Cleavage of a Dibenzotetraazafulvalene to Yield a Rh(I) Carbene Complex

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The reaction of the dibenzotetraazafulvalene $C_6H_4(NC_2H_5)_2C{=}C(NC_2H_5)_2C_6H_4$, $\mathbf{1} = \mathbf{1}$, with $[(COD)Rh(\mu\text{-}Cl)_2Rh(COD)]$ proceeds *via* cleavage of the C=C double bond and yields the carbene complex [(COD)RhCl(**1**)], **2**. The X-ray structure analysis shows **2** to be a mononuclear complex with a rhodium(I) center coordinated in a slightly distorted square-planar fashion.

Key words: Carbene Ligand, Rhodium(I), Crystal Structure

Introduction

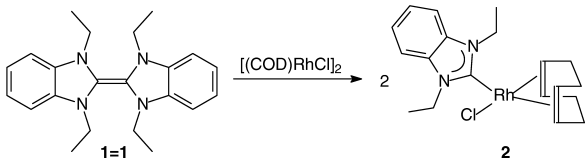
A large number of carbene complexes has been reported since the first synthesis of a complex with a heteroatom stabilized carbene ligand by Fischer in 1964 [1]. Various methods exist for the introduction of carbene ligands into transition metal complexes [2]. The development of stable free carbenes [3] brought about a resurgence of carbene coordination chemistry [4]. Carbene complexes with N,N'-dialkylbenzimidazol-2-ylidene ligands can be synthesized by the reaction of free stable benzannulated carbenes with transition metal complexes [5], by *in situ* deprotonation of N,N'-dialkylbenzimidazolium salts with metal complexes, containing basic ligands [6] or by insertion of a transition metal complex into the C=C double bond of a dibenzotetraazafulvalene [7]. The last method is particularly useful for the generation of carbene complexes under mild conditions as no deprotonation is required. Here we describe the preparation of the carbene complex [(COD)RhCl(**1**)] **2** (**1** = N,N'-diethylbenzimidazol-2-ylidene) by cleavage of the dibenzotetraazafulvalene $\mathbf{1} = \mathbf{1}$ with $[(COD)Rh(\mu\text{-}Cl)_2Rh(COD)]$.

Experimental Section

All manipulations were performed in an atmosphere of dry argon by standard Schlenk techniques. Solvents were dried by standard methods und freshly distilled prior to use. The dibenzotetraazafulvalene **1** was prepared according to a published procedure [5].

*(N,N'–Diethylbenzimidazol–2–ylidene–(1,5–cyclooctadiene)-rhodium) chloride **2**:* A solution of $\mathbf{1} = \mathbf{1}$ (190 mg, 0.55 mmol) in THF (20 ml) was treated with $[(COD)RhCl]_2$ (280 mg, 0.57 mmol) at room temperature. The reaction mixture was stirred for 17 h and then the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (4 ml) and purified by flash column chromatography (hexane/dichloromethane, 3:1, v:v). Yellow crystals of $\mathbf{2}\cdot 1/2CH_2Cl_2$, suitable for an X-ray diffraction analysis, were obtained from a concentrated dichloromethane solution. Yield: 370 mg (0.88 mmol, 81%) of solvent-free **2**. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): $\delta = 7.32 - 7.21$ (m, 4 H, Ar-H), 5.11 (m, 2 H, $CH_2CH{=}CHCH_2$), 5.05 (m, 2 H, $CH_2CH{=}CHCH_2$), 4.79 (m, 2 H, $CH_2CH{=}CHCH_2$), 3.38 (m, 2 H, $CH_2CH{=}CHCH_2$), 2.46 (q, 4 H, NCH_2), 1.99 (m, 4 H, $CH_2CH{=}CHCH_2$), 1.63 (t, 6 H, CH_3). – ^{13}C NMR (50.3 MHz, $[D_6]$DMSO, ppm): $\delta = 195.0$ (^1J(Rh-C) = 50.2 Hz, N-C-N), 134.3 0 (^1J(Rh-C) = 1.3 Hz, *i*Ar-C), 122.0 (Ar-C), 109.8 (Ar-C), 99.7 (^1J(Rh-C) = 6.1 Hz, $CH_2CH = CHCH_2$), 68.5 (^1J(Rh-C) = 14.4 Hz, $CH_2CH = CHCH_2$), 43.4 (N-CH_2), 32.7 ($CH_2CH = CHCH_2$), 28.7 ($CH_2CH = CHCH_2$), 14.8 (CH_3). – EI-MS: $m/z(\%) = 420$ (74.3) $[M^+]$, 384 (8.5) $[M - Cl]^+$, 276 (10.2) $[M - Cl - C_8H_{12}]^+$, 175 (100) $[\mathbf{1} + H]^+$.

X-ray structure determination: Formula $\mathbf{2}\cdot 1/2CH_2Cl_2$, $C_{19.5}H_{27}N_2Cl_2Rh$, $M = 463.2$, yellow crystal $0.60 \times 0.35 \times 0.35$ mm^3, $a = 15.683(2)$, $b = 15.339(2)$, $c = 16.475(4)$ Å, $\beta = 94.65(1)^\circ$, $V = 3963.3(12)$ Å^3, $\rho_{calcd} = 1.553$ g cm^{-3}, $\mu = 11.36$ cm^{-1}, empirical absorption correction *via* ψ scan data $(0.549 \leq T \leq 0.692)$, $Z = 8$, orthorhombic, space group *Pbca* (No. 61), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4017 reflections collected $(+h, +k, +l)$, $[(\sin\theta)/\lambda] =$



Scheme 1. Preparation of complex [Rh(COD)Cl(**1**)], **2** from **1** = **1**.

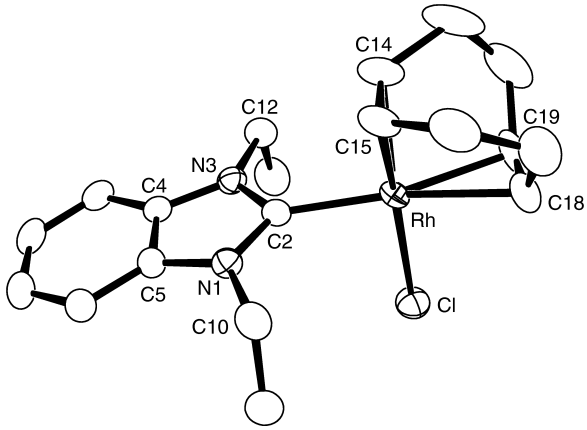


Fig. 1. Molecular structure of complex **2**. Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°]: Rh-Cl 2.3673(11), Rh-C2 2.018(4), Rh-C14 2.119(4), Rh-C15 2.100(4), Rh-C18 2.228(4), Rh-C19 2.195(4), N1-C2 1.350(5), N1-C5 1.389(5), N1-C10 1.463(5), N3-C2 1.360(5), N3-C4 1.386(5), N3-C12 1.469(5), Cl-Rh-C2 88.19(11), Rh-C2-N1 127.4(3), Rh-C2-N3 126.8(3), N1-C2-N3 105.8(3).

0.62 $Å^{-1}$, 4017 independent and 2815 observed reflections $[I \geq 2\sigma(I)]$, 237 refined parameters, $R = 0.038$, $wR2 = 0.088$ (for 2815 observed intensities), max. residual electron density 0.79(−0.90) e $Å^{-3}$ close to the disordered CH_2Cl_2 molecule, hydrogen atoms on calculated positions and refined as riding atoms. The data set was collected with a Nonius MACH3 diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection EXPRES [8], data reduction MolEN [9], structure solution SHELXS-97 [10], structure refinement SHELXL-97 [11], graphics ORTEP [12]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 233003. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

The reaction of $[(COD)RhCl]_2$ with one equivalent of the dibenzotetraazafulvalene **1** = **1** causes cleavage of the C=C double bond in **1** = **1** and yields complex **2** with one carbene ligand as a yellow solid (Scheme 1). Complex **2** is stable in air. Substitution of the chloro ligand was not observed. This is in contrast to the behaviour described for imidazol-2-ylidenes, where an excess of carbene ligand leads to the formation of the insoluble complex $[(COD)Rh(carbene)_2]$ [13]. The chemical shift of the carbene carbon atoms in **2** (δ = 195.0 ppm) correlates well with the value observed for the analogous complex with the N,N'-dimethyl substituted benzimidazol-2-ylidene ligand (δ = 195.9 ppm) [14]. It is, however, shifted to lower field when compared to those of the complexes with imidazol-2-ylidene ligands (δ = 180.1 ppm) [15]. Compared to complexes with imidazolin-2-ylidene ligands (δ = 212.8 and 212.3 ppm) [16] the carbene carbon resonance in **2** is shifted to higher field.

The molecular structure of **2** is depicted in Fig. 1. The rhodium atom is coordinated in a slightly distorted square-planar fashion by the midpoints of the COD C=C bonds, one chloro ligand and the carbene ligand. The bond distance Rh-$C_{carbene}$ in **2** falls in the range observed for similar complexes with imidazol-2-ylidene [15] and imidazolin-2-ylidene ligands [16]. There are different bond lengths found for the C=C bonds of the cyclooctadiene ligand. The double bond *trans* to the carbene ligand (C18-C19 1.354(6) Å) is shorter than the C=C bond *trans* to the chloro ligand (C14-C15 1.389(6) Å). The carbene plane is oriented almost perpendicular (dihedral angle 92.9°) to the square-planar rhodium coordination plane.

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