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Note

Reactivity variations within Group 4 complexes of 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene: Structures of $[(C_5H_5)TiCl\{(t\text{-}BuNCH)_2\}]$ and $[(C_5H_5)_2Zr\{(t\text{-}BuNCH)_2\}]$

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Abstract

The reactions of the metallocene dichlorides $[(\eta^5\text{-}C_5H_5)_2MCl_2]$, M = Ti and Zr, with the 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene radical anion (lithium complex) in diethyl ether reveal a reactivity difference within the series, yielding $[(C_5H_5)TiCl\{(t\text{-}BuNCH)_2\}]$ and $[(C_5H_5)_2Zr\{(t\text{-}BuNCH)_2\}]$ through the elimination of $Li(C_5H_5)$ and/or LiCl, respectively. We report the X-ray crystal structures of these complexes, and discuss their reactivity patterns and solution fluxional properties.

Keywords: Metallocene; Zirconocene; Cyclopentadienyl; 1,4-Diazabuta-1,3-diene; α-Diimine; Crystal structure

1. Introduction

The organometallic chemistry of 1,4-disubstituted 1,4-diazabuta-1,3-dienes (R-DAB) has been studied intensively [1]. The impetus driving the research has been based largely on the discovery that these molecules are not innocent ligands, and that this should lead to highly novel chemistry and useful reactivity properties of the complexes in synthesis and catalysis. More recently they have received most attention as ligands in the polymerisation of alkenes in late-transition metal chemistry [2]. The 1,4-diazabuta-1,3-dienes can bind as neutral Lewis bases, as the singly reduced radical anions or as the dianionic species. Further flexibility is shown by the fact that they can form chelate complexes in all these oxidation states, bind a single metal through only one nitrogen centre or bridge two metal centres through both nitrogen centres in different oxidation states. Homoleptic mono-, bis- and tris(1,4-diazabuta-1,3-diene)metal complexes are known for a large range of metals (the mono-derivatives being better known as Arduengo-type carbene analogues), as are heteroleptic complexes [1,3]. Herein, we report on new syntheses and further characterisation of a series of Group 4 heteroleptic complexes of *t*-Bu-DAB and discuss the chemistry of these complexes (previous syntheses and some fluxional behaviour of these complexes have been reported [4–6]).

2. Experimental

2.1. General

Unless stated, all manipulations of complexes were carried out under an argon atmosphere by the use of standard Schlenk techniques. *t*-Bu-DAB and $[Li(t\text{-}Bu\text{-}DAB)_2]$ were prepared according to the literature procedures [7,8]. $[(C_5H_5)_2TiCl_2]$ and $[(C_5H_5)_2ZrCl_2]$ were purchased from

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Aldrich and sublimed prior to use. All solvents were dried over Na or Na/K and distilled. All other chemicals were obtained from Aldrich and used as received. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AC-200 spectrometer at 200.132 (^{1}H) and 50.323 MHz (^{13}C), internally referenced to the residual ^{1}H resonances of C_6D_6 (δ 7.15) or the ^{13}C resonance (δ 128.0: broad band proton decoupling). Elemental analyses were performed by Chemical and MicroAnalytical Services Pty. Ltd., Melbourne. Melting points were determined in sealed glass capillaries under argon and are uncorrected. I.R. spectra were recorded as Nujol mulls on NaCl plates using a Perkin–Elmer 1725X Fourier-transform infra-red spectrometer.

*2.2. Synthesis of [(C_5H_5)Ti(Cl)(t-Bu-DAB)] (**1**)*

To a diethyl ether solution (40 mL) of [$(C_5H_5)_2TiCl_2$] (0.21 g, 0.84 mmol), a diethyl ether solution (20 mL) of [Li(*t*-Bu-DAB)$_2$] (0.57 g, 1.66 mmol) was added dropwise with stirring at −40 °C. The solution was allowed to warm to room temperature and let stir overnight. The solvent and any uncoordinated *t*-Bu-DAB were removed in vacuo and the product was sublimed (110 °C, 10^{-1} mbar) from the remaining dark solid as dark purple crystals (0.20 g, 76%). M.p. 116–119 °C. ^{1}H NMR (298 K, C_6D_6, major isomer only): δ 1.17 (br s, 18H, C*H*$_3$), 5.20 (br s, 2H, C*H*, *t*-Bu-DAB), 5.62 (br s, 5H, C*H*, Cp). Fluxionality prevented assignment of the ^{13}C NMR spectrum at 298 K. Anal. Calc. for $C_{15}H_{25}N_2ClTi$: C, 56.88; H, 7.96; N, 8.85. Found: C, 56.45; H, 7.86; N, 9.23%.

*2.3. Synthesis of [$(C_5H_5)_2$Zr(t-Bu-DAB)] (**2**)*

To a diethyl ether solution (40 mL) of [$(C_5H_5)_2ZrCl_2$] (0.21 g, 0.72 mmol), a diethyl ether solution (20 mL) of [Li(*t*-Bu-DAB)$_2$] (0.50 g, 1.46 mmol) was added dropwise with stirring at −40 °C. The solution was allowed to warm to room temperature and let stir overnight. The solvent and any uncoordinated *t*-Bu-DAB were removed in vacuo and the product was sublimed (200 °C, 10^{-1} mbar) from the remaining orange solid as orange crystals (0.23 g, 83%). M.p. 162 °C. ^{1}H NMR (298 K, C_6D_6): δ 1.18 (s, 18H, C*H*$_3$), 5.41 (s, 2H, C*H*, *t*-Bu-DAB), 5.41 (s, 5H, C*H*, Cp), 5.90 (s, 5H, C*H*, Cp). ^{13}C NMR (298 K, C_6D_6): δ 31.7 (*C*H$_3$), 57.2 (*C*Me$_3$), 100.9 (*C*H, Cp), 107.1 (*C*H, *t*-Bu-DAB), 108.0 (*C*H, Cp). Anal. Calc. for $C_{20}H_{30}N_2Zr$: C, 61.64; H, 7.76; N, 7.19. Found: C, 61.66; H, 7.68; N, 7.29%.

*2.4. X-ray structure determinations for compounds **1** and **2***

Initial studies were conducted using a single-counter instrument with capillary mounted specimens at ca. 295 K; in the case of **2**, aspirations were thwarted by apparent disorder of a pair of superimposed components. The problems were revisited some years later with the advent of a CCD instrument with 'low'-temperature facility. For **2**, substantial well-formed crystals of a freshly sublimed sample were available; the specimen selected for the experiment was a chip, carefully chosen so as not to include any immediately obvious potential twin plane.

Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo Kα radiation; $\lambda = 0.7107_3$ Å; T ca. 153 K), yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after 'empirical/multiscan' absorption correction (proprietary software), N_o with $I > 2\sigma(I)$ being considered 'observed'. All reflections were used in the full matrix least squares refinements on F^2, refining anisotropic displacement parameters for the non-hydrogen atoms, hydrogen atoms being included in a riding model; for **2**, 'Friedel' data were retained distinct and the absolute structure refined ($x_{abs} = -0.03(6)$), the *t*-butyl carbon displacement parameter forms being refined isotropically (reflections weights were $(\sigma^2(F^2) + (aP)^2 + bP)^{-1}(P = F_o{}^2 + 2F_c{}^2)/3)$. Neutral atom complex scattering factors were employed within the SHELX97 program system [9]. Pertinent results are given below and in Tables 1–3 and Figs. 1 and 2, the latter showing non-hydrogen atoms with 50% probability amplitude displacement envelopes.

3. Results and discussion

[(C_5H_5)TiCl(*t*-Bu-DAB)] (**1**) and [$(C_5H_5)_2$Zr(*t*-Bu-DAB)] (**2**) were prepared by metathetical exchange reactions between the metallocene dichlorides [$(C_5H_5)_2MCl_2$], M = Ti and Zr, and two equivalents of [Li(*t*-Bu-DAB)$_2$] in diethyl ether, Scheme 1. The reactions occurred quickly at −40 °C and the products were isolated as dark purple and orange crystalline solids, respectively, by sublimation

Table 1
Crystal data and refinement details for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{15}H_{25}N_2ClTi$	$C_{20}H_{30}N_2Zr$
Formula weight (g mol^{-1})	316.7	389.7
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c* (No. 15)	$P2_12_12_1$ (No. 19)
a (Å)	28.391(3)	8.611(2)
b (Å)	10.962(1)	14.685(3)
c (Å)	22.577(2)	15.233(3)
β (°)	103.071(2)	90
V (Å^3)	6844(1)	1926.3(7)
Z	16	4
Crystal size (mm)	0.40 × 0.35 × 0.25	0.40 × 0.17 × 0.13
Crystal colour, habit	Purple, prismatic	Orange, prismatic
Reflections collected, N_t	34267	37991
Independent reflections, *N*	8744	10072
R_{int}	0.032	0.022
Reflections with $I > 2\sigma(I)$, N_o	6313	8263
2θ Range (°)	3–58	4–75
Completeness of data (%)	96.1	99.6
Parameters	355	323
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.039$	$R_1 = 0.050$
R indices (all data)	$wR_2 = 0.107$	$wR_2 = 0.145$
Goodness-of-fit	0.979	$R_1 = 1.036$