

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 $[\text{W}(\text{CO})_5(\text{THF})]$ to give the anionic ylidene complex (**1**). Treatment of **1** with allyl bromide yields complex $[\text{W}(\text{CO})_5(1\text{-allylbenzothiazolin-2-ylidene})]$ (**2**) while the reaction in wet CH_2Cl_2 leads to the formation of a mixture of **2** (major) and $[\text{W}(\text{CO})_5(1\text{-H-benzothiazolin-2-ylidene})]$ (**3**) (minor). Complex **2** reacts in a transmetallation reaction with $[\text{Rh}(\text{coe})_2(\mu\text{-Cl})]_2$ (coe = cyclooctene) to give the dicarbene complex $[\text{Rh}(\text{Cl})(\eta^1\text{-NHC})(\eta^2\text{-NHC})]$ (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-ylidene, 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 $[\text{Ir}(\text{cod})(\mu\text{-OR})]_2$ [3a] or $[\text{Pd}(\text{OAc})_2]$ [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 $[\text{Pd}(\text{OAc})_2]$ under deprotonation of the C2 carbon atom of the cation and formation of a *trans* dicarbene complex [5]. The cleavage of bis(*N*-methylbenzothiazolinyldene) by transition metal complexes has also been reported [6]. N-Allyl substituted benzothiazolium salts, however, behave differently. *In situ* deprotonation of N-allylbenzothiazolium bromide with $[\text{Ir}(\text{cod})(\mu\text{-OMe})]_2$ does not yield the expected benzothiazolin-2-ylidene complex. Instead the immediately formed benzothiazolin-2-ylidene dimerizes before complex formation occurs, and the dimer rear-

ranges 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 benzoxazole 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-ylidenes.

We report here on the reaction of 2-lithiobenzothiazole with $[\text{W}(\text{CO})_5(\text{THF})]$ 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 Rh^{I} .

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, 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 $[\text{W}(\text{CO})_5(\text{THF})]$ obtained by irradiation of $[\text{W}(\text{CO})_6]$ (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 **1** was not isolated. Subsequently, the reaction mixture was cooled to 0°C and allyl bromide (0.5 ml, 0.70 g, 5.8 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 Al_2O_3 , 4% H_2O) with ethyl acetate/hexane 1 : 12 as eluent. Recrystallization of the yellow residue from CH_2Cl_2 at -15°C gave complex **2** (1.757 g, 62%) as yellow, light sensitive crystals. – ^1H NMR (200.1 MHz, $\text{THF}-d_8$): δ = 7.88 (d, 1 H, Ar- H_{meta}), 7.76 (d, 1 H, Ar- H_{meta}), 7.47 (m, 2 H, Ar- H_{ortho}), 6.09 (m, 1 H, $\text{CH}_2\text{-CH=CH}_2$), 5.48 (d, 2 H, N- CH_2), 5.29 (d, 1 H, $^3J_{\text{HH}}$ = 10.8 Hz, $\text{CH}_2\text{-CH=CHH}_{\text{cis}}$), 5.02 (d, 1 H, $^3J_{\text{HH}}$ = 17.0 Hz, $\text{CH}_2\text{-CH=CHH}_{\text{trans}}$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, $\text{THF}-d_8$): δ = 217.9 (NCS), 202.2 (CO_{trans}), 198.0 (CO_{cis}), 144.9, 137.8 (Ar- C_{ipso}), 132.5 (N- $\text{CH}_2\text{-CH}$), 127.7, 126.2 (Ar- C_{meta}), 121.9 (Ar- C_{ortho}), 118.5 (N- $\text{CH}_2\text{-CH=CH}_2$), 116.1 (Ar- C_{ortho}), 57.4 (NCH₂). – MS (EI, 70 eV): m/z (%) = 499 (45.1) $[\text{M}]^+$, 471 (13.9) $[\text{M}-\text{CO}]^+$, 443 (50.9) $[\text{M}-2\text{CO}]^+$, 415 (100) $[\text{M}-3\text{CO}]^+$, 387 (76.5) $[\text{M}-4\text{CO}]^+$, 359 (76.1) $[\text{M}-5\text{CO}]^+$. – $\text{C}_{15}\text{H}_9\text{NO}_5\text{SW}$ (499.15): calcd. C 36.09, H 1.82, N 2.81, S 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 CH_2Cl_2 . Treatment of this solution with al-

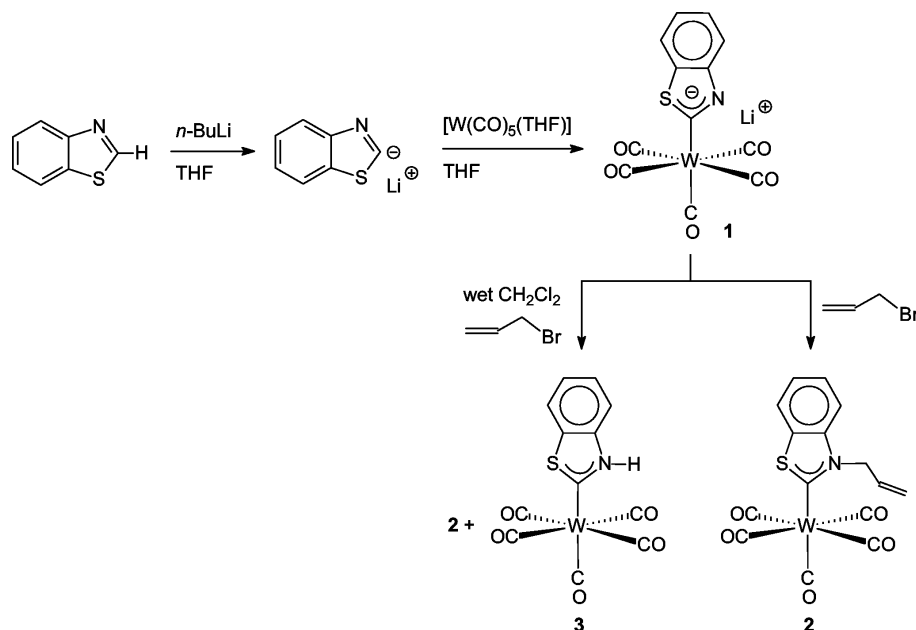
lyl bromide afforded a low yield of **2** (40%) and a small amount (23%) of pentacarbonyl(3-*H*-benzimidazolin-2-ylidene) tungsten(0) **3**. Apparently, complex **3** was formed from water and HCl present in the unpurified dichloromethane. – ^1H NMR (200.1 MHz, $\text{THF}-d_8$): δ = 13.38 (s, br, 1 H, NH), 7.86 (d, 1 H, Ar- H_{meta}), 7.71 (d, 1 H, Ar- H_{meta}), 7.51–7.35 (m, 2 H, Ar- H_{ortho}). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, $\text{THF}-d_8$): δ = 215.1 (NCS), 202.7 (CO_{trans}), 198.3 (CO_{cis}), 146.1, 137.3 (Ar- C_{ipso}), 127.8, 125.8 (Ar- C_{meta}), 121.9, 114.6 (Ar- C_{ortho}). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3394 (s, NH), 2063, 1950, 1909, 1882 (vs, CO). – MS (EI, 70 eV): m/z (%) = 459 (62) $[\text{M}]^+$. – $\text{C}_{12}\text{H}_5\text{NO}_5\text{SW}$ (459.08): calcd. 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]- η^2 -[3-(2-propenyl)benzothiazolin-2-ylidene] chloro rhodium(I) (**4**)

A mixture of **2** (99.8 mg, 0.2 mmol) and $[\text{Rh}(\text{coe})_2(\mu\text{-Cl})_2]$ (35.9 mg, 0.05 mmol) was stirred in CH_2Cl_2 (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, $\text{THF}-d_8$, primed groups represent the ylidene ligand with an uncoordinated allyl group, see also Fig. 1): δ = 7.76 (d, 1 H, Ar- $\text{H}'_{\text{S-ortho}}$), 7.73 (d, 1 H, Ar- $\text{H}_{\text{S-ortho}}$), 7.59 (d, 1 H, Ar- $\text{H}'_{\text{N-ortho}}$), 7.51–7.46 (m, 3 H, Ar- $\text{H}_{\text{N-ortho}}$, Ar- $\text{H}'_{\text{N-meta}}$, Ar- $\text{H}_{\text{N-meta}}$), 7.45–7.42 (m, 1 H, Ar- $\text{H}'_{\text{S-meta}}$), 7.40–7.37 (m, 1 H, Ar- $\text{H}_{\text{S-meta}}$), 6.09–6.03 (m, 1 H, N- $\text{CH}_2\text{-CH' = CH}_2$), 5.41–5.39 (m, 2 H, N- CH_2), 5.35 (dt, 1 H, $^3J_{\text{HH}}$ = 10.8 Hz, N- $\text{CH}_2\text{-CH=CHH'}_{\text{cis}}$), 5.06 (dt, $^3J_{\text{HH}}$ = 16.8 Hz, N- $\text{CH}_2\text{-CH=CHH'}_{\text{trans}}$), 4.98–4.93 (m, 1 H, N- $\text{CH}_2\text{-CH=CH}_2$), 4.90 (dd, 1 H, NCHH), 4.70 (dd, 1 H, NCHH), 3.55 (dd, 1 H, $^3J_{\text{HH}}$ = 9.0 Hz, N- $\text{CH}_2\text{-CH=CHH}_{\text{cis}}$), 3.37 (dd, $^3J_{\text{HH}}$ = 12.6 Hz, N- $\text{CH}_2\text{-CH=CHH}_{\text{trans}}$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (150.8 MHz, $\text{THF}-d_8$, primed groups represent the ylidene ligand with an uncoordinated allyl group): δ = 224.3 (NCS), 218.1 (NC'S), 143.9 (Ar- $\text{C}'_{\text{N-ipso}}$), 143.4 (Ar- $\text{C}_{\text{N-ipso}}$), 137.1 (Ar- $\text{C}'_{\text{S-ipso}}$), 136.6 (Ar- $\text{C}_{\text{S-ipso}}$), 131.0 (N- $\text{CH}_2\text{-C'H=CH}_2$), 127.0 (Ar- C'_{meta}), 126.9 (Ar- C_{meta}), 125.3 (Ar- C'_{ortho}), 124.9 (Ar- C_{ortho}), 121.9 (Ar- C'_{ortho}), 121.0 (Ar- C_{ortho}), 118.6 (N- $\text{CH}_2\text{-CH=C'H}_2$), 114.9 (Ar- C'_{ortho}), 113.6 (Ar- C_{ortho}), 71.1 (N- $\text{CH}_2\text{-CH=CH}_2$), 57.8 (N- $\text{CH}_2\text{-CH=CH}_2$), 56.9 (N- C'H_2), 54.0 (N- CH_2). – MALDI MS (DCTB matrix): m/z (%) = 453 (100) $[\text{M}-\text{Cl}]^+$.

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 $4.1 \leq 2\theta \leq 60.0^{\circ}$. Structure solution [11] and



Scheme 1. Preparation of complexes 1–3.

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 $C_{15}H_9NO_5SW$, $M = 499.15$, yellow crystal, $0.24 \times 0.13 \times 0.10$ mm, $a = 8.8706(12)$, $b = 9.5852(13)$, $c = 9.8660(13)$ Å, $\alpha = 92.129(3)$, $\beta = 90.410(3)$, $\gamma = 99.004(3)^\circ$, $V = 827.9(2)$ Å³, $\rho_{\text{calcd.}} = 2.002$ g cm⁻³, $\mu = 7.125$ mm⁻¹, empirical absorption correction ($0.2797 \leq T \leq 0.5360$), $Z = 2$, triclinic, space group $P\bar{1}$, 9689 intensities collected ($\pm h, \pm k, \pm l$), 4774 independent ($R_{\text{int}} = 0.027$) and 4452 observed intensities [$I \geq 2\sigma(I)$], 208 refined parameters, residuals for all data $R = 0.0260$, $wR2 = 0.0513$, 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

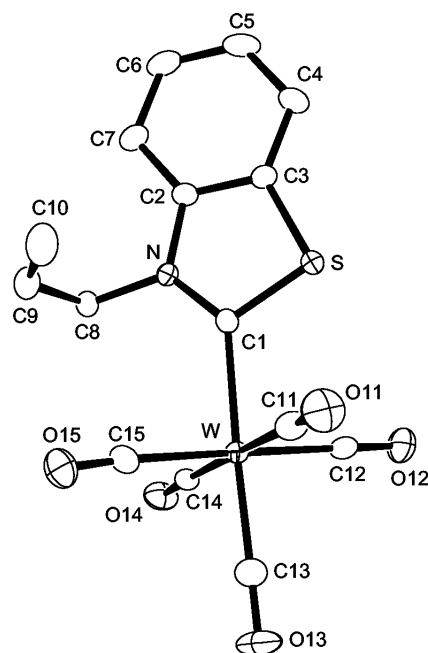
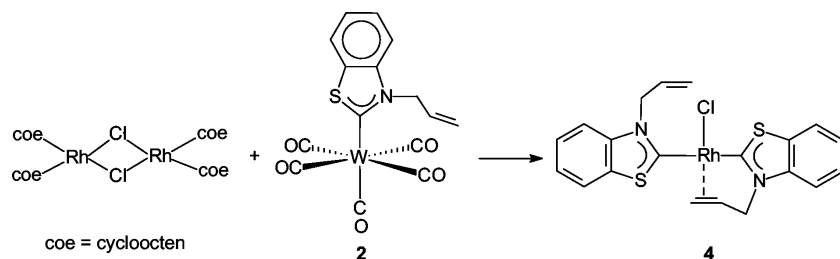


Fig. 1. Molecular structure of complex **2**. Hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: W–C1 2.231(3), W–C11 2.055(3), W–C12 2.036(3), W–C13 2.006(3), W–C14 2.031(3), W–C15 2.059(3), S–C1 1.727(3), S–C3 1.734(3), N–C1 1.342(4), N–C2 1.408(3), N–C8 1.465(3), C2–C3 1.388(4), 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).



Scheme 2. Transfer of the benzothiazolin-2-ylidene ligand from tungsten(0) to rhodium(I).

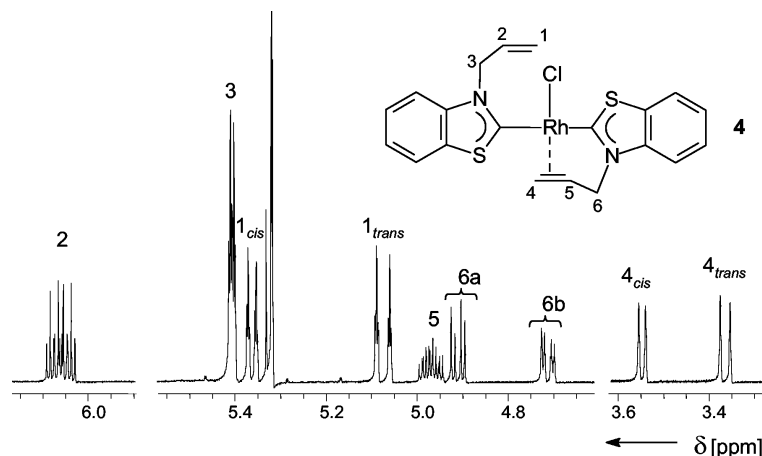


Fig. 2. ¹H NMR spectrum of complex 4 (aromatic protons have been omitted).

complex **2** was confirmed by the appearance of a resonance at $\delta = 217.9$ ppm in the ¹³C 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 conditions complex **3** (23%) containing the N-protonated carbene ligand (Scheme 1) was obtained together with complex **2** (40%). The ¹³C 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 °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'-diallylbenzimidazolin-2-ylidene ligand (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 σ -donor properties which are comparable to N,N'-dialkylated benzimidazolin-2-ylidenes. The major difference between benzimidazolin-2-ylidene and benzothiazolin-2-ylidene 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)°) and a large W-C1-N (133.6(2)°) 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)° and 128.8(2)° [13]). In addition, a large N-C1-S angle (108.3(2)°) was observed for **2** while the corresponding N-C-N angle in the [W(CO)₅] complex with the N,N'-diallylbenzimidazolin-2-ylidene ligand measures only 104.0(2)° [13].

The transmetalation 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 transmetalation 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 transmetalation reaction with [Rh(coe)₂(μ-Cl)₂] (coe = cyclooctene). Stirring of a stoichiometric

mixture of **2** and $[\text{Rh}(\text{coe})(\mu\text{-Cl})_2]$ 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 ^{13}C NMR spectrum exhibits two carbene NCS signals at $\delta = 224.3$ and 218.1 ppm assigned to the different η^1 - and η^2 -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 $[\text{W}(\text{CO})_5(\text{THF})]$ followed by N-alkylation with allyl bromide. The tungsten complex **2** obtained in this way serves as a transmetallation agent. The Rh^{I} complex **4** obtained by transmetallation contains two ligands coordinated in the η^1 - and η^2 -modes.

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