was based on ¹H NMR correlation with **2**; formation of both metallacycles causes the two Cp rings and the two methyl groups on the aniline moiety to become diastereotopic. We were pleased to find that heating **5** for 12 h at 105 °C yielded the α,β-unsaturated imine **3a** in quantitative yield (Scheme 2). Related tosyl imines **4b**,**c** reacted similarly to **4a** and provided the expected α,β-unsaturated imines **7** and **8** in excellent yields (Table 1). Interestingly, the qualitative rate of imine Zr−C insertion was faster for more electron-deficient imines, such that rate₄ᵦ > rate₄ₐ > rate₄ᵧ; however, the rate of α,β-unsaturated imine extrusion from the corresponding expanded zirconacycles displayed the opposite trend, in which rate₄ᵦ < rate₄ₐ < rate₄ᵧ.

Extrusion of α,β-unsaturated imines **3a**, **7**, and **8** should be accompanied by generation of the previously unstudied *N*-tosyl imido complex **6**.[5] We were unable to detect this imido species by NMR but observed a white semicrystalline precipitate in the reaction vessel. This solid failed to dissolve in any solvents typically compatible with zirconium complexes, and no catalytic turnover was observed when the reaction was conducted in the presence of excess imine and 1-phenyl-1-propyne. Insertion of *N*-(*p*-bromobenzenesulfonyl)benzaldimine (**10**),[6] however, led to crystallization of the *p*-bromoben-

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(1) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705.

(2) Standard condensation methods for the preparation of α,β-unsaturated imines have not been shown to be successful in the syntheses of these highly arylated α,β-disubstituted derivatives.

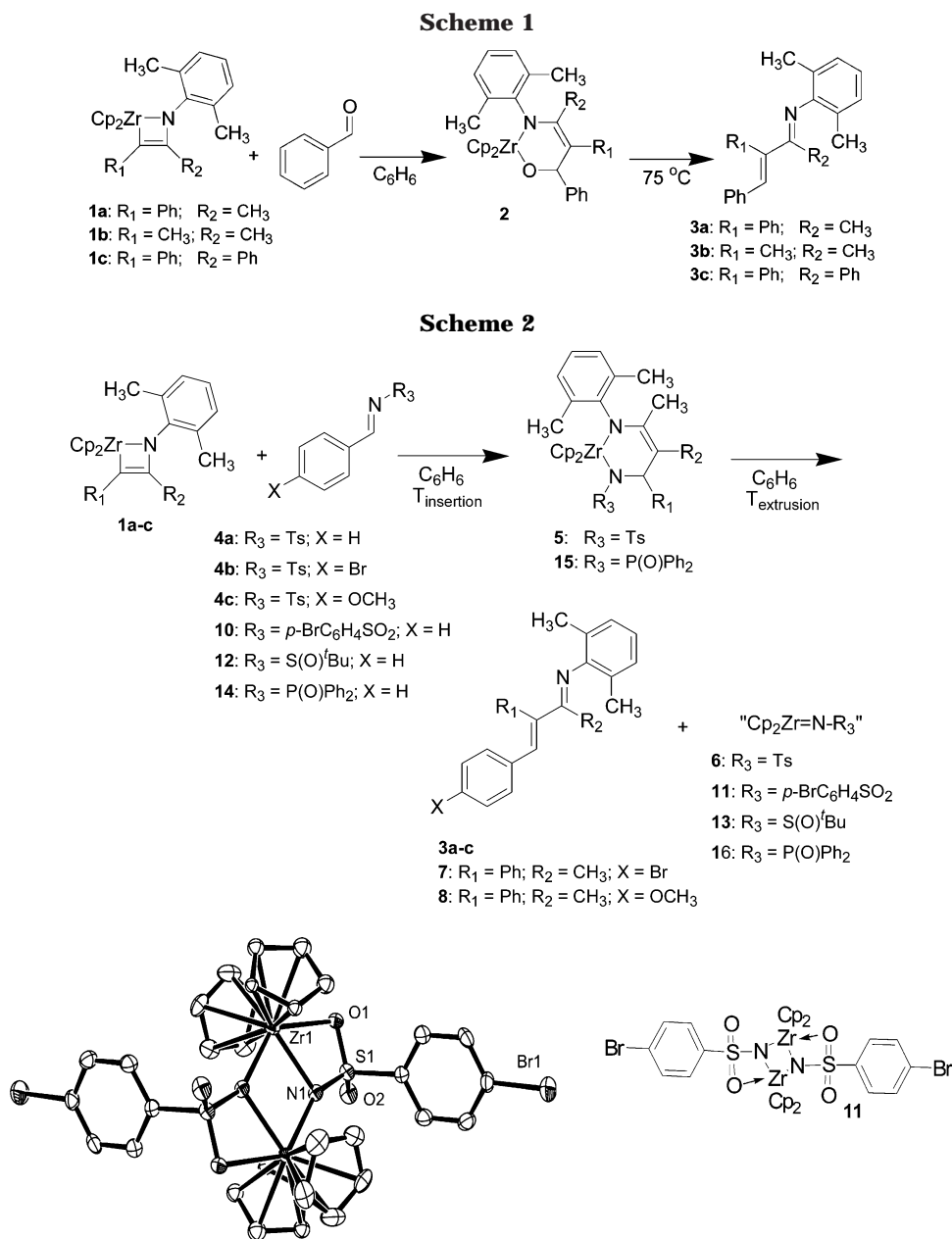(3) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *J. Org. Chem.* **1996**, *61*, 4532.

(4) Love, B. E.; Raje, P. S.; Williams, T. C., II. *Synlett* **1994**, 493.

Scheme 1

1a: R_1 = Ph; R_2 = CH_3
1b: R_1 = CH_3; R_2 = CH_3
1c: R_1 = Ph; R_2 = Ph

3a: R_1 = Ph; R_2 = CH_3
3b: R_1 = CH_3; R_2 = CH_3
3c: R_1 = Ph; R_2 = Ph

Scheme 2

4a: R_3 = Ts; X = H
4b: R_3 = Ts; X = Br
4c: R_3 = Ts; X = OCH_3
10: R_3 = p-BrC$_6$H$_4$SO$_2$; X = H
12: R_3 = S(O)^{t}Bu; X = H
14: R_3 = P(O)Ph$_2$; X = H

5: R_3 = Ts
15: R_3 = P(O)Ph$_2$

"Cp$_2$Zr=N-R$_3$"

6: R_3 = Ts
11: R_3 = p-BrC$_6$H$_4$SO$_2$
13: R_3 = S(O)^{t}Bu
16: R_3 = P(O)Ph$_2$

3a-c
7: R_1 = Ph; R_2 = CH_3; X = Br
8: R_1 = Ph; R_2 = CH_3; X = OCH_3

Figure 1. ORTEP and line drawings of the *N*-sulfonyl imido dimer **11**.

zenesulfonyl imido dimer **11** directly from the reaction mixture.[7] An X-ray diffraction study carried out on this material showed that one sulfonyl oxygen of each monomeric unit is coordinated to each zirconium in this dimeric complex to generate an 18-electron pentacoordinate compound (Figure 1). The connectivity in this structure suggests that the sulfonyl protecting group in the starting imine may coordinate to the zirconium center to facilitate insertion but also indicates that subsequent insertion of alkyne to generate a new azazirconacyclobutene will be difficult energetically. Even highly sterically hindered N-protecting groups, such as (2,4,6-triisopropylphenyl)sulfonyl, failed to prevent dimerization of the *N*-sulfonyl imidozirconocene monomer.

We next considered the case of *N*-sulfinyl imines for the insertion/extrusion sequence. This functional group possesses only one oxygen atom per sulfur atom, retaining the sulfonyl's ability to coordinate to zirconium while potentially decreasing the propensity of the resulting *N*-sulfinyl imidozirconocene complex to dimerize. *N-tert*-Butylsulfinylbenzaldimine (**12**)[8] inserted into the zirconium–carbon bond of metallacycle **1a** at 105 °C. The

(5) There are no examples of early-transition metal−*N*-tosyl imido complexes in the literature. Mid-to-late-transition-metal−*N*-tosyl imido complexes have been shown to participate in group transfer chemistry. For more information, see: (a) Liang, J.-L.; Huang, J.-S.; Yu, X.-Q.; Zhu, N.; Che, C.-M. *Chem. Eur. J.* **2002**, *8*, 1563. (b) Smieja, J. A.; Shirzad, K.; Roy, M.; Kittilstved, K.; Twamley, B. *Inorg. Chim. Acta* **2002**, *335*, 141. (c) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120. (d) Au, S.-M.; Fung, W.-H.; Huang, J.-S.; Cheung, K.-K.; Che, C.-M. *Inorg. Chem.* **1998**, *37*, 6564. (e) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889. (f) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.

(6) Alper, P. B.; Meyers, C.; Lerchner, A.; Siegel, D. R.; Carriera, E. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3186.

(7) An analogous structure was determined on the precipitate in the tosyl reaction; however, the crystal for this species decomposed on the diffractometer, and only a partial data set was collected.

(8) Liu, G.; Cogan, D. A.; Ellman, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 9913.
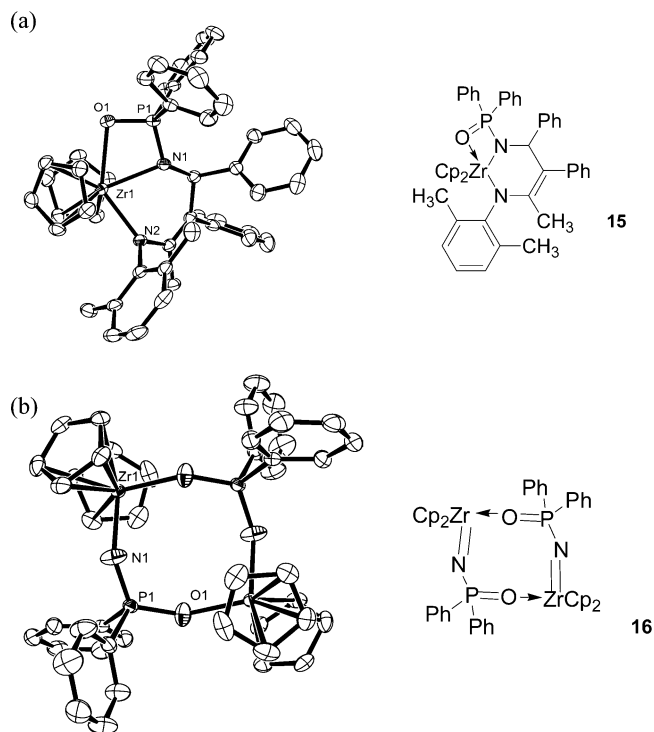
(a)

(b)

Figure 2. ORTEP and line drawings of (a) the expanded zirconacycle **15** and (b) the *N*-phosphinyl imidozirconocene dimer **16**.

expanded zirconacycle subsequently extruded imine **3a** at 135 °C. Unfortunately, no evidence of the newly formed sulfinyl imido complex **13** was observed by ^{1}H NMR spectroscopy, and no corresponding precipitation from the reaction mixture was noted. The starting imine was unstable above 115 °C, suggesting that the sulfinyl functional group might not survive the 135 °C temperature required for the retro-[4 + 2] cycloaddition.[9]

In a further exploration of N-substituents with main-group oxygen donors, we decided to pursue *N*-phosphinyl imines as substrates; phosphine oxides have been shown to coordinate *reversibly* to imidozirconocene complexes.[1] *N*-(Diphenylphosphinyl)benzaldimine (**14**)[10] reacted with zirconacycle **1a** at room temperature to generate the expanded metallacycle **15**. A crystal structure of the intermediate confirmed its six-membered-ring structure and showed that the phosphinyl oxygen is coordinated to zirconium (Figure 2a). Heating **15** to 135 °C led to extrusion of the α,β-unsaturated imine **3a** in 96% yield and generated a new species bearing a single Cp resonance in the ^{1}H spectrum and a new resonance in the [31]P{[1]H} spectrum. There are no reports on *N*-phosphinylmetal–imido complexes in the literature; thus, we were unable to compare these spectral data to those of any known compounds.[11] However, we were able to grow X-ray-quality crystals of this new *N*-phosphinyl imidozirconocene complex (**16**). The X-ray structure showed that this compound is an eight-membered ring, in which dimerization has occurred through the oxygen atom of the bulky phosphinyl protecting group instead of via a [2 + 2] cycloaddition

as in the *N*-sulfonyl imido complex. Heating this soluble imidozirconcene species in the presence of external Lewis bases, such as trimethylphosphine oxide and alkynes, failed to cleave the dimer.

This chemistry was shown to be general with respect to the azazirconacyclobutene. Imine **14** reacted with metallacycles **1b,c** at 45 and 10 °C, respectively. Heating the corresponding zirconacycles to 145 and 135 °C generated the α,β-unsaturated imines **3b,c** in excellent yields.[12] Only one double-bond geometrical isomer was observed for all α,β-unsaturated imines generated; however, the product **3c** was generated as a 7:4 mixture of (*E*)- and (*Z*)-imine isomers, presumably due to the increased steric bulk α to the imine.

In summary, we have succeeded in developing an effective method for inserting imines into azametalla-cycle zirconium–carbon bonds and generating α,β-unsaturated imines from the resulting expanded zir-conacycles in high yields. The presence of an oxygen-bearing substituent on nitrogen was critical in effecting the reaction between imine and azazirconacyclobutene. However, the role of the oxygen substituent in effecting this chemistry is, at present, unknown.[13] Simulta-neously, we have developed reactions that access several new electron-deficient imidozirconocene complexes, two of which were shown to dimerize even in dilute solu-tions. Because of this dimerization process, we are not yet able to generate α,β-unsaturated imines and imido-zirconocene complexes catalytically in these systems. We are continuing to explore the classes of imines best suited to reactions with azazirconacyclobutenes and to further develop the chemistry of electron-deficient im-idozirconocene complexes.

Supporting Information Available: Text giving experimental procedures and characterization data for all new compounds and CIF files giving X-ray crystallographic data for **11**, **15**, and **16**. This information is available free of charge via the Internet at http://pubs.acs.org.

OM0497994

(9) Decomposition was not limited to *N-tert*-butylsulfinylbenzaldi-mine; *N*-(*p*-toluenesulfinyl)benzaldimine began to decompose at 90 °C.

(10) Yamada, K.; Harwood, S. J.; Gröger, H.; Shibasaki, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3504.

(11) We have also generated the *N*-phosphinyl imidozirconocene complex **16** by an alternative method. All spectral data for **16** generated in this manner correlate with those observed by the methodology above.
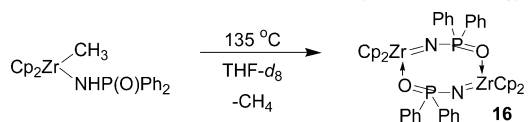
(12) The rate of phosphinyl imine insertion into the azazirconacylo-butenes Zr–C bond followed the order rate$_{1b}$ > rate$_{1a}$ > rate$_{1c}$.

(13) We propose three possible roles for the oxygen substituent: (1) in withdrawing electron density from the imine C=N bond, the oxygen substituent may facilitate insertion by making the imine more elec-trophilic and, thus, higher in energy and more reactive; (2) the oxygen substituent may be required to coordinate to zirconium and, therefore, direct the insertion; (3) the protecting group on nitrogen may increase the distance between the imine and the bulk of the protecting group, thus facilitating insertion.