DOI: 10.1002/ejic.201000370

Facile Formation of a Rhenium Allenylcarbene Complex with an Internal Dithioalkyne

Wolfram W. Seidel,*[a] Matthias J. Meel,[b] David Schallenberg,[a] Tania Pape,[b] Alexander Villinger,[a] and Dirk Michalik[a]

Dedicated to Prof. Uwe Rosenthal on the occasion of his 60th birthday

Keywords: Rhenium / Alkynes / Carbene complexes / Cycloaddition

The η^2-alkyne complex $[(\eta^5\text{-}C_5H_5)Re(\mathbf{1})Br_2]$, **2**, (**1** = $BnSC_2SBn$) reacts with an excess of the dithioalkyne **1** to give the addition product $[(\eta^5\text{-}C_5H_5)ReBr_2\{\eta^3\text{-}(BnS)_2C_2C(SBn)\text{-}C(SBn)\}]$, **3**, displaying a ReC_3 ring with an exocyclic double bond. The molecular structures of the complexes **2** and **3** were determined by single-crystal X-ray diffraction. The nonplanarity of the ReC_3 ring and the largely equal C–C bond lengths within the ring reveal **3** to be a resonance hybrid of an allenylcarbene complex and a folded rhenacyclobutene system. DFT calculations show that complex type **3** is favorable over the isomeric η^4-cyclobutadiene complex **3a** with four thiobenzyl substituents, while the opposite holds true for the phenyl-substituted derivative. According to calculations on potential intermediates and transition states, the rate-determining step is the conversion of a bis(alkyne) into a mixed alkyne/vinylidene complex by 1,2-SBn shift, while the formation of **3** via the η^4-cyclobutadiene complex **3a** is improbable. Allenyl carbene complexes are of great interest as alkyne polymerization intermediates.

Introduction

Cyclooligomerization reactions promoted by transition-metal complexes are well established in the synthesis of ring systems containing alternate single and double bonds. Within this scheme metallacyclopentadienes generated by dimerization of alkynes at the metal are widely accepted central intermediates.[1] In many cases either these metallacyclopentadienes[2] or η^4-complexes of cyclobutadienes[3] are stable enough to be isolated. A third less frequent reaction path, combining two alkynes and a metal, results in so-called allenylcarbene complexes. Complexes of this type are discussed as potential intermediates in the polymerization of alkynes.[4] In fact, in recent years allenylcarbene complexes could be isolated with $[(C_5H_5)Ru(PR_3)]^+$ and $[Os(PR_3)_2Cl_2]$ fragments,[5] which also show alkyne oligomerization activity.[6] However, the straightforward formation of allenylcarbene complexes from alkynes has been confined so far to terminal alkynes, which is attributed to the alkyne vinylidene rearrangement in the complex as a prerequisite for a subsequent [2+2] cycloaddition step. In the course of our studies with sulfide-substituted alkynes[7] we observed a cyclodimerization reaction of two internal dithioalkynes at the $[(C_5H_5)ReBr_2]$ fragment leading to a folded ReC3 ring skeleton. This finding is surprising because investigations by Green et al. with the identical metal complex system but diphenylacetylene showed the formation of a stable η^4-cyclobutadiene complex.[8] This diverse behavior raises the question, whether the formation of allenylcarbene complexes is really limited to systems with alkyne vinylidene rearrangement. In this communication we try to address this problem by comparing our results with related systems.

Results and Discussion

Adapting a procedure described by Green,[9] the reaction of $[(\eta^5\text{-}C_5H_5)Re(CO)_2Br_2]$ with bis(benzylthio)acetylene (**1**) at elevated temperature leads to the formation of the η^2-alkyne complex $[(\eta^5\text{-}C_5H_5)Re(\mathbf{1})Br_2]$ (**2**) in good yield. The intense green, air-stable complex **2** was characterized by a ^{13}C NMR resonance at δ = 207.5 ppm, which is consistent with a side-on four-electron donor alkyne complex. In addition, the identity of **2** is proven by X-ray structure analysis (Figure 1). In general, the structure is similar to related Re^{III} alkyne complexes.[9,10] The C1–C2 vector lies parallel to one of the rhenium bromide bonds leading to signifi-

---

[a] Institut für Chemie, Universität Rostock,
Albert-Einstein-Straße 3a, 18059 Rostock, Germany
Fax: +49-381-4986382
E-mail: wolfram.seidel@uni-rostock.de
[b] Institut für Anorganische und Analytische Chemie,
Westfälische Wilhelms-Universität Münster,
Corrensstraße 30, 48149 Münster, Germany

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000370.

cantly different Re–Br distances [Re–Br1 2.575(1) Å, Re–Br2 2.507(1) Å], the shorter one pointing away from the ReC1C2 plane. Consequently, the alkyne is coordinated slightly unsymmetrically [Re–C1 1.930(6) Å, Re–C2 1.971(7) Å] with a noticeably long C1–C2 bond [1.354(2) Å] indicating conjugation with the sulfur lone pairs.

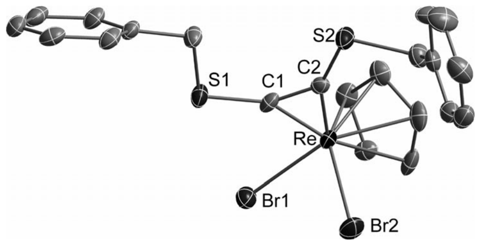


Figure 1. Molecular structure of **2** with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Re–C1 1.930(6), Re–C2 1.971(7), C1–C2 1.354(10), Re–Br1 2.575(1), Re–Br2 2.507(1), C1–C2–S2 138.1(6), C2–C1–S1 142.5(6).

Further reaction of complex **2** with an excess of alkyne **1** in refluxing toluene led to the formation of a new red compound **3**, which was isolated in analytically pure form by crystallization. Mass spectrometry indicated **3** to be an addition product of **1** and **2**, while the NMR spectroscopic data of **3** appeared hard to elucidate. Finally, X-ray diffraction analysis of **3** uncovered a C_1-symmetric complex displaying a ReC3 four-atom cycle with an exocyclic C–C double bond attached to it. The molecular structure of **3** is depicted in Figure 2 and selected interatomic distances are listed in Table 1.

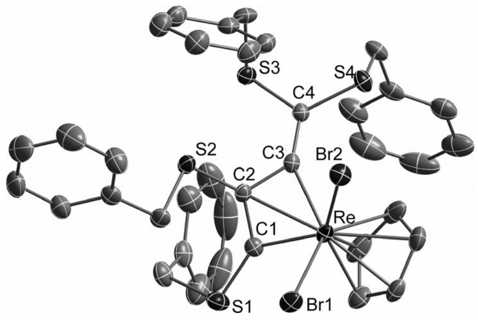


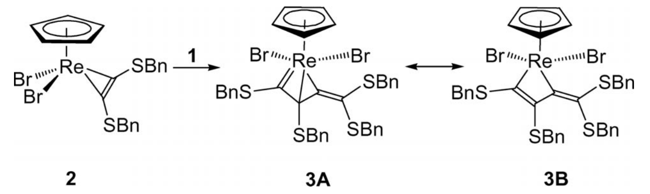
Figure 2. Molecular structure of complex **3** with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Re–Br1 2.5851(3), Re–Br2 2.5323(3), C1–Re–C3 68.6(1), Re–C1–C2 85.8(4), Re–C1–S1 135.8(1), C1–C2–S2 129.2(2), C3–C2–S2 122.1(2), C1–C2–C3 107.9(2), Re–C3–C4 146.3(2), C2–C3–C4 132.6(2), C3–C4–S3 118.1(2), C3–C4–S4 122.0(2).

Complex **3** could formally be considered as a [2+2] cycloaddition product of alkyne **1** with an intermediate vinylidene complex [(η^5-C_5H_5)Br_2Re=C=C(SBn)$_2$] (**2a**) formed by isomerization of **2** to **2a** via 1,2-shift of a benzylthio moiety. However, the two C–C bonds within the rhenacyclobutene ring exhibit very similar lengths (Table 1), typical for aromatic C–C bonds, and the ring is folded about the C1–C3 vector by 46.6°.[11] This feature allows a Re–C2 distance of 2.324 Å indicating an unambiguous bonding interaction. In addition, the Re–C1 distance of 1.980 Å falls in the range of Re carbene bonds,[12] while the Re–C3 bond of 2.101 Å is typical for internal Re–C bonds in η^2-allene complexes.[13] Accordingly, compound **3** is regarded as a η^3-allenyl carbene complex **3A** (Scheme 1). Related structures with Ru and Os exhibit similar metrical parameters,[5] while the strongest variation applies to the M–C2 bond {2.167 Å in [Os(PPh$_3$)$_2$Cl$_2$(PhCCHCCHPh)]}. The description of **3** as a η^3-allenylcarbene complex is corroborated by the ^{13}C NMR resonances of the rhenium-bound carbon atoms. The C1 atom at δ = 242.1 ppm is highly deshielded, which is typical for carbene complexes.[14] Similar structural motifs were found in corresponding vinyl carbene complexes.[15]

Table 1. Selected bond lengths of **3** determined by X-ray structure determination and corresponding calculated values.

[a]	Exp.	Calcd.[b]	Calcd.[c]
Re–C1	1.980	2.005	1.995
Re–C2	2.324	2.343	2.336
Re–C3	2.101	2.136	2.123
C1–C2	1.415	1.406	1.398
C2–C3	1.433	1.439	1.435
C3–C4	1.321	1.339	1.336
C1–S2	1.671	1.690	1.690
C2–S2	1.768	1.775	1.777

[a] Numbering scheme used for the X-ray structure determination. [b] Basis set 6-311G(d,p), ECP and 8s7p6d/[6s5p3d] for Re. [c] cc-pvtz, ECP and 37s33p22d2f1g/[5s5p4d2fg] for Re.



Scheme 1. Preparation and resonance structures of **3**.

However, a contribution of the rhenacyclobutene canonical form **3B** is evident by the short C1–C2 bond indicating resonance of the metal-bound allene moiety with the carbene center and by the long Re–C2 bond. In addition, the rigorous description of **3** as an allenyl carbene complex is problematic for geometric reasons, because the π-systems and hence the terminal substituent planes of an allene should form an angle of 90°.[16] The planes ReC2C3 (σ-donation of the allene π-orbital) and C1C2S2 (corresponding substituent plane) form an angle of 40.4° resulting from the direct C1–Re linkage allowing resonance of the allene and carbene π-system. Consequently, the rhenacyclobutene model **3B** involves a bent Re–C2 bond[12a] comprising an orbital of π-symmetry at C2. The angles between the planes ReS1C2, C1C3S2, and ReC2C4, respectively, implying the relative direction of the corresponding π-orbitals at C1, C2, and C3, amount to 39.9° and 39.8°. Obviously, compound **3** represents a compromise between bonding modes **3A** (major) and **3B** (minor), in which the coordination structure is stabilized by resonance. The ^{13}C NMR resonance of the central C2 atom serves as a spectroscopic indication for the significance of resonance form **3B**. While in Re η^2-allene complexes chemical shifts around 0 ppm are found for the metal-bound terminal C atom,[13] δ_C values between 120 and 160 ppm are typical for the C atom opposite the metal in rhenacyclobutenes.[11] The corresponding C atom in $[Os(PPh_3)_2Cl_2(PhCCHCCHPh)]$ was detected at δ = 36.1 ppm, while C2 in **3** resonates at δ = 86.8 ppm. This relatively low field shift and the longer metal–C2 bond indicate that the contribution of the metallacyclobutene form is larger in **3** compared with related Ru and Os complexes described by Kirchner, Jia and others[5].

This perception of the binding forces in **3** is corroborated by molecular orbital calculations using DFT methods. The optimized geometry of **3** is in reasonable agreement with the experimentally determined structure. The important metrical parameters of the central metallacycle are given in Table 1 together with the corresponding values derived from the X-ray structure determination. Important frontier orbitals are depicted in Figure 3. The HOMO–1 reveals major contributions from the exocyclic C–C π-bond and the Re–C π-bond at the C1 carbene center. The HOMO is mainly centered at Re and the bromide substituents. However, a bonding interaction between Re and C2 is evident by an overlap of a metal d-orbital with an orbital of π-symmetry at C2. The latter is characterized by an antibonding interaction with electron density at S2, which is mirrored by a conspicuously long C2–S2 distance. A NBO analysis resulted in occupations for the Re–C bonds of 1.74 (Re–C1), 1.40 (Re–C2), and 1.73 (Re–C3) reflecting substantial Re–C2 bonding interaction despite the comparatively long distance. The Re–C2 bond is composed of an orbital at C2 with 97.3% p-character and at Re with 79.4% d-character.

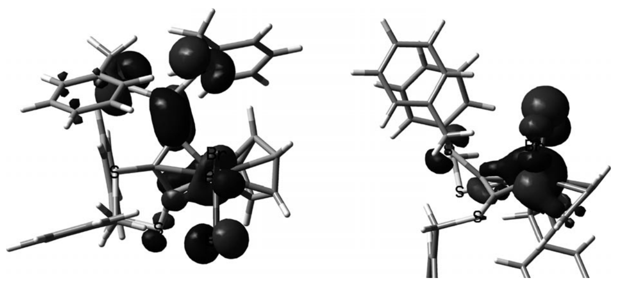


Figure 3. Frontier Kohn–Sham orbitals of **3**: HOMO–1 (left, top view on ReC3 cycle) and HOMO (right, side view on ReC3 cycle).

Interestingly, Green et al. observed the formation of the η^4-tetraphenylcyclobutadiene complex **4a** by addition of tolane to $[(\eta^5\text{-}C_5H_5)Re(\eta^2\text{-}PhC_2Ph)Br_2]$.[8] To determine the reasons for the different behavior of carbon-based and thioether-substituted alkynes we performed DFT calculations with **3** and the hypothetical phenyl derivative **4** and the respective η^4-cyclobutadiene complex isomers **3a** and **4a**. We found **3** to be more stable than **3a** by ΔH = 13.3 kcal/mol. In contrast, for the carbon-based alkyne the situation is the inverse, but the difference of ΔH = 4 kcal/mol between favorable **4a** and its isomer **4** is quite small. Thus, in both cases the crystallographically characterized isomers are the thermodynamically stable products. Therefore, kinetic reasons are unlikely for the different behavior in the addition reaction. The proven stability of the η^4-cyclobutadiene complex **4a** raises the question, whether the corresponding isomer **3a** with the dithioalkyne is a more likely intermediate on the reaction path than the vinylidene complex **2a**. To shed light on this problem we calculated the energy profile of possible reaction coordinates with a slightly reduced model bearing methyl instead of benzyl substituents at all sulfur atoms. The results are summarized in Figure 4.

The calculations clearly show that even the formation of the η^4-cyclobutadiene complex $\mathbf{3a^{Me}}$ from $\mathbf{1^{Me}}$ and $\mathbf{2^{Me}}$ is slightly exothermic, which does not apply to the formation of the vinylidene complex $\mathbf{2a^{Me}}$. In addition, the calculated barrier of 47.6 kcal/mol for an uncatalyzed conversion of $\mathbf{2^{Me}}$ into $\mathbf{2a^{Me}}$ by 1,2-SMe shift renders this step unlikely. The alternative formation of the bis(alkyne) complex **IM1** as an initiating step is likewise considerably endothermic. However, the additional coordination of the second alkyne is accompanied by a hapticity change of the C_5H_5 ligand from η^5 to η^2, which may account for the energy rise. Consistently, transfer of one bromide ion to the C_5H_5 system to form **IM2** with one sp^2 center and one noncoordinating double bond within the C_5H_5 ring implicates a stabilization of 3.9 kcal/mol. Related examples of cyclopentadienyl[17] and cyclopentadiene[18] complexes displaying η^2-coordination are known and usually stabilized in restricted environ-

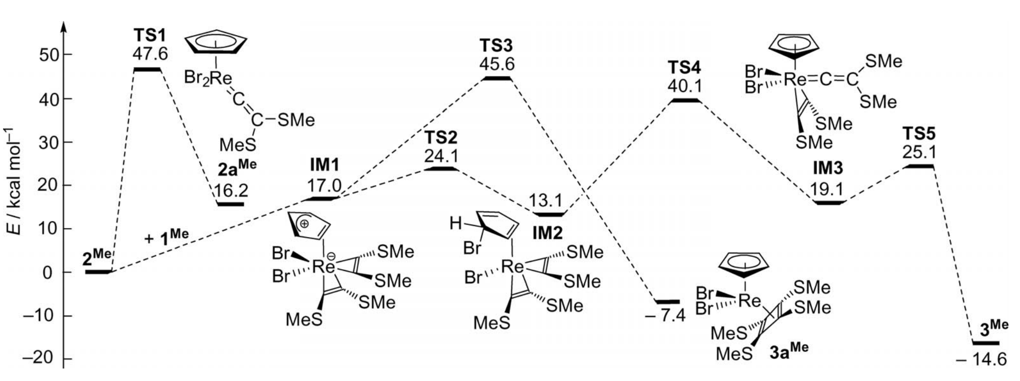


Figure 4. Schematic representation (calculated energy vs. reaction coordinate) for the formation of $\mathbf{3^{Me}}$.

ments.[17a,18] The assumed significance of intermediate **IM2** (or a similar type of dissociation keeping an ion pair in toluene) is supported by the fact that stable bis(alkyne) complexes were isolated by Herrmann et al. in the form of the cation $[(C_5Me_5)ReBr(MeC_2Me)_2]^+$.[19] The calculated barrier for the subsequent conversion of **IM2** to **IM3** by 1,2-MeS shift now amounts to 27 kcal/mol being within a realistic range for the rate-determining step, if the high reaction temperature and the overestimation of barriers due to the lack of solvent stabilization in the calculation are considered. Interestingly, in the transition-state structure (Figure S9) the C_5H_5 ring is bound in a η^5-fashion, indicating a concerted step. In addition, an experimental example of a 1,2-migration of a methylsulfanyl moiety was already observed with Ru^{II}.[20] Within this scheme the barrier for the [2+2] cycloaddition in the bis(alkyne) complex **IM1** to yield hypothetical **3a^{Me}** falls in a similar range. The feasibility of the latter step has been shown experimentally at least for the tolane system. Taking this as a measure, the reaction path including formation of the bis(alkyne) complex, subsequent 1,2-SBn shift and final [C_2+ReC] cycloaddition to yield **3** seems reasonable. According to preliminary results, the energy profile for the alternative conversion of the η^4-cyclobutadiene complex **3a/3a^{Me}** into the product **3/3^{Me}** is quite intricate. This path cannot be ruled out by the calculations, but there is no indication for markedly lower barriers on this coordinate so far.

Finally, we sought experimental evidence on the proposed mechanism. The question of a catalytic alkyne/vinylidene rearrangement **2/2a** by proton sources has been addressed by experiments with acids. The addition of catalytic amounts of HBF_4 to the reaction mixture neither resulted in an acceleration of the reaction nor in an increase of yield. If complex **2** with the 4e-donor alkyne and complex **2a** with the 2e-donor vinylidene were at equilibrium in boiling toluene, **2a** should be trapped by addition of donor ligands. However, reaction of the alkyne complex **2** with PPh_3 under respective reaction conditions led to the stoichiometric formation of $[Ph_3PBn]Br$ instead of a rhenium vinylidene complex. In addition, ^1H NMR experiments with pure **2** did not indicate any transformation up to 90 °C. In contrast, a 1:1 mixture of **2** and **1** at 80 °C showed consumption of **1** in the course of hours, while only traces of **3** were formed and the bulk of **2** persisted in solution (Figure S4). Consistently, heating a solution of **1** with only 10% of **2** resulted in the complete consumption of **1** yielding an unidentified mixture of oligomers. Obviously, **2** is an active oligomerization catalyst, while complex **3** constitutes the most stable final rhenium product. Variation of the solvent is somewhat restricted by the necessarily high reaction temperature. Increasing polarity from toluene across fluorobenzene to propionitrile resulted in moderately improved yields (35, 47, 63%). This observation can be attributed to the stabilization of intermediates with high polarity or even ion pairs, which form by dissociation of one bromide ion from Re. Within this context it must be pointed out that there is no experimental confirmation for the ring slippage of the C_5H_5 ring suggested by the calculations. Finally, cross experiments with the alkyne complex **2** and tolane (PhC_2Ph) lead to the isolation of **3** as the exclusive C–C coupling product. This result proved the preliminary substitution of the acetylene disulfide **1** by tolane. Cross products could not be isolated.

Conclusions

The alkyne complex $[(\eta^5\text{-}C_5H_5)Re(\mathbf{1})Br_2]$ (**2**) – **1** being bis(benzylthio)acetylene – reacts with an excess of the alkyne **1** at elevated temperatures to give **3**, which has a folded ReC3 ring skeleton. The molecular structure of complex **3** is best rationalized by two resonance forms being primarily an allenylcarbene complex and with minor contribution a folded rhenacyclobutene. This perception is corroborated by results of DFT calculations. In addition, the calculations show that isomeric η^4-cyclobutadiene complexes at the $[(\eta^5\text{-}C_5H_5)ReBr_2]$ fragment are less stable with thioether substituents, but favorable with aryl groups.

The formation of **3** includes a 1,2-SBn shift. Our calculations on potential intermediates and respective transition states indicate high barriers for the observed transformation. However, in comparison the rearrangement of the η^2-alkyne in a corresponding vinylidene complex needs less energy in the bis(alkyne) complex $[(\eta^5\text{-}C_5H_5)Re(\mathbf{1})_2Br_2]$ than in the mono(alkyne) complex **2**. In addition, the dissociation of one bromide substituent seems to play an important role in the stabilization of reaction intermediates. The calculated energies of transition states for the 1,2-SMe-migration considered and the alternative [2+2] cycloaddition yielding a hypothetical η^4-cyclobutadiene complex are comparable. Therefore, a subsequent rearrangement of a η^4-cyclobutadiene complex into the final product by 1,2-SBn shift is improbable.

Allenylcarbene complexes with $[Os(PPh_3)_3Cl_2]$ have been shown to be excellent precursors for the preparation of osmabenzene systems.[5c] Very recently, Jia et al. presented the first rhenabenzene ring synthesized by a slightly different strategy.[21] The authors pointed out that donor substitution at the carbon ring atoms is essential for the stability with respect to the corresponding rhenium cyclopentadienyl complexes. In this regard complex **3** seems to be a promising precursor for the preparation of further rhenabenzene systems.

Experimental Section

General: All operations were carried out in an atmosphere of dry argon using Schlenk and glove box techniques. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded with a Bruker Avance 400 or 500 MHz spectrometer. Mass spectra were obtained with a Bruker Reflex IV.

$[(\eta^5\text{-}C_5H_5)ReBr_2(BnSCCSBn)]$ (2): A solution of bis(benzylthio)-acetylene[22] (435 mg, 1.61 mmol) in toluene (5 mL) was added to a solution of $[CpReBr_2(CO)_2]$[23] (500 mg, 1.07 mmol) in toluene (70 mL). The reaction mixture was heated under reflux for 2 h. After removal of the solvent the product was recrystallized from

CH_2Cl_2/*n*-hexane. Complex **2** was obtained as a deep green solid in 67% yield (490 mg). $C_{21}H_{19}Br_2ReS_2$ (681.52): calcd. C 37.01, H 2.81, S 9.41; found C 37.00, H 3.21, S 9.36. ^1H NMR (400 MHz, $CDCl_3$): δ_H = 7.40–7.30 (m, 10 H, Ph-*H*), 5.69 (s, 5 H, C_5H_5), 4.93 (s, 4 H, SCH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ_C = 207.5 ($C{\equiv}C$), 135.2, 129.1, 129.0, 128.2 (Ph-*C*), 94.8 (C_5H_5), 43.4 (SCH_2Ph) ppm. MS (MALDI): *m*/*z* = 682 [M], 601 [M – Br]$^+$.

[(η^5-C_5H_5)$ReBr_2$\{η^3-C(SBn)C(SBn)CC(SBn)$_2$\}] (3): A solution of bis(benzylthio)acetylene (1.8 g, 6.67 mmol) in toluene (20 mL) was added to a solution of [$CpReBr_2(CO)_2$] (620 mg, 1.33 mmol) in toluene (40 mL). The reaction mixture was heated under reflux overnight. The solvent was removed in vacuo and the residue redissolved in dichloromethane (10 mL) and precipitated with *n*-hexane (50 mL). Complex **3** was obtained as orange red needles from CH_2Cl_2/*n*-hexane (430 mg, 34%). Alternatively **3** was obtained by refluxing pure **2** (99 mg, 0.15 mmol) and **1** (161 mg, 0.6 mmol) in toluene (5 mL) for 7 h. Yield after crystallization: 42 mg (30%). $C_{37}H_{33}Br_2ReS_4$ (951.93): calcd. C 46.68, H 3.49; found C 46.60, H 3.48. ^1H NMR (400 MHz, CD_2Cl_2, 300 K): δ_H = 7.47–7.08 (m, 20 H, Ph-*H*), 5.11 (br., 1 H, SCH*H*), 4.97 (s, 5 H, C_5H_5), 4.40 (d, ^2J = 12 Hz, 1 H, SCH*H*), 4.33 (m, 3 H, SCH*H*), 4.17 (m, 2 H, SCH*H*), 3.77 (d, ^2J = 12 Hz, 1 H, SCH*H*) ppm. ^1H NMR (500 MHz, $C_6D_5CD_3$, 363 K): δ_H = 7.31 (m, 2 H, Ph-*H*), 7.16–6.85 (m, 18 H, Ph-*H*), 4.88 (d, ^2J = 13.2 Hz, 1 H, SCH*H*), 4.74 (s, 5 H, C_5H_5), 4.61 (d, ^2J = 12.0 Hz, 1 H, SCH*H*), 4.28–4.23 (m, 3 H, SCH*H*), 4.09 (d, ^2J = 12.9 Hz, 2 H, SCH*H*), 3.98 (d, ^2J = 13.3 Hz, 2 H, SCH*H*), 3.60 (d, ^2J = 13.3 Hz, 1 H, SCH*H*) ppm. $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_2Cl_2, 300 K): δ_C = 242.1 (Re*C*1), 162.3 (Re*C*3), 138.9–135.5 (4 signals, Ph-C_{ipso}), 128.8–126.2 (12 signals, Ph-*C*), 118.9 (C=*C*SBn$_2$), 91.1 (C_5H_5), 86.8 (C*C*C), 41.0, 39.3, 36.2, 35.5 (S*C*H$_2$Ph) ppm. MS (MALDI): *m*/*z* = 950 [M], 871 [M – Br]$^+$, 861 [M – Bn]$^+$, 780 [M – Br – Bn]$^+$, 689 [M – 2Bn – Br]$^+$, 601 [M – 2Bn – 2Br]$^+$.

Crystal Structure Determination: Single crystals suitable for X-ray diffraction analysis were coated in perfluoropolyether oil and mounted on a glass fiber. Diffraction data were collected at T = 153 K for **2** and at T = 173 K for **3** with a Bruker AXS Apex CCD diffractometer equipped with a rotating anode using graphite-monochromated Mo-K_α radiation. Data collection, cell refinement, data reduction and integration as well as absorption correction were performed with the Bruker AXS program packages SMART, SAINT, and SADABS. Structure solutions were obtained with SHELXS[24] by direct methods and were refined with SHELXL[25] against F_o^2 by using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with fixed thermal parameters.

CCDC-771678 (for **2**) and -771679 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for [(η^5-C_5H_5)$ReBr_2$(BnSC$_2$SBn)] (2): $C_{21}H_{19}Br_2ReS_2$, M = 681.51 g mol^{-1}, green plates, space group *Cc*, a = 8.4042(12), b = 21.696(3), c = 11.4504(16) Å, V = 2081.8(5) Å^3, β = 94.350(3)°, ρ = 2.174 g cm^{-3}, μ = 9.879 mm^{-1}, Z = 4, 11840 measured reflections, 5830 unique reflections (R_{int} = 0.0518), 4961 observed reflections [$I \geq 2\sigma(I)$], 235 parameters, R(all) = 0.0467, wR(all) = 0.0682, GOF = 0.885, largest peak/hole 1.727/–1.040 e$^-$ Å^{-3}.

Crystal Data for [(η^5-C_5H_5)$ReBr_2$\{η^3-(BnS)$_2$C$_2$C(SBn)C(SBn)\}] (3): $C_{37}H_{33}Br_2ReS_4$, M = 951.89 g mol^{-1}, brown blocks, space group $P2_1/c$, a = 18.2367(10), b = 18.5086(10), c = 10.8359(6) Å, V = 3504.5(3) Å^3, β = 106.632(1)°, ρ = 1.804 g cm^{-3}, μ = 6.012 mm^{-1}, Z = 4, 23815 measured reflections, 10107 unique reflections (R_{int} = 0.0186), 8605 observed reflections [$I \geq 2\sigma(I)$], 397 parameters, R(all) = 0.0327, wR(all) = 0.0526, GOF = 1.003, largest peak/hole 1.696/–0.712 e$^-$ Å^{-3}.

Calculations: Molecular geometries of model complexes were optimized without constraints by DFT using the hybrid B3LYP functional.[26] Frequency calculations were performed to identify all the stationary points as minima or transition states. Intrinsic reaction coordinates (IRC)[27] were calculated for the transition states to confirm that such structures indeed connect two relevant minima. Rhenium was described by the pseudo-relativistic effective core potential (ECP) of the Stuttgart/Cologne group for 60 core electrons and a 8s7p6d/[6s5p3d2] basis set for the valence shell.[28] The 6-311G(d,p) basis set was used for H, C, N, and Br in the calculations of **3**, **3a**, **4**, and **4a**. The smaller 6-31G(d,p) basis set was used for the same elements in the calculations with the methyl-substituted model compounds $\mathbf{1^{Me}}$, $\mathbf{2^{Me}}$, $\mathbf{2a^{Me}}$, $\mathbf{3^{Me}}$, $\mathbf{3a^{Me}}$ and all intermediates (**IM**) and transition states (**TS**). The relative energies stated are zero point corrected. All calculations were performed with the Gaussian 03 software package.

Supporting Information (see also the footnote on the first page of this article): Two-dimensional and high-temperature NMR characterization of **3** and reaction mixtures, DFT calculation details and optimized structures.

Acknowledgments

This work was supported by a PhD fellowship of the Fonds der Chemischen Industrie (to M. J. M.). The authors thank Prof. F. E. Hahn for his generous support.

---

[1] a) B. R. Galan, T. Rovis, *Angew. Chem. Int. Ed.* **2009**, *48*, 2830–2834; b) B. Heller, M. Harpke, *Chem. Soc. Rev.* **2007**, *36*, 1085–1094.

[2] a) U. Rosenthal, V. V. Burlakow, M. A. Bach, T. Beweries, *Chem. Soc. Rev.* **2007**, *36*, 719–728; b) F. M. Dolgushin, A. I. Yanovsky, M. Y. Antipin, *Russ. Chem. Rev.* **2004**, *73*, 517; recent examples: c) L. Canovese, F. Visentin, G. Chessa, P. Uguagliati, C. Levi, A. Dolmella, *Organometallics* **2005**, *24*, 5537–5548; d) E. I. Ison, K. A. Abboud, J. M. Boncella, *Organometallics* **2006**, *25*, 1557–1564; e) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, E. Álvarez, K. Mereiter, *Chem. Eur. J.* **2007**, *13*, 5160–5172; f) A. F. Hill, A. D. Rae, M. Schultz, A. C. Willis, *Organometallics* **2007**, *26*, 1325–1338; g) M. Zirngast, C. Marschner, J. Baumgartner, *Organometallics* **2008**, *27*, 2570–2538.

[3] a) A. Efraty, *Chem. Rev.* **1977**, *77*, 691–744; b) D. Seyferth, *Organometallics* **2003**, *22*, 2–20; c) A. R. Kudinov, E. V. Mutseneck, D. A. Loginov, *Coord. Chem. Rev.* **2004**, *248*, 571–585; recent examples: d) C. Schaefer, R. Gleiter, F. Rominger, *Organometallics* **2004**, *23*, 2225–2227; e) A. Goswami, T. H. Staeb, F. Rominger, R. Gleiter, W. Siebert, *Eur. J. Inorg. Chem.* **2005**, 4086–4089.

[4] J. Liu, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2009**, *109*, 5799–5867.

[5] a) E. Rüba, K. Mereiter, R. Schmid, K. Kirchner, H. Schottenberger, *J. Organomet. Chem.* **2001**, *637–639*, 70–74; b) E. Rüba, K. Mereiter, R. Schmid, V. N. Sapunov, K. Kirchner, H. Schottenberger, M. J. Calhorda, L. F. Veiros, *Chem. Eur. J.* **2002**, *8*, 3948–3961; c) T. B. Wen, W. Y. Hung, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 2856–2857; d) M. A. Esteruelas, Y. A. Herdández, A. M. López, E. Onate, *Organometallics* **2007**, *26*, 6009–6013.

[6] T. B. Wen, W. Y. Hung, H. H.-Y. Sung, Z. Zhou, I. D. Williams, G. Jia, *Eur. J. Inorg. Chem.* **2007**, 2693–2701.

[7] a) W. W. Seidel, M. J. Meel, F. Hupka, J. J. Weigand, *Dalton Trans.* **2010**, *39*, 624–631; b) W. W. Seidel, B. López Sánchez,

M. J. Meel, A. Hepp, T. Pape, *Eur. J. Inorg. Chem.* **2007**, 936–943; c) W. W. Seidel, M. D. Ibarra Arias, M. Schaffrath, M. C. Jahnke, A. Hepp, T. Pape, *Inorg. Chem.* **2006**, *45*, 4791–4800; d) W. W. Seidel, M. Schaffrath, T. Pape, *Chem. Commun.* **2006**, 3999–4000.

[8] S. J. Dossett, M. Green, M. F. Mahon, J. M. McInnes, C. Vaughan, *J. Chem. Soc., Dalton Trans.* **1997**, 3671–3682.

[9] C. Carfagna, N. Carr, R. J. Deeth, S. J. Dossett, M. Green, M. F. Mahon, C. Vaughan, *J. Chem. Soc., Dalton Trans.* **1996**, 415–430.

[10] a) W. A. Herrmann, R. A. Fischer, E. Herdtweck, *Organometallics* **1989**, *8*, 2821–2831; b) W. A. Herrmann, R. A. Fischer, W. Amslinger, E. Herdtweck, *J. Organomet. Chem.* **1989**, *362*, 333–343.

[11] For planar rhenacyclobutene complexes, see: a) L. L. Padolik, J. C. Gallucci, A. Wojcicki, *J. Organomet. Chem.* **1990**, *383*, C1–C6; b) L. L. Padolik, J. C. Gallucci, A. Wojcicki, *J. Am. Chem. Soc.* **1993**, *115*, 9986–9996; c) C. P. Casey, J. R. Nash, C. S. Yi, A. D. Selmeczy, S. Chung, D. R. Powell, R. K. Hayashi, *J. Am. Chem. Soc.* **1998**, *120*, 722–733.

[12] For related systems, see: a) R. J. Deeth, S. J. Dossett, M. Green, M. F. Mahon, S. R. Rumble, *J. Chem. Soc., Chem. Commun.* **1995**, 593–595; b) Z. Qiu, J. Sun, J. Chen, *Organometallics* **1998**, *17*, 600–606; c) C. P. Casey, S. Kraft, D. R. Powell, *J. Am. Chem. Soc.* **2000**, *122*, 3771–3772.

[13] a) J. Pu, T. S. Peng, A. M. Arif, J. A. Gladysz, *Organometallics* **1992**, *11*, 3232–3241; b) C. P. Casey, T. L. Underiner, P. C. Vosejpka, J. A. Gavney Jr., P. Kiprof, *J. Am. Chem. Soc.* **1992**, *114*, 10826–10834.

[14] a) C. F. Bernasconi, S. Bhattacharya, P. J. Wenzel, M. M. Olmstead, *Organometallics* **2006**, *25*, 4322–4330; b) O. Kaufhold, A. Stasch, T. Pape, A. Hepp, P. G. Edwards, P. D. Newman, F. E. Hahn, *J. Am. Chem. Soc.* **2009**, *131*, 306–317; O. Hiltner, E. Herdtweck, M. Drees, W. A. Herrmann, F. E. Kühn, *Eur. J. Inorg. Chem.* **2009**, 1825–1831.

[15] a) J. Klimes, E. Weiss, *Angew. Chem.* **1982**, *94*, 207; b) W. A. Herrmann, R. A. Fischer, E. Herdtweck, *Angew. Chem.* **1987**, *99*, 1286–1290; c) K. E. Garrett, J. B. Sheridan, D. B. Pourreau, W. C. Feng, G. L. Geoffroy, D. L. Staley, A. L. Rheingold, *J. Am. Chem. Soc.* **1989**, *111*, 8383–8391.

[16] B. M. Foxman, *J. Chem. Soc., Chem. Commun.* **1975**, 221–222.

[17] a) F. Bottomley, D. E. Paez, L. Sutin, P. S. White, *J. Chem. Soc., Chem. Commun.* **1985**, 597–598; b) D. Barr, A. J. Edwards, P. R. Raithby, M.-A. Rennie, K. L. Verhorevoort, D. S. Wright, *J. Organomet. Chem.* **1995**, *493*, 175–179; c) P. Jutzi, W. Wieland, B. Neumann, H.-G. Stammler, *J. Organomet. Chem.* **1995**, *501*, 369–374; d) M. M. Corradi, D. J. Duncalf, G. A. Lawless, M. P. Waugh, *Chem. Commun.* **1997**, 203–204.

[18] a) M. Enders, P. Fernández, M. Kaschke, G. Kohl, G. Ludwig, H. Pritzkow, R. Rudolph, *J. Organomet. Chem.* **2002**, *641*, 81–89; b) M. Theil, P. Jutzi, B. Neumann, A. Stammler, H.-G. Stammler, *J. Organomet. Chem.* **2002**, *662*, 34–42; c) M. Enders, G. Ludwig, H. Pritzkow, *Eur. J. Inorg. Chem.* **2002**, 539–542.

[19] W. A. Herrmann, R. A. Fischer, J. K. Felixberger, R. A. Paciello, P. Kiprof, E. Herdtweck, *Z. Naturforsch., Teil B* **1988**, *43*, 3191–1404.

[20] D. C. Miller, R. J. Angelici, *Organometallics* **1991**, *10*, 79–89.

[21] K. C. Poon, L. Liu, T. Guo, J. Li, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem. Int. Ed.* **2010**, *49*, 2759–2762.

[22] W. W. Seidel, M. J. Meel, M. Schaffrath, T. Pape, *Eur. J. Org. Chem.* **2007**, 3526–3532.

[23] R. B. King, H. Reimann, *Inorg. Chem.* **1976**, *15*, 179–183.

[24] *SHELXS-97*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[25] *SHELXL-97*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

[26] a) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200.

[27] a) K. Fukui, *J. Phys. Chem.* **1970**, *74*, 4161; b) K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363.

[28] a) D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, *77*, 123–141; b) J. M. L. Martin, A. Sundermann, *J. Chem. Phys.* **2001**, *114*, 3408–3420.

Received: April 1, 2010