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Cyclization of adiponitrile in the reaction with diphenylzirconocene

Maxim V. Andreev, Iuliia A. Akishkina, Vyacheslav S. Bogdanov,
Alexander F. Smol'yakov and Vladimir V. Burlakov

Table of Contents:

Table S1. Crystal data and structure refinement parameters for **7**.

Empirical formula	$C_{25}H_{25}N_2Zr$
Formula weight	444.69
Temperature/K	100
Crystal system	Monoclinic
Space group	C2/c
a (Å)	25.0016(8)
b (Å)	12.4893(4)
c (Å)	16.1038(5)
α (deg)	90
β (deg)	127.8810(10)
γ (deg)	90
V (Å^3)	3968.9(2)
Z	8
ρ_{calc}g/cm^3	1.488
μ/mm^{-1}	0.567
F(000)	1832.0
Crystal size/mm^3	0.38 × 0.19 × 0.14
Radiation	MoKα (λ = 0.71073)
$2\theta_{max}$ (deg)	3.86 to 60
Index ranges	$-35 \leq h \leq 31$, $-17 \leq k \leq 16$, $-22 \leq l \leq 22$
Reflections collected	52038
Independent reflections	5803 [R_{int} = 0.0473, R_{sigma} = 0.0241]
Data/restraints/parameters	5803/0/258
Goodness-of-fit on F^2	1.062
Final R indexes ($I>=2\sigma(I)$)	R_1 = 0.0232, wR_2 = 0.0608
Final R indexes [all data]	R_1 = 0.0241, wR_2 = 0.0614
Largest diff. peak/hole / e Å^{-3}	0.48/-0.77

2. EXPERIMENTAL SECTION

Experiments were carried out under Ar with careful exclusion of air and moisture using standard Schlenk techniques. The starting bromobenzene (Sigma Aldrich) was washed with sulfuric acid, then with sodium carbonate (aq.), dried with CaH_2, and distilled under argon. Solvents (*n*-hexane, toluene, THF, MTBE) were purified by conventional methods and freshly distilled prior to use under Ar. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Av-400 spectrometer. Chemical shifts (^1H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of benzene-d_6 (δ_H 7.16 ppm, δ_C 128.0 ppm as solvent). The Raman spectrum were registered on a JY LABRAM 300 spectrometer (He−Ne laser, 632.8 nm, 5 mW). The mass spectra were recorded on a Finnigan Polaris Q instrument. Phenyllithium and diphenylzirconocene were synthesized according to the literature.[S1,S2]

Reaction of diphenylzirconocene with adiponitrile. Synthesis of 7.

A mixture of Cp_2ZrPh_2 (0.359 g, 0.96 mmol) and adiponitrile (0.1 ml, 0.91 mmol) in toluene (25 ml) was heated at 80°C for 2.5 hours. The obtained yellow solution was evaporated to dryness and the residue was dissolved in MTBE (10 ml) at 50°C. The formed solution were placed at -40°C overnight for crystallization. The next day colorless crystals of **7** were filtered, washed with cold *n*-hexane and dried *in vacuo*. Yield of **7**: 0.302 g (82%). Mp: 150°C (dec) under Ar. Anal. Calcd for $C_{22}H_{22}ZrN_2$: C: 65.14; H: 5.47, N: 6.91%. Found C: 65.20; H: 5.55, N: 6.74%. ^1H NMR (297 K, benzene-d_6, δ, ppm): 1.51 (m, 2H, CH_2), 1.91-1.94 (m, 2H, CH_2); 2.26 (q, 2H, CH_2); 3.93 (br.s, 1H, NH); 5.54 (t, 1H, (HC=), J=5.1 Hz); 5.65 (s, 10H, Cp); 7.19-7.26, 7.38-7.40, 7.68-7.70 (m, 4H, arom.). ^{13}C NMR (296 K, benzene-d_6, δ, ppm): 21.8, 29,5 38.6 ($\underline{C}H_2$); 98.2 (H$\underline{C}$=); 108.7 (Cp); 122.1, 123.6, 124.62, 140.14 (arom.); 147.9, 148.5 ($\underline{C}$=); 174.7($\underline{C}$=NH), 183.5 ($\underline{C}$-Zr). IR (ν, cm^{-1}): 799, 751 (δCHAr), 1496 (νC=N), 1628 (νC=C), 3367 (νNH). Raman spectrum (ν, cm^{-1}): 1004 (Ph), 1121 (Cp), 1625 (νC=C), 3371 (νN–H). MS (70 eV, *m/z*): 405 $[M+H]^+$, 220 $[Cp_2Zr]^+$. Single crystals of **7** for the X-ray diffraction study were obtained by cooling a benzene/n-hexane (1:1) mixture, were not washed and were not dried and contained one cocrystallized benzene molecule per two molecules of **7**.

Protolysis of zirconamidinate complex 7.

Synthesis of 7-phenyl-1,3,4,5-tetrahydro-2*H*-azepin-2-imine hydrochloride 8.

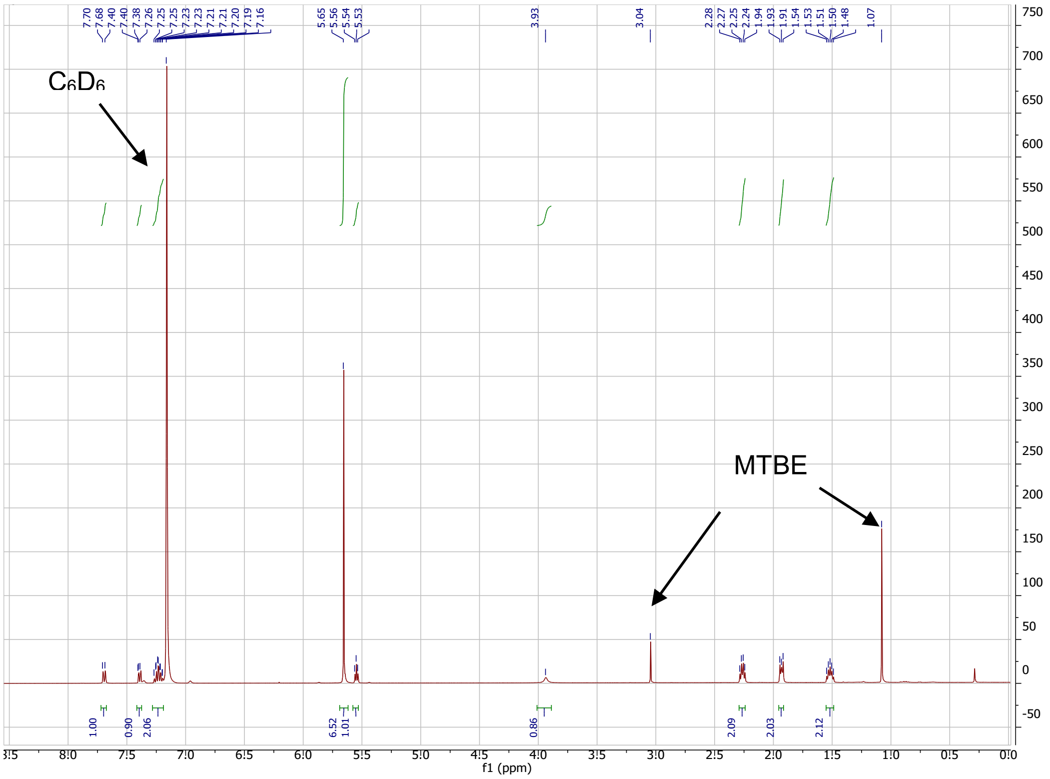
To complex **7** (0.125 g, 0.31 mmol) in THF (10 ml), a solution of HCl in dioxane (2.3 M, 0.415 ml, 0.96 mmol) was added at room temperature. The mixture was then evaporated to dryness, and the residue was washed with toluene (20 ml) at 65°C. The residue was extracted with methanol (35 ml), and the extract was filtered through Al_2O_3. The obtained filtrate was evaporated to dryness, the residue was dissolved in THF (0.4 ml) and acetone (3 ml), and the solution was allowed to stand at room temperature for several days for crystallization. Yield of **8**: 0.05 g (73%). Mp: 155-156°C (dec) under Ar. Anal. Calcd for $C_{12}H_{15}ClN_2$: C 64.72; H 6.79, N 12.58%. Found C 64.40; H 6.83, N 12.4%. ^{1}H NMR (297 K, CD_3OD, δ, ppm): 2.34-2.38, 2.67-2.71 (m, 6H, CH_2); 6.38 (t, 1H, (HC=), J=6.9 Hz); 7.37-7.43 (m, 3H, *m,p*-Ph); 7.48-7.51 (m, 2H, *o*-Ph). ^{13}C NMR (297 K, CD_3OD, δ, ppm): 25.1, 30.7, 32.4 ($\underline{C}H_2$); 121.4 (H$\underline{C}$=); 126.9, 129.8 (*o,m*-C, Ph); 130.1 (*p*-C, Ph); 139.1, 163.6 ($\underline{C}$=); 173.1 ($\underline{C}$-NH_2). IR (ν, cm^{-1}): 1662 ($\delta_{NH}+\nu_{C=N}$), 3244 (νNH), 3244 (νNH). MS (70 eV, *m/z*): 223 $[M+H]^+$, 187 $[M-Cl]^+$.

X-ray Diffraction Study. Diffraction data for **7** was collected on a Bruker Kappa APEX II Duo diffractometer using graphite-monochromated Mo-Kα radiation. Semiempirical absorption correction based on equivalent reflections was applied using the SADABS program.[S3] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[S4,S5] Molecular graphics were drawn using the OLEX2/Linux-amd64 program.[S6]

3. ^{1}H and ^{13}C NMR spectra of 7 and 8

Figure S1. ^{1}H and ^{13}C NMR spectra of **7** in C_6D_6.

a. ^{1}H NMR



b. ^{13}C NMR

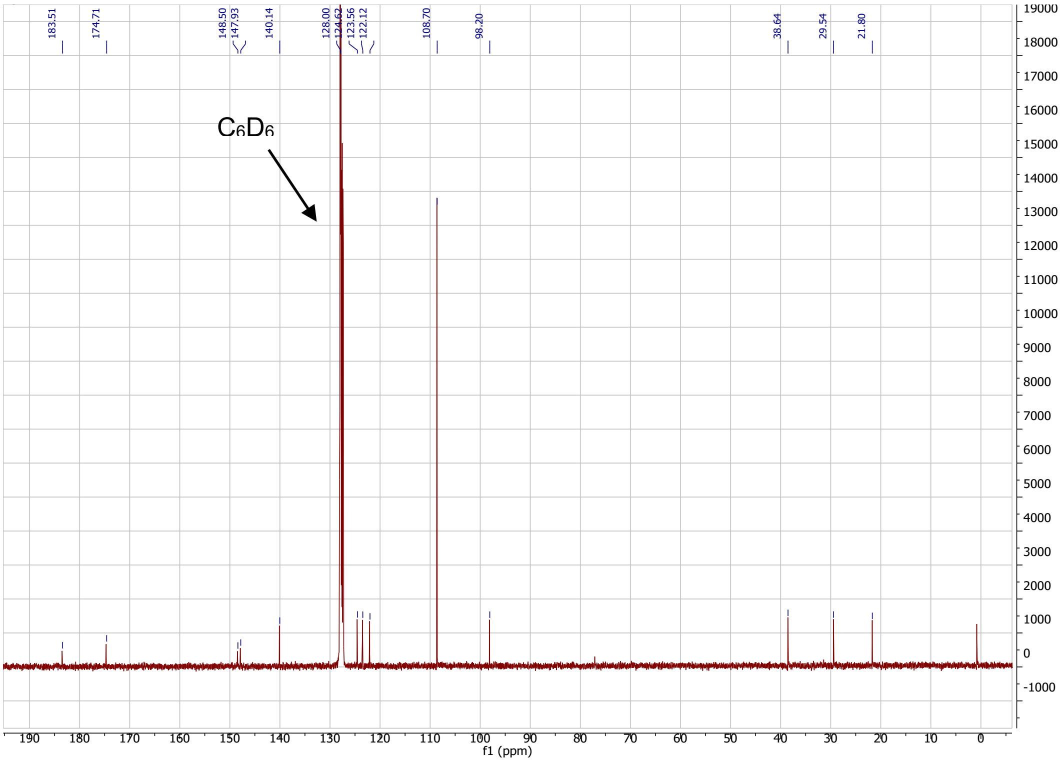
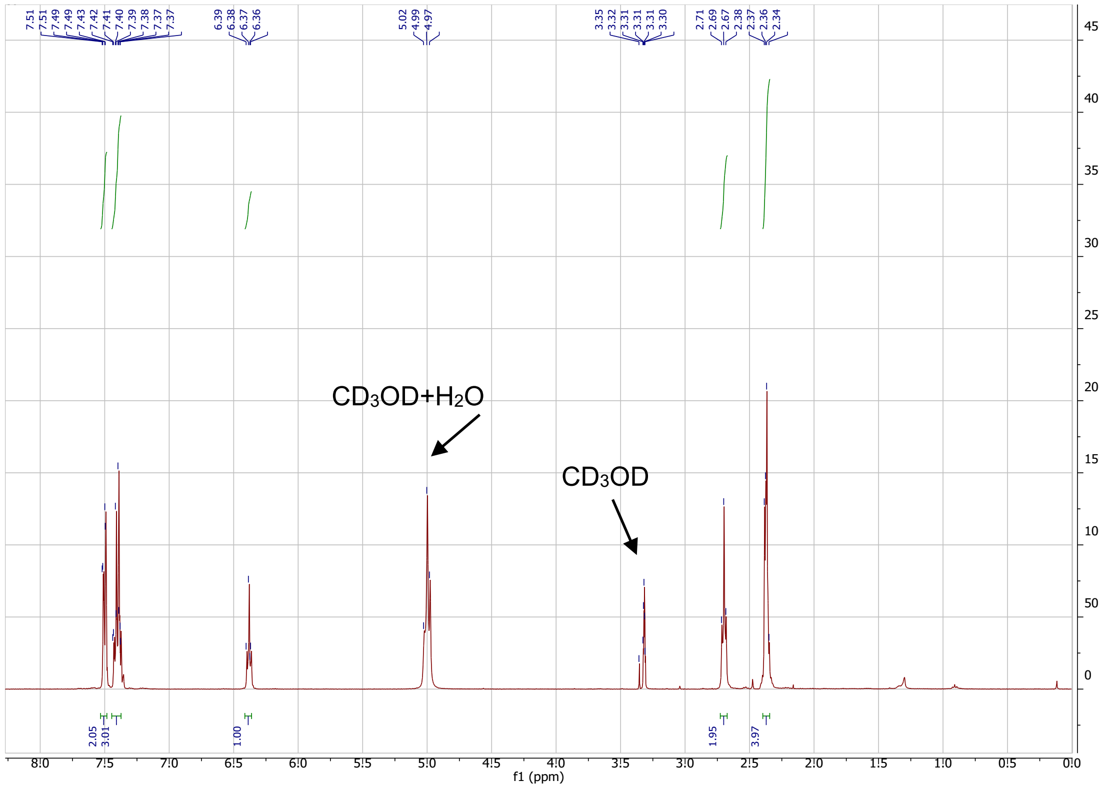
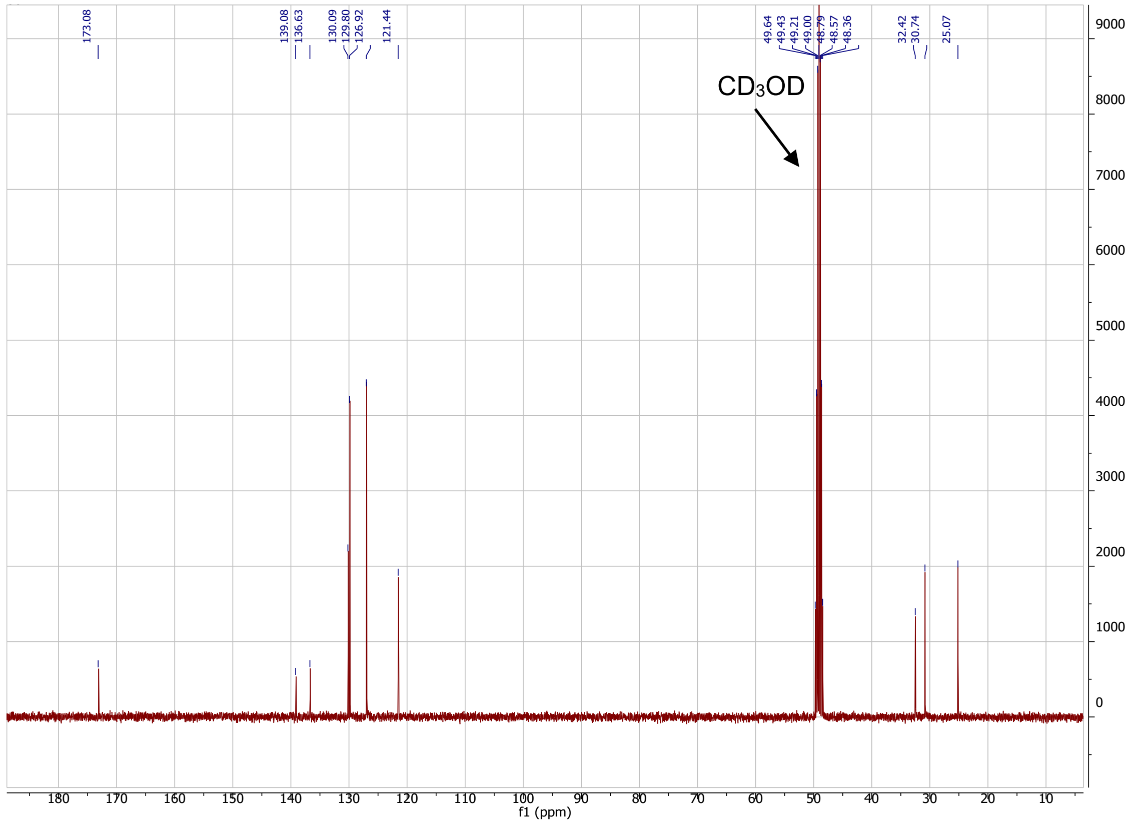


Figure S2. ^{1}H and ^{13}C NMR spectra of **8** in CD_3OD.

a. ^{1}H NMR



b. ^{13}C NMR



References:

S1 T. V. Talalaeva, K. A. Kocheshkov, *Metody elementoorganicheskoi khimii. Litii, natrii, kalii, rubidii, tsezii* (*Methods of Organoelement Chemistry. Lithium, Sodium, Potassium, Rubidium, Cesium*), Nauka, Moscow, 1971 (in Russian).

S2 K. C. Jantunen, B. L. Scott and J. L. Kiplinger, *J. Alloys Compd.*, 2007, **444-445**, 363.

S3 *SADABS, Version 2016/5*, Bruker AXS, Madison, WI, USA.

S4 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

S5 G. Sheldrick, *Acta Cryst. Sect. C*, 2015, **C71**, 3.

S6 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.,* 2009, **42**, 339.