Synthesis of a Benzothiazol-2-ylidene Complex of Tungsten(0) and Transfer of the Ylidene Ligand to Rhodium(I)

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

2-Lithiobenzothiazole reacts with freshly generated [W(CO)5(THF)] to give the anionic ylidene complex (1). Treatment of 1 with allyl bromide yields complex [W(CO)5(1-allylbenzothiazolin-2-ylidene)] (2) while the reaction in wet CH2Cl2 leads to the formation of a mixture of 2 (major) and [W(CO)5(1-H-benzothiazolin-2-ylidene)] (3) (minor). Complex 2 reacts in a transmetallation reaction with [Rh(coe)(µ-Cl)]2 (coe = cyclooctone) to give the dicarbene complex [Rh(Cl)(η1-NHC)(η2-NHC)] (NHC = 1-allylbenzothiazolin-2-ylidene) with one carbene ligand coordinated via the C2 carbon atom and the other one coordinating with both the C2 carbon atom and the allyl group.

Key words: Benzothiazole, Benzothiazolin-2-yldiene, Tungsten, Rhodium, Crystal Structure

Introduction

Complexes with benzimidazolin-2-ylidene ligands can be prepared from the free carbene ligand [1], from dibenzotetraazafulvalenes and coordinatively unsaturated transition metal complexes [2] or by reaction of benzimidazolium salts with complexes containing basic ligands like [Ir(cod)(µ-OR)]2 [3a] or [Pd(OAc)2] [3b, 3c]. The latter method was employed successfully even for N-allyl substituted benzimidazolium salts which otherwise upon deprotonation in the absence of transition metals tend to dimerize followed by sigmatropic rearrangement and radical degradation reactions [4]. N-Methyl benzothiazolium salts react with [Pd(OAc)2] under deprotonation of the C2 carbon atom of the cation and formation of a trans dicarbene complex [5]. The cleavage of bis(N-methylbenzothiazolinylidene) by transition metal complexes has also been reported [6]. N-Allyl substituted benzothiazolium salts, however, behave differently. In situ deprotonation of N-allylbenzothiazolinium bromide with [Ir(cod)(µ-OME)]2 does not yield the expected benzothiazolin-2-ylidene complex. Instead the immediately formed benzothiazolin-2-ylidene dimerizes before complex formation occurs, and the dimer rearranges under N-allyl cleavage to give benzothiazole [7] which is found coordinating with the nitrogen atom to the iridium center [8].

Owing to this rapid degradation and in contrast to the preparation of complexes with N-allyl benzimidazolin-2-ylidene ligands, the preparation of complexes with the N-allyl benzothiazolin-2-ylidene ligand is not possible by in situ deprotonation of the azolium salt. Raubenheimer and coworkers have reported an alternative route for the preparation of benzothiazolin-2-ylidene complexes. Deprotonation of the C2 carbon of benzoazole with n-BuLi leads under ring opening to the phenyl isocyanide derivative [9], while benzothiazole gives under these conditions 2-lithiobenzothiazole [10] which can be transmetallated by various transition metal reagents. Subsequent N-alkylation yields complexes with N-alkyl benzothiazolin-2-ylidenes. We have adapted this procedure to the preparation of complexes with N-allyl substituted benzothiazolin-2-ylidene.

We report here on the reaction of 2-lithiobenzothiazole with [W(CO)5(THF)] followed by N-allylation with allyl bromide to give the tungsten(0) complex with the N-allyl benzothiazolin-2-ylidene ligand and on the transfer of this ligand to RhI.
Experimental Section

Chemicals and solvents were purchased from Aldrich, Acros and Merck. THF was distilled prior to use from sodium/benzophenone under argon. NMR spectra were recorded on Bruker AC 200 or Varian Unity Plus 600 NMR spectrometers, IR spectra on a Bruker Vector 22 FT spectrometer with KBr pellets. MALDI and EI mass spectra were obtained on Bruker Reflex IV or Varian MAT 212 spectrometers, respectively. Elemental analyses were obtained with a Vario EL III CHNS Elemental Analyzer at the Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster.

Pentacarbonyl[1-(2-propenyl)benzothiazolin-2-ylidene]-tungsten(0) (2)

A solution of benzothiazole (0.77 g, 0.62 ml, 5.7 mmol) in THF (30 ml) was cooled to −78 °C and n-BuLi (3.0 ml of a 2.0 M solution in cyclohexane, 6.0 mmol) was added. The reaction mixture was stirred for 2 h at −78 °C and was then added dropwise with a syringe to a freshly prepared solution of [W(CO)5(THF)] obtained by irradiation of [W(CO)6] (2.0 g, 5.7 mmol) in THF (112 ml) for 6 h in a photoreactor (high-pressure mercury vapour lamp). An orange solution was obtained which was stirred at ambient temperature over night under exclusion of light. The generated complex I was not isolated. Subsequently, the reaction mixture was cooled to 0 °C and allyl bromide (0.5 ml, 0.70 g, 0.58 mmol) was added. The reaction mixture was stirred for another 5 h at ambient temperature. The solvent was removed in vacuo and the resulting brown oil was purified by column chromatography (neutral Al2O3, 4% H2O) with ethyl acetate/hexane 1:12 as eluent. Recrystallization of the yellow residue from CH2Cl2 at −15 °C gave complex 2 (1.757 g, 62%) as yellow, light sensitive crystals. – 1H NMR (200.1 MHz, THF-d8): δ = 7.88 (d, 1 H, Ar-Hmeta), 7.76 (d, 1 H, Ar-Hmeta), 7.47 (m, 2 H, Ar-Hortho), 6.09 (m, 1 H, CH2=CH-CH2), 5.48 (d, 2 H, N-CH2), 5.29 (d, 1 H, JHH = 10.8 Hz, CH2-CH=CH2), 5.02 (d, 1 H, JHH = 17.0 Hz, CH2=CH(CH2)trans), – 13C{1H} NMR (50.3 MHz, THF-d8): δ = 217.9 (NCS), 202.2 (COtrans), 198.0 (COcis), 144.9, 137.8 (Ar-Cpno), 132.5 (N-CH2-CH2), 127.7, 126.2 (Ar-Cmeta), 121.9 (Ar-Cortho), 118.5 (N-CH2=CH2), 116.1 (Ar-Cortho), 57.4 (NCH2), – MS (EI, 70 eV): m/z (%) = 495 (45.1) [M]+, 471 (13.9) [M-CO]+, 443 (50.9) [M-2CO]+, 415 (100) [M-3CO]+, 387 (76.5) [M-4CO]+, 359 (76.1) [M-5CO]+. – C13H8NO3SW (499.15) calcld: C 36.09, H 1.82, S 2.81, O 6.42; found C 35.94, H 1.69, N 2.71, S 5.99.

Pentacarbonyl[3-H-benzothiazolin-2-ylidene]tungsten(0) (3)

Compound 1 was isolated in one instance and redissolved in wet CH2Cl2. Treatment of this solution with allyl bromide afforded a low yield of 2 (40%) and a small amount (23%) of pentacarbonyl[3-H-benzimidazolin-2-ylidene]tungsten(0) 3. Apparently, complex 3 was formed from water and HCl present in the unpurified dichloromethane. – 1H NMR (200.1 MHz, THF-d8): δ = 13.38 (s, br, 1 H, NH), 7.86 (d, 1 H, Ar-Hmeta), 7.71 (d, 1 H, Ar-Hmeta), 7.51 – 7.35 (m, 2 H, Ar-Hortho), – 13C{1H} NMR (50.3 MHz, THF-d8): δ = 215.1 (NCS), 202.7 (COtrans), 198.3 (COcis), 146.1, 137.3 (Ar-Cipso), 127.8, 125.8 (Ar-Cmeta), 121.9, 114.6 (Ar-Cortho). – IR (KBr, cm−1): ν = 3394 (s, NH), 2063, 1950, 1909, 1882 (vs, CO). – MS (EI, 70 eV): m/z (%) = 459 (62) [M]+. – C12H8NO3SW (459.08): calcld. C 31.40, H 1.10, N 3.05, S 6.98; found C 31.34, H 1.22, N 3.30, S 7.09.

{3-(2-Propenyl)benzothiazolin-2-ylidene}-η7-{3-(2-propenyl)benzothiazolin-2-ylidene} chloride rhodium(I) (4)

A mixture of 2 (99.8 mg, 0.2 mmol) and [Rh(coe)2(µ-Cl)]2 (35.9 mg, 0.05 mmol) was stirred in CH2Cl2 (20 ml) at ambient temperature for 20 h. During the reaction time a black precipitate of elemental tungsten was formed. The reaction mixture was filtered over silica and the resulting yellow solution was concentrated to give complex 3 as a yellow powder (27.4 mg, 56%). – 1H NMR (600 MHz, THF-d8), primed groups represent the ylide ligand with an uncoordinated allyl group, see also Fig. 1): δ = 7.76 (d, 1 H, Ar-HSortho), 7.73 (d, 1 H, Ar-Hsortho), 7.59 (d, 1 H, Ar-HNortho), 7.51 – 7.46 (m, 3 H, Ar-HNmeta, Ar-HNmeta-trans), 7.45 – 7.42 (m, 1 H, Ar-Hsmeta), 7.40 – 7.37 (m, 1 H, Ar-Hsmeta), 6.09 – 6.03 (m, 1 H, N-CH2-CH=CH2), 5.41 – 5.39 (m, 2 H, N-CH'2), 5.35 (dd, 1 H, JHH = 10.8 Hz, N-CH2-CH(CH2)trans), 5.06 (dd, 1 JHH = 16.8 Hz, N-CH2-CH(CH2)trans), 4.98 – 4.93 (m, 1 H, N-CH2-CH=CH2), 4.90 (dd, 1 H, NCH2), 4.70 (dd, 1 H, NCH2), 3.55 (dd, 1 H, JHH = 9.0 Hz, N-CH2-CH(CH2)trans), 3.37 (dd, 1 JHH = 12.6 Hz, N-CH2-CH(CH2)trans), – 13C{1H} NMR (150.8 MHz, THF-d8), primed groups represent the ylide ligand with an uncoordinated allyl group): δ = 224.3 (NCS), 218.1 (NCS), 143.9 (Ar-Cipso), 143.4 (Ar-Cipso), 136.6 (Ar-Cipso), 131.0 (N-CH2-C=CH2), 127.0 (Ar-Cmeta), 126.9 (Ar-Cmeta), 125.3 (Ar-Cmeta), 124.9 (Ar-Cmeta), 121.9 (Ar-Cortho), 118.6 (N-CH2-CH=CH2), 114.9 (Ar-Cortho), 113.6 (Ar-Cortho), 71.1 (N-CH2-CH=CH2), 57.8 (N-CH2-CH=CH2), 56.9 (N-CH2), 54.0 (N-C3), – MALDI MS (DCTB matrix): m/z (%) = 453 (100) [M-Cl]+.

X-ray structure determination

A crystal of 2 was mounted on a Bruker AXS 2000 CCD diffractometer equipped with a rotating molybdenum anode (λ = 0.71073 Å) and a CCD area detector. Diffraction data were measured at 153(2) K in the range 4.1 ≤ 2θ ≤ 60.0°. Structure solution [11] and
refinement [12] were achieved with standard Patterson and Fourier techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure models in calculated positions. Formula C_{15}H_{9}NO_{5}SW, M = 499.15, yellow crystal, 0.24 × 0.13 × 0.10 mm, \( a = 8.8706(12), b = 9.5852(13), \ c = 9.8660(13) \text{ Å}, \alpha = 92.129(3), \beta = 90.410(3), \gamma = 99.004(3) \text{°}, \ V = 827.9(2) \text{ Å}^3, \rho_{\text{calc}} = 2.002 \text{ g cm}^{-3}, \mu = 7.125 \text{ mm}^{-1}, \) empirical absorption correction (0.2797 ≤ \( T \leq 0.5360), Z = 2, \) triclinic, space group \( P\bar{1}, \) 9689 intensities collected (±h, ±k, ±l), 4774 independent (\( R_{\text{int}} = 0.027) \) and 4452 observed intensities \[ I \geq 2\sigma(I)\], 208 refined parameters, residuals for all data \( R = 0.0260, wR^2 = 0.0513, \) max. residual electron density 1.458 (−1.489) e Å\(^{-3}\).

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-299060. 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)3 36-033, e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

Benzothiazole was deprotonated with \( n\)-BuLi in THF and added to a freshly prepared solution of [W(CO)\(_5\)](THF) to give complex 1 (Scheme 1). Complex 1 was normally not isolated but was treated with an equimolar amount of allyl bromide to give complex 2 in good yield (62%). The formation of the carbene

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Scheme 1. Preparation of complexes 1–3.

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Fig. 1. Molecular structure of complex 2. Hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: W-C1 2.231(3), W-C11 2.055(3), W-C12 2.036(3), W-C13 2.006(3), W-C14 2.031(3), C-W-C15 2.059(3), S-C1 1.727(3), S-C3 1.734(3), N-C1 1.342(4), N-C2 1.408(3), N-C8 1.465(3), C2-C3 1.388(4), C8-C9 1.492(4), C9-C10 1.311(5); C1-S-C3 93.93(14), C1-N-C2 117.0(2), C1-N-C8 123.0(2), C2-N-C8 120.0(2), W-C1-S 118.16(14), W-C1-N 133.6(2), N-C1-S 108.3(2).
complex 2 was confirmed by the appearance of a resonance at $\delta = 217.9$ ppm in the $^{13}$C NMR spectrum, which was assigned to the NCS carbon atom. In one instance complex 1 was isolated before N-allylation. To achieve the allylation, complex 1 was redissolved in wet dichloromethane and treated with allyl bromide. Under these condition complex 3 (23%) containing the N-protonated carbene ligand (Scheme 1) was obtained together with complex 2 (40%). The $^{13}$C NMR chemical shift for the NCS carbon atom in 3 ($\delta = 215.1$ ppm) differs only slightly from the value for the corresponding resonance in 2.

Crystals of 2 suitable for an X-ray diffraction study were obtained by recrystallization from dichloromethane at $-15^\circ$C. The structure analysis has confirmed the proposed composition and connectivity pattern in 2 (Fig. 1). The tungsten atom in 2 is surrounded by five carbonyl ligands and the carbon atom of the N-allylbenzothiazolin-2-ylidene in a slightly distorted octahedral fashion. The W-C1 separation (2.231(3) Å) falls in the range observed for complexes with the N,N’-diallyl-benzimidazolin-2-ylidene (2.256 Å [13] and 2.242(3) [14]). The same holds for the W-CO$_{cis}$ and W-CO$_{trans}$ bond distances which demonstrates, that the benzothiazolin-2-ylidene exhibits $\sigma$-donor properties which are comparable to N,N’-dialkylated benzimidazolin-2-ylidenes. The major difference between benzimidazolin-2-ylidene and benzothiazolin-2-ylidine ligands is the distortion of the geometry of the heterocycle of the latter owing to the long S-C bonds. This and the lack of a third substituent at the sulphur atom lead to a small W-C1-S (118.16(14)$^\circ$) and a large W-C1-N (133.6(2)$^\circ$) angle in 2 while these angles are of similar size in the [W(CO)$_5$] complex with the N,N’-diallylbenzimidazolin-2-ylidene (127.1(2)$^\circ$ and 128.8(2)$^\circ$ [13]). In addition, a large N-C1-S angle (108.3(2)$^\circ$) was observed for 2 while the corresponding N-C-N angle in the [W(CO)$_5$] complex with the N,N’-diallylbenzimidazolin-2-ylidene measures only 104.0(2)$^\circ$ [13].

The transmetallation of carbene ligands from silver complexes to other metals is a standard procedure for the generation of transition metal carbene complexes [15]. Few examples for such transmetallation reactions are known to start from carbene complexes of other metals, although some examples have been described [16]. We have tested the carbene complex 2 in the transmetallation reaction with [Rh(coe)$_2$(µ-Cl)]$_2$ (coe = cyclooctene). Stirring of a stoichiometric
mixture of 2 and [Rh(coe)(μ-Cl)]2 in dichloromethane at ambient temperature for 20 h yields the rhodium dicarbene complex 4 (Scheme 2) in moderate (56%) yield.

Carbene complex 4 was unambiguously identified by NMR spectroscopy. The 13C NMR spectrum exhibits two carbene NCS signals at δ = 224.3 and 218.1 ppm assigned to the different η1- and η2-coordinated benzimidazolin-2-ylidene ligands. The 1H NMR spectrum is even more informative. It shows well separated resonances for both the coordinated and the non-coordinated allyl group. As expected, the spectrum exhibits an upfield shift for all protons associated with the coordinated allyl group.

We have demonstrated, that N-allyl substituted benzothiazolin-2-ylidene ligands can be generated at W 0 from 2-lithiobenzothiazole and [W(CO)5(THF)] followed by N-alkylation with allyl bromide. The tungsten complex 2 obtained in this way serves as a transmetallation agent. The RhI complex 4 obtained by transmetallation contains two ligands coordinated in the η1- and η2-modes.

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