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Journal of Organometallic Chemistry 591 (1999) 2–7

Reversible C–H activation of an *N*-methyl group in a bis-Zr(IV) diazametallacycle: generation of an end-on, side-on coordinated bridging alkylideneamido ligand

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Received 15 July 1999; accepted 27 August 1999

Abstract

The complex $(Cp_2Zr)_2(\mu\text{-}NH^tBu)(\mu\text{-}N{=}CH_2)$ was obtained when the stoichiometric reaction between $Cp_2(THF)Zr{=}N^tBu$ and PhCH=NMe was carried out. The crystal structure of this dinuclear species shows two Cp_2Zr fragments bridged in a moderately symmetric fashion by a $-NH^tBu$ group, and in an extremely asymmetric fashion by a $-N{=}CH_2$ (methyleneamido) group. The methyleneamido fragment exhibits an unusual coordination mode: it is bound to one Zr atom in a linear fashion ($\angle$Zr1–N1–C21 = 176.9(6)°) and to the second Zr atom (Zr2) in a side-on fashion. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: C–H activation; Imido complexes; Dinuclear complexes; Imines

1. Introduction

There are now many Group IV imido complexes known [1–11]. Among the most chemically interesting of these molecules are ones in which the M=N multiple bond (M = Ti, Zr, Hf) is reactive toward strong linkages in organic compounds, such as C=O, C=N and C–H bonds. This has resulted in a rich array of reaction chemistry, much of which leads to the formation of organic and organometallic compounds with new carbon–nitrogen bonds.

Previous work in our laboratories has focused on the class of reactive imido complexes of formula $Cp_2Zr{=}NR$. In addition to reacting with arene C–H bonds [1], the Zr–N bond in this molecule participates in overall cycloaddition reactions with organic imines, leading to isolable 2,4-diazametallacycles (Scheme 1) [12,13]. These reactions are reversible, a property which has allowed us to convert the stoichiometric cycloaddition reaction into a series of catalytic imine metathesis reactions, which are mechanistically analogous to olefin metathesis [14].

The imine metathesis reactions work well between *N*-aryl aldimines, but their *N*-alkyl analogues were found to be unreactive toward cross metathesis with *N*-aryl aldimines. Attempted metathesis reactions involving the two *N*-alkyl imines TolCH=NMe (**2b**) and PhCH=NPr (**2c**) gave slow or erratic results, depending on the catalyst used. This paper reports the results of our attempt to obtain a better understanding of these reactions.

2. Results and discussion

To obtain direct information about the reactivity of *N*-alkyl imines with zirconocene imido complexes, the stoichiometric reaction between $Cp_2(THF)Zr{=}N^tBu$ (**1**) and *N*-methyl benzaldimine (**2b**) was studied. When **1** was treated with two equivalents of **2b** at 45°C for 6 h, ^{1}H-NMR spectroscopic analysis of the reaction mixture supported the initial formation of diazametallacycle **3** in ca. 80% yield, with the balance of **1** remaining unreacted (Scheme 2). The ^{1}H-NMR spectrum of **3** in C_6D_6 contained diastereotopic Cp resonances at δ 6.16 and 5.91 ppm, a singlet at 3.86 ppm integrating to one proton (assigned to the C–H group α to the two N

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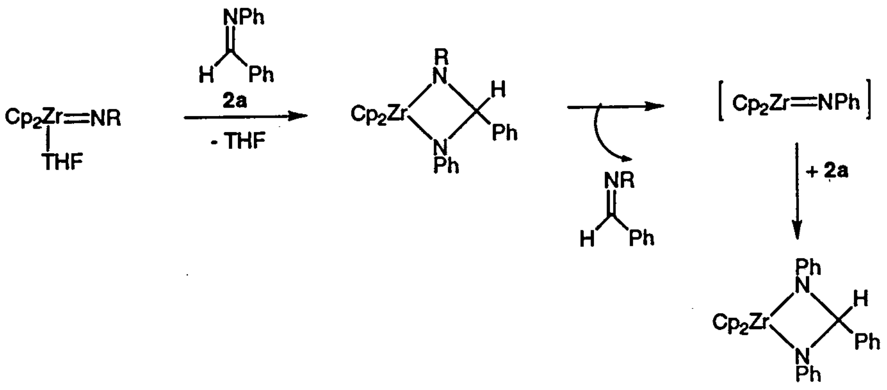
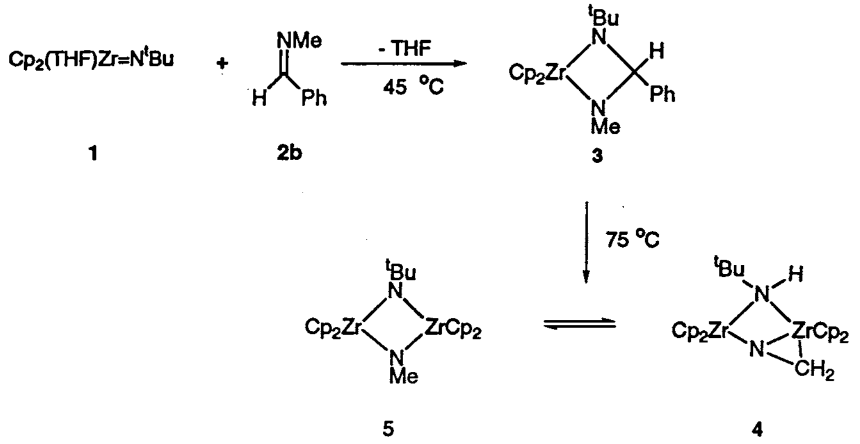
PII: S0022-328X(99)00505-7



Scheme 1.



Scheme 2.

atoms in metallacycle **3**), an *N*-Me resonance at 2.53 ppm and a *N*-ᵗBu resonance at 0.81 ppm. The formation of diazametallacyclobutane (**3**) from the formal [2 + 2] cycloaddition of the transient '$Cp_2Zr{=}N^tBu$' species with **2b** is analogous to the reactivity observed with *N*-phenyl imines (Scheme 1).

When the reaction mixture was heated further at 75°C, *N*-methyl and *N*-ᵗbutyl benzaldimine and two new organometallic products were obtained, as determined by ¹H-NMR spectroscopy. Brown homogeneous crystals were isolated in 25% yield from this reaction mixture. Analysis of these crystals by X-ray diffraction revealed that one of the compounds present in the product mixture was dinuclear complex **4** (Scheme 2). An ORTEP diagram of complex **4** is shown in Fig. 1. There are two molecules of the compound in the asymmetric unit of the structure. The hydrogen atom attached to N2 was not located in the final difference map, but is clearly visible in the ¹H-NMR spectrum as a broad singlet at δ 2.2 ppm. The two Cp_2Zr fragments in **4** are bridged in a moderately symmetric fashion by an $-NH^tBu$ group, and in an extremely asymmetric fashion by an $-N{=}CH_2$ (methyleneamido) group. The Zr1–N2 and Zr2–N2 bond lengths associated with the bridging ᵗBu amido group (2.247(6)/2.209(6) and 2.394(6)/2.326(7) Å, respectively) indicate a stronger interaction between Zr1 and N2. The methyleneamido fragment coordinates to Zr1 in a linear fashion

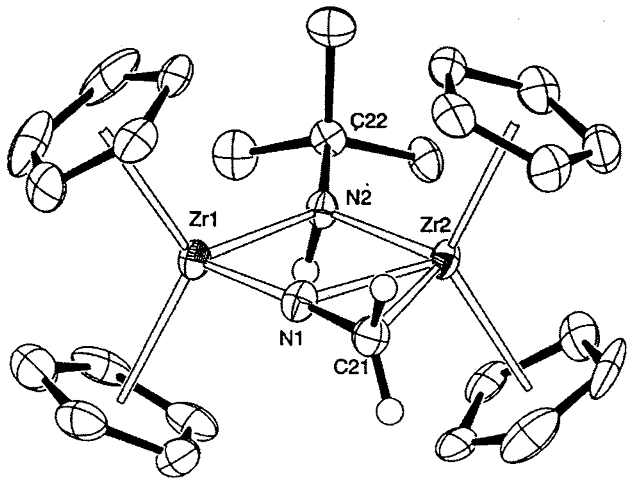


Fig. 1. ORTEP diagram of the zirconium dinuclear species **4** with thermal ellipsoids scaled to represent the 50% probability surface.

Table 1
Selected bond lengths (Å) [a] and angles (°) [a] of compound **4**

Bond lengths			
Zr(1)–N(1)	1.929(6) /1.965(7)	Zr(2)–N(1)	2.196(6) /2.169(7)
Zr(1)–N(2)	2.247(6) /2.209(6)	Zr(2)–N(2)	2.394(6) /2.326(7)
N(1)–C(21)	1.390(9) /1.31(1)	Zr(2)–C(21)	2.334(8) /2.42(1)
Bond angles			
Zr(1)–N(1)–C(21)	176.9(6) /171.3(8)	Zr(2)–N(1)–C(21)	35.6(2) /32.5(4)
Zr(1)–N(2)–Zr(2)	47.0(2) /45.5(2)		

[a] The values of the two crystallographically independent molecules are separated by a slash (/).

(∠Zr1–N1–C21 = 176.9(6)/171.3(8)°), indicating a high degree of π-interaction between N1 and Zr1 [15,16] (see Table 1). The Zr1–N1 bond length of 1.929(6)/1.965(7) Å is somewhat shorter than that seen in other Zr alkylideneamido complexes (2.013(5) [15] to 2.063(2) Å) [16] and lies midway between the typical values for Zr–N single (2.07–2.16 Å) [6,17] and double (1.826(4) Å) [3] bonds. The second Zr atom (Zr2) is coordinated to the bridging methyleneamido group in a side-on fashion. The Zr2–N1, Zr2–C21 and N1–C21 bond lengths (2.196(6)/2.169(7), 2.334(8)/2.42(1) and 1.390(9)/1.31(1) Å, respectively) are similar to those observed in the zirconocene imine complex, $Cp_2(THF)Zr(\eta^2\text{-}PhCH{=}NSiMe_3)$ (2.11(1), 2.26(1), and 1.41(1) Å) [18]. This end-on, side-on bridging mode represents a rare binding mode for this ligand.

When crystalline **4** was redissolved in C_6D_6, the ^{1}H-NMR spectrum showed the same ca. 3:1 mixture of **4** and **5** that existed prior to crystallization, suggesting that **4** and **5** are in dynamic equilibrium in solution. Complex **5** formally arises from the reaction between $[Cp_2Zr{=}NMe]$ and $[Cp_2Zr{=}N^tBu]$, and complex **4** from proton transfer between the bridging *N*-Me and *N*-^{t}Bu imido groups of **5**. Thus, it appears that the cycloreversion of **3** is capable of generating either the $[Cp_2Zr{=}N^tBu]$ or the $[Cp_2Zr{=}NMe]$ fragment, implying that a similar mechanism is operative for both *N*-alkyl and *N*-aryl imine metathesis [14]. The equilibrium between **4** and **5** is established very quickly, as demonstrated by warming a frozen (−196°C) mixture of solid **4** and toluene-d_8 to −42°C in the probe of a NMR spectrometer. The resulting ^{1}H-NMR spectrum was identical to that obtained at room temperature.

Surprisingly, the 3:1 equilibrium ratio of **4** to **5** did not vary significantly over a temperature range of 25–100°C (Fig. 2). This indicates that $\Delta H° \cong 0$ for the equilibration, and thus dominance of **4** is the result of a slightly positive $\Delta S°$. Consistent with this conclusion, over the investigated temperature range complex **4** ex-

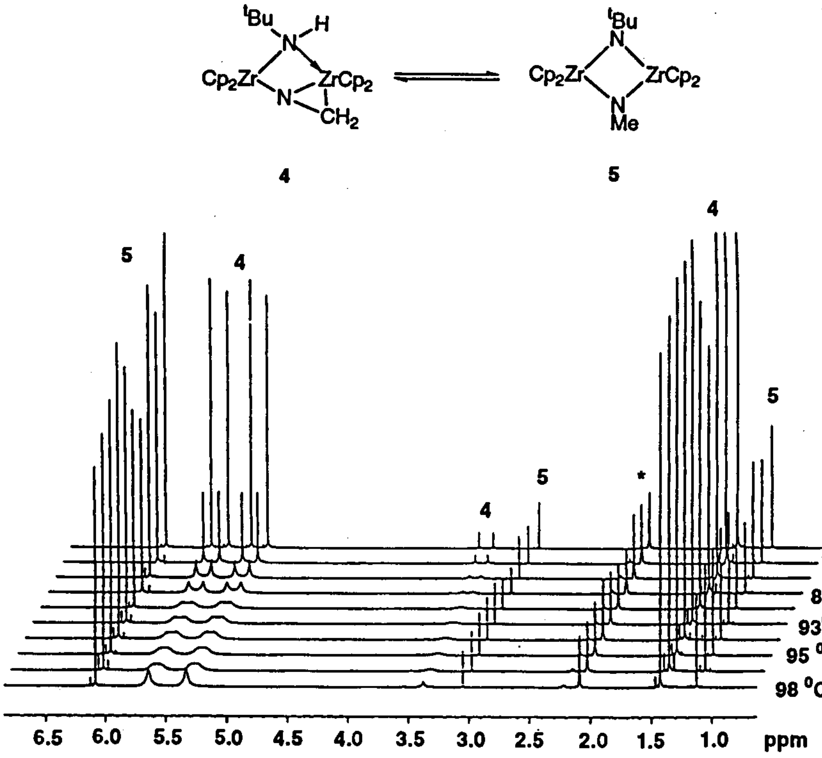
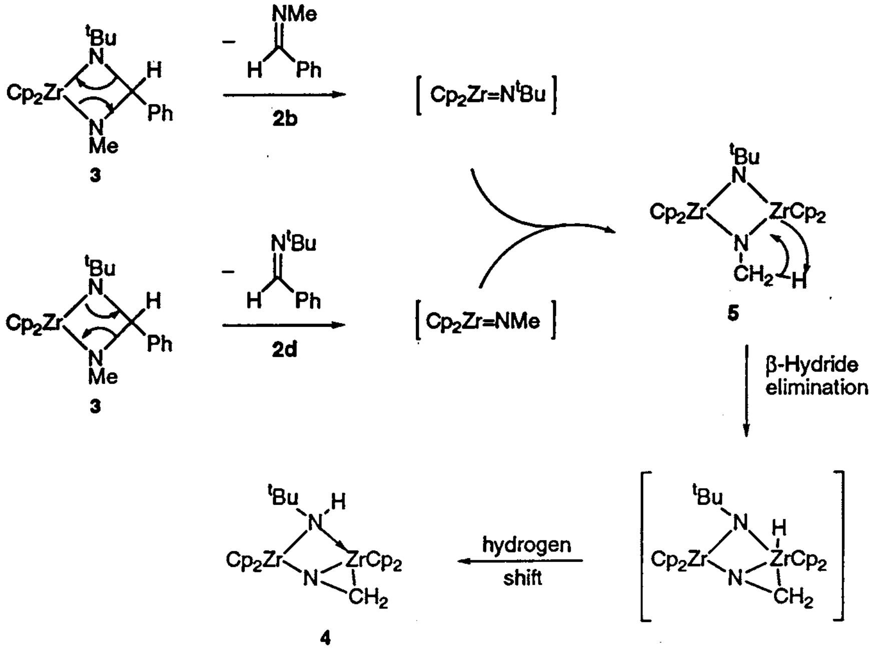


Fig. 2. ^{1}H-NMR spectra of **4** and **5** over a 70°C temperature range (* denotes a signal from the residual protiated solvent; spectra are not normalized).



Scheme 3.

hibited fluxional behavior but **5** did not. Each of the two sets of diastereotopic cyclopentadienyl resonances of **4** coalesced into a single signal ($T_c = 87.1$°C, $\Delta G^{\ddagger}_{360} = 15.5$ kcal mol^{-1}), as did the two methylene proton resonances ($T_c = 91.9$°C, $\Delta G^{\ddagger}_{365} = 14.9$ kcal mol^{-1}). This result implies that the bridging –NH^{t}Bu group in **4** is able to rotate about one of the Zr–N bonds, causing the top and bottom halves of the dimer to become equivalent on the NMR timescale.

Analogous results were obtained when imido complex **1** was heated with two equivalents of *N*-propyl benzaldimine (**2c**) in C_6D_6 at 75°C. Red crystals precipitated from the reaction mixture during the course of the reaction. Attempts to analyze these crystals by X-ray crystallography proved unsuccessful due to the large amount of disorder in the structure. However, the ^{1}H-NMR spectrum of these crystals in THF-d_8 was similar to that of the mixture of **4** and **5** discussed above.

The concurrent formation of **4** and **5** raises interesting mechanistic questions. Scheme 3 outlines a pathway for the formation of these materials that we consider most reasonable. Based on spectroscopic evidence, we believe that metallacyclobutane (**3**) is the initially formed species, as it is in the *N*-phenyl imine reaction. Cycloreversion of **3** can occur in two directions to afford the corresponding imido complexes [Cp_2Zr=NMe] and [Cp_2Zr=N^{t}Bu] with the extrusion of the organic imines **2b** and **2d**. An overall [2 + 2] cycloaddition between the two imido fragments would generate the dinuclear species **5**. Complex **5** could undergo β-hydride elimination reaction followed by rapid hydrogen shift to yield **4**.

3. Conclusions

Previously, it has been observed that treatment of imidozirconocene complex **1** with a stoichiometric amount of *N*-phenyl imines results in the formation of mono-metallic diazacyclobutane complexes that are isolable. Heating these complexes with excess imines results in the metathetical exchange of imines with the concurrent formation of the corresponding diazametallacycle complex (Scheme 1). In contrast to the overall reactivity of *N*-phenyl imines, treatment of **1** with a stoichiometric amount of imine **2b** leads to the dinuclear species **4** and **5**. Complex **4** has an unusual end-on, side-on binding mode.

Compound **5** results from overall C–H activation of the *N*-methyl group, with transfer of the activated hydrogen to the second ^{t}Bu substituted nitrogen atom. At present we do not know how this two-atom hydrogen migration occurs, but any proposed pathway would have to account for the rapid interconversion of **4** and **5** in solution at low temperature. Further work will also be required to understand why product **5**, rather than the related symmetrical Zr=NR dimers, is formed in this process, and to elucidate the factors that promote activation of the *N*-methyl hydrogens.

4. Experimental

4.1. General procedures

Unless otherwise noted, reactions and manipulations were performed using standard drybox or Schlenk techniques. Glassware was dried overnight at 150°C before use. Unless otherwise noted, ^{1}H-NMR spectra were recorded at 500 MHz and chemical shifts (δ) are reported in parts per million (ppm) relative to residual protiated solvent: C_6D_6 (7.15 ppm). The ^{13}C{^{1}H}-NMR were recorded at 100 MHz and are reported in ppm relative to the carbon resonance of the deuterated solvent: C_6D_6 (128.0 ppm).

Table 2
Crystal and data collection parameters for **4**

Crystal data	
Empirical formula	$C_{25}H_{32}N_2Zr_2$
Formula weight	542.98
Crystal color, habit	Orange, bladelike
Crystal dimensions (mm)	0.16 × 0.12 × 0.05
Crystal system	Triclinic
Lattice type	Primitive
Lattice parameters	
a (Å)	9.8781(6)
b (Å)	13.9726(9)
c (Å)	16.0956(10)
V (Å^3)	2219.7(2)
Space group	$P\bar{1}$ (no. 2)
Z value	4
D_{calc} (g cm^{-3})	1.625
F_{000}	1104.00
μ(Mo–K$_\alpha$) (cm^{-1})	9.52
Intensity measurements	
Diffractometer	SMART
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å), graphite monochromated
Crystal to detector distance (mm)	60.00
Temperature (°C)	-105 ± 1
Scan type	ω (0.30° per frame)
Exposure time	20.0 s per frame
2θ max (°)	52.1
Total no. of reflections measured	12 026
Corrections	Lorentz-polarization, absorption ($T_{max} = 0.96$, $T_{min} = 0.70$)
Structure solution and refinement	
Structure solution	Direct methods (SIR-92)
Refinement	Full-matrix least-squares
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$1/[\sigma^2(F_o)] = [\sigma_c^2(F_o) + p^2F_o^2/4]^{-1}$
p-factor	0.0310
Anomalous dispersion	All non-hydrogen atoms
No. observations ($I > 3.00\sigma(I)$)	4549
No. variables	535
Reflection/parameter ratio	8.50
Residuals: R; R_w; R_{all}	0.050; 0.050; 0.008
Goodness-of-fit indicator	1.48
Max. shift/error in final cycle	0.00
Largest difference peak and hole (e Å^{-3})	1.06 and -0.81

4.2. Materials

Solvents were distilled from the appropriate drying agents under N_2 or passed through a column of activated alumina and sparged with N_2 prior to use. Complexes **1** [3], **2b** [19], and **2c** [19] were synthesized according to literature procedures.

4.3. $(Cp_2Zr)_2(\mu\text{-}NH^tBu)(\mu\text{-}N{=}CH_2)$ and $(Cp_2Zr)_2(\mu\text{-}NH^tBu)(\mu\text{-}NCH_3)$ (**4** and **5**)

To a stirred solution of $Cp_2(THF)Zr({=}N^tBu)$ (**1**) (269 mg, 0.739 mmol) in 5 ml of C_6H_6 was added PhCH=NMe (174 mg, 1.47 mmol, two equivalents) resulting in an immediate color change from yellow to purple. The solution was heated to 75°C for 14 h. During heating, the reaction mixture developed a brown color. The solvent was removed at reduced pressure to obtain 450 mg of a brown residue which was dissolved in toluene (5 ml), layered with hexanes (5 ml) and stored at −35°C for two months. After this time, light brown crystals had formed (100 mg, 25% yield) that were suitable for X-ray crystallographic analysis. The ORTEP that was obtained is shown in Fig. 1 (compound **4**). However, spectroscopic data indicate the presence of a second compound in solution, which is tentatively assigned as the dinuclear species **5**. We believe that there is a rapid equilibrium between **4** and **5** in solution to give ca. a 3:1 ratio of **4**:**5** but **4** crystallizes selectively under the conditions employed. Since the crystals obtained appeared homogeneous, the implication is that only one compound was present in the solid state.

We have tentatively assigned the solution ^{1}H-NMR data to complexes **4** and **5**. Complex **4**: ^{1}H-NMR (C_6D_6): δ 5.74 (s, 14H, C_5H_5), 5.59 (s, 14H, C_5H_5), 5.40 (s, 14H, C_5H_5), 5.27 (s, 14H, C_5H_5), 3.55 (d, $J = 3$ Hz, 1.5H, vinyl), 3.43 (d, $J = -3.5$ Hz, 1.5H, vinyl), 2.18 (s, 2.5H, NH), 1.34 (s, 25H, C(CH_3)$_3$) ppm. Compound **5**: ^{1}H-NMR (C_6D_6): δ 6.10 (s, 20H, C_5H_5), 2.98 (s, 3H, CH_3), 1.07 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C-NMR for **4** and **5** (C_6D_6): δ 128.29, 127.81, 111.80, 111.60, 108.48, 108.38, 104.63, 104.41, 67.33, 58.10, 45.78, 44.90, 37.06, 36.29 ppm. HRMS (EI): m/z calc. for $C_{25}H_{32}N_2Zr_2$ 540.0652 [M$^+$]. Found 540.0660.

Crystal and data collection parameters for **4** are listed in Table 2.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 132687 for compound **4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK by fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgements

The authors thank Drs Frederick Hollander and Ryan Powers for solving the crystal structure of **4** and the US National Institutes of Health (Grant No. GM-25459) for financial support of this work.

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