Benzothiazolin-2-ylidene Complexes of Iridium(I)

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The reaction of allyl bromide with benzothiazole under neat conditions furnished 3-(2-propenyl)-benzothiazolium bromide, (H-**1**)Br, in high yield. Attempts to synthesize the corresponding carbene dimer by deprotonation of $(H\text{-}\mathbf{1})^+$ led to the isolation of the rearrangement product 2,3-di(2-propenyl)-2′,3′-dihydro-2,2′-bisbenzothiazole (**2**). The reaction of $[Ir(\mu\text{-}OMe)(cod)]_2$ with the salt (H-**1**)Br unexpectedly afforded [IrBr(cod)(benzothiazole)] (**3**) (cod = 1,5-cyclooctadiene), which contained an *N*-coordinated unsubstituted benzothiazole ligand. The formation of carbene complexes of Ir^I with the benzothiazolin-2-ylidene ligand could be achieved via precoordination of the allyl substituent of $(H\text{-}\mathbf{1})^+$ to $[Ir(cod)(MeCN)_2]BF_4$ and subsequent deprotonation at the C2 position of $(H\text{-}\mathbf{1})^+$ by addition of base. The use of NaH as external base yielded the square planar Ir^I complex **4** with an *N*-propyl-substituted carbene ligand, while deprotonation with KO^{t}Bu gave the five-coordinated Ir^I complex $[IrBr(cod)(\eta^2\text{-}\mathbf{1})]$, **5**. Displacement of the cod ligand in complex **4** by two CO ligands afforded the complex $[IrBr(CO)_2(NHC)]$ (NHC = 3-propylbenzothiazolin-2-ylidene), **6**, which allowed an estimation of the σ-donor capabilities of benzothiazolin-2-ylidene ligands. Compounds **1**−**6** have been characterized spectroscopically, and the molecular structures of (H-**1**)Br and **2**−**5** were determined by X-ray diffraction.

Introduction

Nucleophilic *N*-heterocyclic carbene ligands (NHCs) and their transition metal complexes have attracted much interest recently due to their applications in catalysis.[1] Particularly diaminocarbenes with an *N*-heterocyclic ring were thoroughly investigated in that respect. On the other hand, less attention has been paid to *N*,*S*-heterocyclic carbenes. Arduengo prepared the first stable thiazolin-2-ylidene and its dimer.[2] Another prominent example is the thiamine-carbene derived from vitamin B1, which is important for the decarboxylation of pyruvate and also acts as co-enzyme for other bio-related reactions.[3] In 1958, Breslow proposed that thiamine derivatives act as catalysts in benzoin condensation reactions.[4] Early work of Lappert describes complexes of *N*,*S*-heterocyclic carbenes derived from reactions involving the electron-rich 3,3′-dimethyldiazadithiofulvalene.[5] Later, Raubenheimer reported a transmetalation method[6] for the preparation of such complexes using lithiated thiazoles. More recently, Calo et al. described the synthesis and catalytic activity of a bis(*N*-methylbenzothiazolin-2-ylidene)palladium(II) complex for a wide range of C−C couplings such as the Heck reaction or the arylation of allylic alcohols in ionic liquids.[7] Most of the complexes reported so far contain *N*-protonated or *N*-alkylated benzothiazolin-2-ylidene ligands. *N*-Functionalization of *N*,*S*-heterocyclic carbenes with donor groups may furnish hemilabile chelating ligands, which can stabilize reactive transition metal centers during the catalytic cycle. Since *N*-functionalized NHCs with *P*-, *N*-, or *O*-donor groups have been used in a range of catalytic reactions,[8] we became interested in the *N*-allyl functionalization of NHCs. Recently, we have reported the preparation of complexes with *N*,*N*′-diallyl-substituted benzannulated[9] and unsaturated[10] carbene ligands via the in situ deprotonation of *N*,*N*′-diallyl-functionalized benzimidazolium or imidazolium salts by metal precursors containing basic ligands. Herein, we wish to report the synthesis and coordination chemistry of an *N*-allyl-functionalized benzothiazolin-2-ylidene ligand.

Results and Discussion

Preparation of 3-(2-Propenyl)benzothiazolium Bromide ((H-1)Br). In general, azolium salts can be easily prepared by reaction of azoles with alkyl halides in organic solvents. However, attempts to react benzothiazole with allyl bromide under these conditions were unsuccessful in our hands, indicat-

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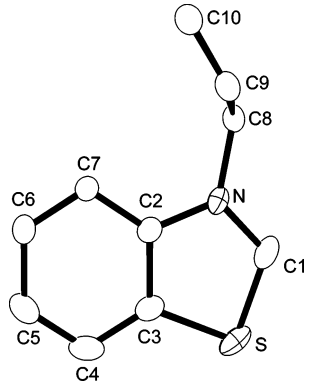

Figure 1. Molecular structure of the cation (H-**1**)$^+$ with the cystallographic numbering scheme. Selected bond lengths (Å) and angles (deg): S−C1 1.685(2), S−C3 1.743(2), N−C1 1.317(3), N−C2 1.394(2), N−C8 1.478(3), C2−C3 1.391(3), C8−C9 1.494-(3), C9−C10 1.316; C1−S−C3 90.30(10), C1−N−C2 113.6(2), C1−N−C8 123.8(2), C2−N−C8 122.6(2).

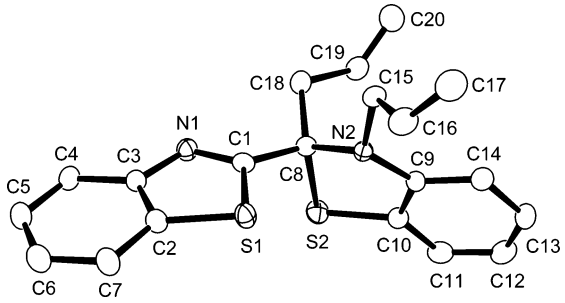

Figure 2. Molecular structure of compound **2** with the crystallographic numbering scheme. Selected bond lengths (Å) and angles (deg): S1−C1 1.750(2), S1−C2 1.734(3), S2−C8 1.850(2), S2−C10 1.758(3), N1−C1 1.287(3), N1−C3 1.396(3), N2−C8 1.471-(3), N2−C9 1.391(3), N2−C15 1.464(3), C1−C8 1.508(3), C2−C3 1.396(3), C8−C18 1.545(3), C9−C10 1.396(3), C15−C16 1.501(3), C16−C17 1.316(4), C18−C19 1.498(3), C19−C20 1.314-(4); C1−S1−C2 88.25(12), C8−S2−C10 91.86(11), C1−N1−C3 110.3(2), C8−N2−C9 113.0(2), C8−N2−C15 117.5(2), C9−N2−C15 120.5(2), S1−C1−N1 116.7(2), S1−C1−C8 118.7(2), N1−C1−C8 124.0(2), S2−C8−N2 103.79(14), S2−C8−C1 104.52(14), S2−C8−C18 111.14(15), N2−C8−C1 110.2(2), N2−C8−C18 114.8(2), C1−C8−C18 111.6(2).

ing that harsher conditions are required to activate benzothiazole. The synthesis of 3-(2-propenyl)benzothiazolium bromide, (H-**1**)Br, was finally accomplished by stirring a neat mixture of benzothiazole and an excess of allyl bromide at ambient temperature. After a few days, the product precipitates from the initially liquid reaction mixture and can be collected by filtration. The crude product can be purified by crystallization from an ethanolic solution upon cooling to −12 °C. Heating of the reaction mixture to 70−80 °C as described by Matsumoto et al.,[11] a method frequently used for the preparation of *N,N′*-dialkylbenzimidazolium salts, should be avoided since this leads to partial decomposition due to deprotonation of the benzothiazolium salt by unreacted benzothiazole. The ^{1}H NMR spectrum of (H-**1**)Br displays signals for the terminal allyl hydrogen atoms at δ 5.61 and 5.57 ppm with typical coupling constants in the range of $^3J_{HH}$ = 10.6 Hz (*cis*) and $^3J_{HH}$ = 16.2 Hz (*trans*). As expected, the NCHN hydrogen atom of the azolium salt gives rise to a singlet at δ 10.37 ppm. An X-ray diffraction study with crystals obtained from a concentrated ethanol solution confirmed the identity of (H-**1**)Br (Figure 1).

Attempted Deprotonation of (H-1)Br with Isolation of 2. Reported methods for the synthesis of complexes with benzothiazolin-2-ylidene ligands involve the electrophilic cleavage of electron-rich olefins with suitable metal precursors,[5] the in situ deprotonation of alkylbenzothiazolium halides[7] with Pd(OAc)$_2$, or the oxidative addition of 2-chlorobenzothiazole to Ir^I complexes.[12] To test the feasibility of the first method for the synthesis of complexes bearing *N*-allyl-functionalized benzothiazolin-2-ylidenes, we intended to prepare the corresponding dibenzodiazadithiofulvalene by deprotonation of (H-**1**)$^+$ followed by dimerization of the resulting ylidene. However, the deprotonation of *N*-benzylbenzothiazolium salts with NEt_3 has been reported to give initially a fulvalene that is unstable toward rearrangement.[13] The reaction of (H-**1**)Br with NEt_3 in DMF gives similar results and yields instead of the carbene dimer the rearrangement product **2** (Scheme 1). The initially obtained dibenzodiazadithiofulvalene can react further in competing [1,3]- or [3,3]-sigmatropic rearrangements. A radical [1,3]-sigmatropic rearrangement has been proposed to occur for similar dibenzodiazadithiofulvalenes,[13] and we assume that compound **2** is also formed in a radical [1,3]-sigmatropic rearrangement. A similar rearrangement for *N*-allyl dibenzotetraazafulvalenes has been shown to proceed via the radical [1,3]-sigmatropic rearrangement.[14] Owing to the rearrangement reaction, the deprotonation of *N*-allyl-substituted benzothiazolium salts proves impractical for the preparation of carbene dimers and thus is not suitable for the synthesis of complexes bearing *N*-allyl-substituted benzothiazolin-2-ylidene ligands.

Compound **2** was fully characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The structure assignment for **2** is corroborated by the NMR spectra, which show two nonequivalent allyl groups. The rotation around the N−CH$_2$ and C−CH$_2$ bonds, respectively, is hindered. The four diastereotopic methylene protons thus give rise to four doublets of doublets in the ^{1}H NMR spectrum. In addition, characteristic signals for the N═CS carbon atom (δ 174.7 ppm) and the quarternary carbon atom (δ 83.2 ppm) were detected. The molecular structure of **2** was unambiguously established by X-ray diffraction (Figure 2). The two five-membered rings in **2** are quite different. The planar ring S1−C1−N1−C3−C2 exhibits molecular parameters similar to a C2-alkylated benzothiazole with a short N1−C2 separation (1.287(3) Å), while the ring S2−C8−N2−C9−C10 is not planar.

Reaction of (H-1)Br with [Ir(μ-OMe)(cod)]$_2$. A rearrangement similar to the one found upon deprotonation of (H-**1**)Br (Scheme 1) has been observed during the deprotonation of *N*-allyl-substituted benzimidazolium[14] and other azolium salts with external bases.[15] However, iridium(I) complexes with *N*-allyl-substituted benzimidazolin-2-ylidene ligands can be obtained by in situ deprotonation of benzimidazolium salts with iridium precursors bearing basic ligands.[9] We therefore assumed that the iridium complex with a benzothiazolin-2-ylidene ligand could be obtained by treatment of the benzothiazolium salt (H-**1**)Br with [Ir(μ-OMe)(cod)]$_2$ in acetone. This reaction gave a

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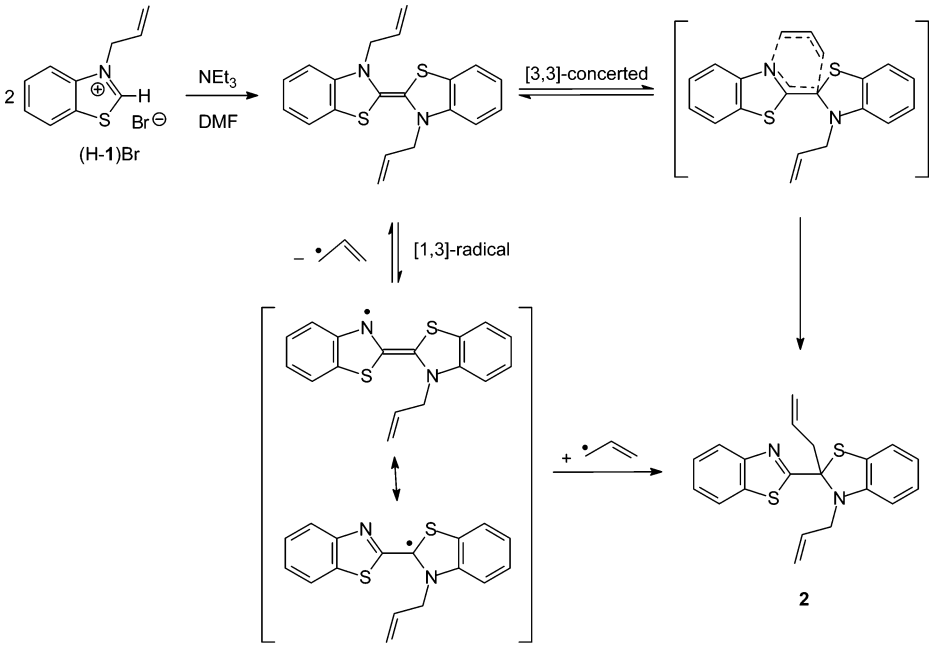
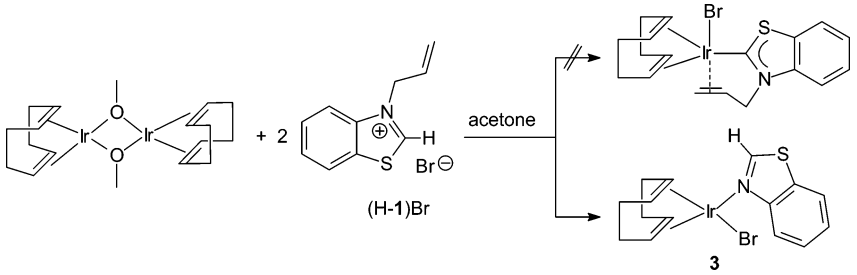
Scheme 1. Deprotonation of (H-1)Br under Formation of a Dimeric Benzothiazolin-2-ylidene and Possible Subsequent Rearrangement Reactions of the Dimer to Give 2



Scheme 2. Reaction of (H-1)Br with [Ir(*μ*-OMe)(cod)]$_2$ under Formation of Complex 3



yellow solid product **3**. Surprisingly, the NMR spectra for complex **3** showed no resonances for an allyl group anymore. The analytical data obtained are consistent with the formation of a complex containing an *N*-coordinated benzothiazole ligand (Scheme 2). For example, the ^{1}H NMR spectrum of **3** showed a singlet at δ 9.16 ppm assigned to the N═CHS proton of benzothiazole.

The molecular structure of **3** was established by an X-ray diffraction study (Figure 3). Complex **3** features an iridium atom coordinated in a square planar fashion by the nitrogen atom of a benzothiazole ligand, a bromo ligand, and two double bonds of one cod ligand. Bond lengths and angles within the coordinated benzothiazole ligand do not differ significantly from those of the benzothiazole moiety in **2**. The Ir−C separations are approximately equidistant, indicating a similar *trans* influence of the bromo and the nitrogen donor. This leads to C═C distances within the cod ligand that are also identical within experimental error.

Since a contamination of the used *N*-allyl benzothiazolium salt with benzothiazole can be ruled out, complex **3** must have formed after deallylation of (H-**1**)Br. We assume that the reaction of (H-**1**)Br with [Ir(*μ*-OMe)(cod)]$_2$ yields initially the C2 deprotonated molecule, which instead of coordinating to the metal center can dimerize and then rearrange to give compound **2** (Scheme 1). The thermal or acid-catalyzed degradation of compounds of type **2** to the free azoles (benzothiazole[13] and benzimidazole[15]) has been demonstrated.

The reasons for the differences in reactivity of *N*-allyl-substituted benzimidazolium[9] and benzothiazolium salts toward [Ir(*μ*-OMe)(cod)]$_2$ remain to be established. After deprotonation of benzothiazolium salts, the dimerization of the resulting benzothiazolin-2-ylidenes is apparently much faster than for

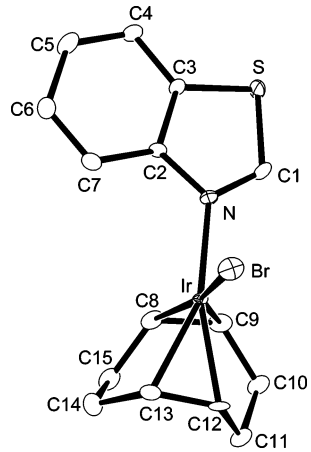
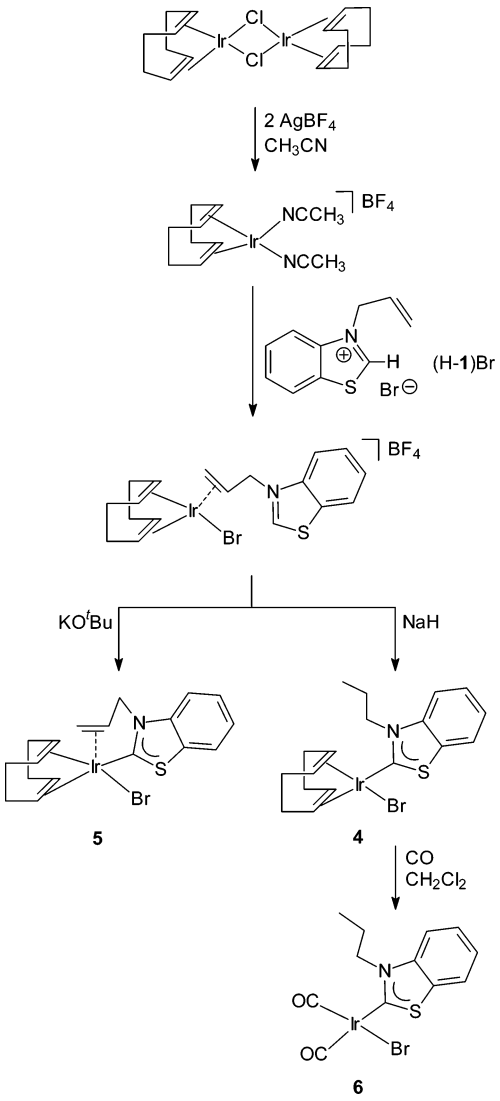


Figure 3. Molecular structure of complex **3** with the crystallographic numbering scheme. Selected bond lengths (Å) and angles (deg): Ir−Br 2.4848(7), Ir−N 2.089(3), Ir−C8 2.128(4), Ir−C9 2.097(4), Ir−C12 2.126(4), Ir−C13 2.117(4), S−C1 1.714(4), S−C3 1.722(4), N−C1 1.307(6), N−C2 1.396(5), C2−C3 1.398(5), C8−C9 1.425(6), C12−C13 1.396(6); Br−Ir−N 88.27(10), Br−Ir−C8 165.30(13), Br−Ir−C9 155.28(13), Br−Ir−C12 93.38(12), Br−Ir−C13 92.02(12), N−Ir−C8 92.6(2), N−Ir−C9 90.1(2), N−Ir−C12 164.2(2), N−Ir−C13 157.3(2), C1−S−C3 89.5(2), Ir−N−C1 125.5(3), Ir−N−C2 124.2(3), C1−N−C2 111.3(3), S−C1−N 115.7(3).

Scheme 3. Syntheses of Ir^{I} Benzothiazolin-2-ylidene Complexes 4−6



benzimidazolin-2-ylidenes. This opens a reaction path for the rearrangement/degradation reactions before coordination to the metal center can occur. The degradation product benzothiazole is then found coordinated to iridium.

Reaction of (H-1)Br with (Ir(cod)(NCCH$_3$)$_2$)BF$_4$ and NaH or KO^{t}Bu as External Base. Since the deprotonation of (H-**1**)$^+$ with NEt_3 or with Ir^{I} complexes containing basic ligands was unsuccessful, we attempted a precoordination of the allyl substituent of cation (H-**1**)$^+$ to the metal center prior to the generation of the carbene center by deprotonation at the C2 carbon atom. To achieve this, [Ir(μ-Cl)(cod)]$_2$ was treated with silver tetrafluoroborate in acetonitrile to remove the chloro ligands and replace them with more labile acetonitrile ligands (Scheme 3). In a second step, the benzothiazolium salt was added in order to precoordinate the allyl substituent to the iridium center. Subsequent addition of sodium hydride as an external base resulted in the unexpected formation of the Ir^{I} carbene complex **4**, which contains an *N*-propylbenzothiazolin-2-ylidene ligand. Apparently, the amount of hydrogen generated in the deprotonation step is already sufficient to hydrogenate the *N*-allyl function and transform it into an *N*-propyl group.

The in situ self-hydrogenation of the *N*-allyl substituent demonstrates that complexes of type **4** are capable of activating molecular hydrogen and thus can be considered potential hydrogenation catalysts. The hydrogenation of both *N*-allyl groups in the Ir^{I} complex with the 1,3-diallylbenzimidazolin-2-ylidene ligand under transfer hydrogenation conditions has been reported.[9b]

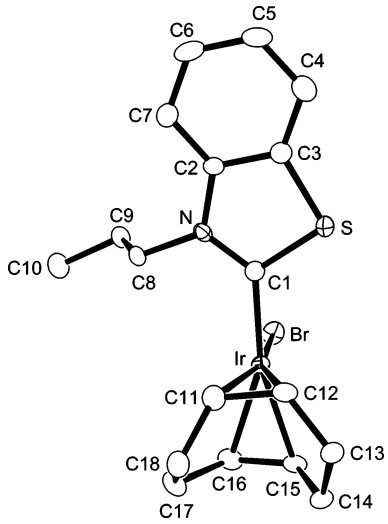


Figure 4. Molecular structure of complex **4** with the crystallographic numbering scheme. Selected bond lengths (Å) and angles (deg): Ir−Br 2.4837(5), Ir−C1 1.981(4), Ir−C11 2.118(4), Ir−C12 2.102(4), Ir−C15 2.211(4), Ir−C16 2.190(4), S−C1 1.726(4), S−C3 1.742(4), N−C1 1.325(5), N−C2 1.395(5), N−C8 1.484(5), C2−C3 1.397(6), C8−C9 1.511(6), C9−C10 1.522(6), C11−C12 1.419(6), C15−C16 1.387(6); Br−Ir−C1 89.08(12), Br−Ir−C11 160.21(12), Br−Ir−C12 160.39(12), Br−Ir−C15 94.07(11), Br−Ir−C16 89.58(11), C1−Ir−C11 93.3(2), C1−Ir−C12 91.3(2), C1−Ir−C15 163.7(2), C1−Ir−C16 159.5(2), C1−S−C3 93.1(2), C1−N−C2 116.9(3), C1−N−C8 121.8(3), C2−N−C8 121.2(3), Ir−C1−S 120.5(2), Ir−C1−N 130.0(3), S−C1−N 109.4(3).

Typical signals for *N*-allyl groups are absent in the ^{1}H NMR spectrum of **4**. Instead, broad multiplets around δ 5.0 and 1.9 ppm and a triplet at δ 1.12 ppm, respectively, are observed for the propyl protons. The ^{13}C{^{1}H] NMR spectrum shows three new signals for the propyl carbon atoms at δ 56.5, 22.3, and 11.6 ppm. The chemical shift for the carbene carbon resonance at δ 218.9 ppm is shifted downfield compared to the analogous complex with the 1,3-di(propyl)benzimidazolin-2-ylidene (δ_{NCN} 191.2 ppm).[9b] The coordination of the carbene ligand to the Ir^{I} center leads to two types of cod−CH resonances with chemical shifts of δ 89.2 (*trans* to carbene) and δ 60.1 ppm (*trans* to bromide). This difference, which has also been observed for the analogous complex with the 1,3-di(propyl)benzimidazolin-2-ylidene ligand,[9b] results from the differences in the *trans* influence of the carbene ligand compared to the bromo ligand.

Single crystals of **4** suitable for an X-ray diffraction analysis were grown from a CH_2Cl_2 solution. The molecular structure of **4** and selected bond parameters are depicted in Figure 4. The structure analysis confirms the hydrogenation of the allyl substituents. The Ir−C1 distance (1.981(4) Å) compares well with the equivalent distance in the analogous benzimidazolin-2-ylidene complex,[9b] which indicates similar σ-donor capabilities of the *N*,*N*- and *N*,*S*-stabilized carbene ligands. The different *trans* influence of the carbene and the bromo ligand in **4** manifests itself in two different sets of Ir−C$_{cod}$ distances. The carbene ligand acts as a stronger σ-donor, which weakens the Ir−C$_{cod}$ interactions *trans* to the carbene. This leads in turn to a short CH═CH bond *trans* to the carbene and a longer one *trans* to the bromo ligand.

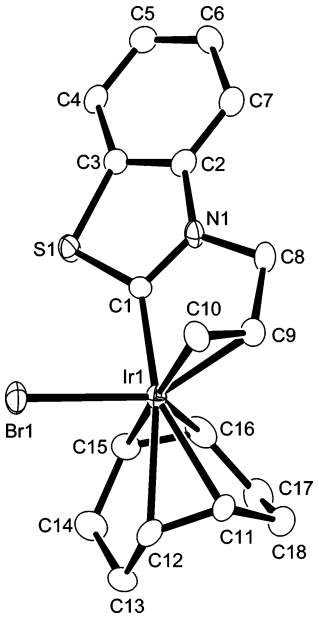


Figure 5. Molecular structure of complex **5** with the crystallographic numbering scheme. Only one of the two essentially identical molecules in the asymmetric unit is depicted. Selected bond lengths (Å) and angles (deg): Ir1−Br1 2.6207(7), Ir1−C1 1.976(6), Ir1−C9 2.153(6), Ir1−C10 2.162(6), Ir1−C11 2.253(6), Ir1−C12 2.279(6), Ir1−C15 2.170(6), Ir1−C16 2.160(6), S1−C1 1.726(6), S1−C3 1.753(6), N1−C1 1.336(7), N1−C2 1.392(7), N1−C8 1.461(7), C2−C3 1.403(9), C8−C9 1.496(8), C9−C10 1.422(8), C11−C12 1.374(8), C15−C16 1.425(9); Br1−Ir1−C1 89.2(2), C1−S1−C3 92.8(3), C1−N1−C2 117.6(5), C1−N1−C8 118.1(5), C2−N1−C8 124.0(5), Ir1−C1−S1 131.6(3), Ir1−C1−N1 119.0(4), S1−C1−N1 109.2(4).

Since the in situ deprotonation of precoordinated (H-**1**)$^+$ with NaH led to the hydrogenation of the *N*-allyl substituent, other bases were employed for the generation of the carbene ligand. The reaction of the precoordinated ligand with KO^{t}Bu was investigated (Scheme 3). This modified procedure led to the isolation of the colorless, air- and moisture-stable complex **5**. Crystals of **5** were obtained after recrystallization from CH_2Cl_2.

The molecular structure of one of the two essentially identical molecules in the asymmetric unit of **5** and selected bond parameters are shown in Figure 5. The iridium atom is pentacoordinated by one bromide, two cod C═C double bonds, the carbene carbon atom, and the C═C double bond of the *N*-allyl group in a distorted trigonal bipyramidal fashion. The carbene carbon atom and one of the cod double bonds (C11═C12) occupy the axial positions. Overall, the molecular structure of **5** resembles that of [IrBr(cod)(η^2-*C*-NHC)] (NHC = 1,3-di(2-propenyl)benzimidazolin-2-ylidene), where only one of the two allyl groups of the 1,3-di(2-propenyl)benzimidazolin-2-ylidene ligand coordinates to the iridium atom.[9b] Comparable molecular parameters of the two complexes are identical within experimental error. As described for the benzimidazolin-2-ylidene complex, the Ir−C distances *trans* to the carbene center in **5** (Ir−C11 and Ir−C12) are longer than those in the equatorial plane (Ir−C15 and Ir−C16). This observation is again attributed to the strong *trans* influence of the carbene ligand. The ^{1}H NMR spectrum of **5** indicates that the coordination of the *N*-allyl substituent is retained in solution. Coordination of the allyl group to iridium leads to diastereotopic N−CH_2 protons, which give rise to two doublets of doublets each at δ 1.99 and 1.86 ppm with geminal $^2J_{HH}$ coupling constants of 2.2 Hz.

Reaction of 4 with CO. Displacement of olefins by CO is a common method used for the synthesis of iridium carbonyl complexes.[16] Similarly, the cod ligand is readily substituted for two CO ligands by bubbling gaseous CO through a dichloromethane solution of **4** (Scheme 3). The formation of the dicarbonyl complex **6** can be monitored by IR and NMR spectroscopy. After complete substitution of the cod ligand, the $^{13}C\{^1H\}$ NMR spectrum shows two nonequivalent CO carbon signals at δ 181.5 and 168.5 ppm, indicating a *cis* arrangement of the two CO ligands. Two CO stretching modes at ν 2071 and 1992 cm^{-1}, with nearly identical intensity, are observed in the IR spectrum of **6**.

Crabtree has shown that the position of the CO valence bands in [Ir(CO)$_2$Cl(L)] complexes gives semiquantitative information about the σ-donor ability of the ligand L in terms of the "Tolman electronic parameter" (TEP).[17] We have used Crabtree's linear fit procedure[18] to determine the TEP for the *N*-propylbenzothiazolin-2-ylidene ligand in complex **6** in order to evaluate and compare its σ-donor character with those of selected imidazolin-2-ylidenes and phosphines.[18] The small influence of different halogeno ligands at the iridium center was neglected. The calculations show that the imidazolin-2-ylidenes (TEP 2050−2051 cm^{-1}) are stronger electron donors than the benzothiazolin-2-ylidene ligand in **6** (TEP 2059.1 cm^{-1}). The benzothiazolin-2-ylidene shows σ-donor properties that are comparable to triisopropylphosphine (TEP 2059.2 cm^{-1}).[18]

Conclusion

Attempts to generate benzothiazolin-2-ylidenes and their iridium(I) complexes by in situ deprotonation of the benzothiazolium salt (H-**1**)Br are presented. The preparation of the free carbene is hampered by the pronounced tendency of the free *N*(allyl),*S*-stabilized ylidene to dimerize and rearrange to compound **2**. Similarly, the use of iridium(I) complexes with basic ligands for the deprotonation of (H-**1**)Br and subsequent complex formation led to deallylation of the ligand and isolation of the Ir^1 benzothiazole complex **3**. Precoordination of the allyl group of (H-**1**)$^+$ to Ir^1 followed by C2-deprotonation with KO^t-Bu allowed the isolation of the carbene complex **5**, while C2-deprotonation of the precoordinated ligand with NaH gave the carbene complex with a hydrogenated *N*-propylbenzothiazolin-2-ylidene ligand, **4**. Replacement of the cod ligand in **4** was accomplished by reaction with gaseous CO, to give the dicarbonyl complex **6**, which allowed the determination of the σ-donor capability of the benzothiazolin-2-ylidene ligand.

Experimental Section

All manipulations were performed in an atmosphere of dry nitrogen/argon by standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on Bruker AC 200, Bruker AMX 400, or Varian U 600 spectrometers using Me_4Si as internal standard. IR spectra were recorded using a Bruker Vektor 22. MALDI mass spectra were obtained using a Bruker Reflex IV spectrometer, and elemental analyses were performed on a Vario EL III CHNS elemental analyzer at the IAAC, University Münster, Germany.

3-(2-Propenyl)benzothiazolium Bromide ((H-1)Br)). Benzothiazole (15.0 mL, 136.5 mmol) is stirred with allyl bromide (11.8 mL, 136.5 mmol) under neat conditions at ambient temperature in

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Table 1. Summary of Crystallographic Data for (H-1)Br and 2−5

	(H-**1**)Br	**2**	**3**	**4**	**5**
formula	$C_{10}H_{10}NBrS$	$C_{20}H_{18}N_2S_2$	$C_{15}H_{17}NBrIrS$	$C_{18}H_{23}NBrIrS$	$C_{18}H_{21}NBrIrS$
M_r	256.16	350.48	515.47	557.54	555.53
cryst size [mm]	0.19 × 0.15 × 0.08	0.23 × 0.09 × 0.04	0.24 × 0.18 × 0.15	0.19 × 0.15 × 0.09	0.14 × 0.07 × 0.05
a [Å]	7.515(2)	13.295(2)	20.455(6)	31.097(6)	15.998(3)
b [Å]	8.107(3)	20.450(3)	11.712(3)	8.033(2)	13.005(2)
c [Å]	9.083(3)	7.3573(12)	14.630(4)	15.710(3)	16.687(3)
α [deg]	100.577(6)	90.0	90.0	90.0	90.0
β [deg]	91.178(6)	121.332(3)	123.502(4)	117.387(3)	106.774(3)
γ [deg]	110.396(5)	90.0	90.0	90.0	90.0
V [Å^3]	507.7(3)	1708.6(5)	2922.5(14)	3484.6(12)	3323.9(9)
Z	2	4	8	8	8
space group	$P\bar{1}$ (no. 2)	*Cc* (no. 9)	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)	$P2_1/c$ (no. 14)
ρ_{calcd} [g cm^{-3}]	1.676	1.363	2.343	2.126	2.220
μ Mo Kα [mm^{-1}]	4.204	0.315	11.999	10.072	10.559
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
2θ range [deg]	$4.6 \le 2\theta \le 60.1$	$2.0 \le 2\theta \le 60.1$	$4.2 \le 2\theta \le 60.0$	$2.9 \le 2\theta \le 60.2$	$4.0 \le 2\theta \le 55.0$
no. of unique data	2931	4811	4266	5082	7636
no. of obsd data [$I \ge 2\sigma(I)$]	2555	4294	3818	4395	6362
R (all)	0.0362	0.0540	0.0339	0.0402	0.0502
wR^2 (all)	0.0728	0.1054	0.0648	0.0644	0.0789
no. of variables	118	217	172	200	397
peak/hole [e Å^{-3}]	0.59/−0.44	0.41/−0.29	1.51/−2.86	2.06/−1.89	1.65/−1.42

a sealed flask. After a few days, the pink crude product precipitates from the reaction mixture and is isolated by filtration. The product is further purified by recrystallization from EtOH. Yield: 31.8 g (91.0%). ^{1}H NMR (200.1 MHz, D_2O): δ 10.37 (s, 1H, CH), 8.19−8.05 (m, 2H, Ar−H$_{ortho}$), 7.67−7.59 (m, 2H, Ar−H$_{meta}$), 6.19 (m, 1H, CH_2CH═CH_2), 5.61 (d, 1H, $^3J_{HH}$ = 10.6 Hz, CH_2CH═CH_{cis}), 5.57 ($^3J_{HH}$ = 16.2 Hz, CH_2CH═CH_{trans}), 5.40 (d, 2H, NCH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, D_2O): δ 165.1 (NCS), 142.3 and 133.7 (Ar−C$_{ipso}$), 132.7, 131.5 (Ar−C$_{meta}$), 131.1 (CH_2CH═CH_2), 127.3, 126.3 (Ar−C$_{ortho}$), 119.7 (CH_2CH═CH_2), 57.8 (NCH_2). Anal. Calcd for $C_{10}H_{10}NBrS$: C, 46.89; H, 3.93; N, 5.47; S, 12.52. Found: C, 46.75; H, 3.94; N, 5.45; S, 12.39.

2,3-Di(2-propenyl)-2′,3′-dihydro-2,2′-bisbenzothiazole (2). 3-(2-Propenyl)benzothiazolium bromide, (H-**1**)Br (1.02 g, 4.0 mmol), is dissolved in DMF (40 mL) and treated with NEt_3 (0.56 mL, 4.0 mmol). The mixture is stirred overnight at ambient temperature. The solvent is removed, and the resulting solid is suspended in toluene. After filtration and removal of the solvent the solid crude product is purified by column chromatography (SiO_2, hexane/ethyl acetate = 8:1). Compound **2** is isolated as a slightly yellow solid. Yield: 567 mg (81%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 8.02 (d, 1H, Ar−H), 7.82 (d, 1H, Ar−H), 7.47 (t, 1H, Ar−H), 7.37 (t, 1H, Ar−H), 7.06 (d, 1H, Ar−H), 6.98 (t, 1H, Ar−H), 6.71 (t, 1H, Ar−H), 6.39 (d, 1H, Ar−H), 6.00 (m, 1H, $C-CH_2CH$═CH_2), 5.77 (m, 1H, $N-CH_2CH$═CH_2), 5.28 (dd, 1H, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 16.9 Hz, $C-CH_2CH$═CH_{trans}), 5.24 (dd, 1H, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 17.3 Hz, $N-CH_2CH$═CH_{trans}), 5.15 (dd, 1H, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 10.2 Hz, $C-CH_2CH$═CH_{cis}), 5.11 (dd, 1H, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 10.3 Hz, $N-CH_2CN$═CH_{cis}), 3.99, 3.85 (dd, 2H, $N-CH_2$), 3.48, 3.34 (dd, $C-CH_2$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 174.7 (N═CS), 153.0, 145.8 (Ar−C$_{ipso,N}$), 136.4 (Ar−C$_{ipso,S}$), 133.8 ($N-CH_2-CH$═CH_2), 132.4 ($C-CH_2-CH$═CH_2), 126.0, 125.9 (Ar−C$_{meta,N}$), 125.5 (Ar−C$_{meta,S}$), 123.6 (Ar−C$_{ortho,N}$), 123.3 (Ar−C$_{ipso,S}$), 121.8, 121.1 (Ar−C$_{ortho,S}$), 119.7 ($C-CH_2-CH$═CH_2), 119.0 (Ar−C$_{meta,S}$), 116.8 ($N-CH_2-CH$═CH_2), 107.8 (Ar−C$_{ortho,N}$), 83.2 (C$_{quart}$), 47.3 ($N-CH_2$), 42.8 ($C-CH_2$). Anal. Calcd for $C_{20}H_{18}N_2S_2$: C, 68.54; H, 5.18; N, 7.99; S, 18.29. Found: C, 68.34; H, 5.42; N, 7.94; S, 18.14.

1,5-Cyclooctadiene(benzothiazole)iridium(I) Bromide (3). A sample of [Ir(μ-OMe)(cod)]$_2$ (200 mg, 0.3 mmol) is stirred with 3-(2-propenyl)benzothiazolium bromide, (H-**1**)Br (154 mg, 0.6 mmol), in acetone (8 mL) for 4 h. Afterward, the solvent is decanted and the crude solid product is washed with methanol (2 × 4 mL). Purification of the yellow solid obtained is achieved by recrystallization from CH_2Cl_2. Complex **3** is obtained as off-white crystals suitable for an X-ray diffraction study. Yield: 230 mg (74%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 9.16 (s, 1H, NCHS), 8.92 (d, 1H, Ar−H), 7.95 (d, 1H, Ar−H), 7.66 (t, 1H, Ar−H), 7.55 (t, 1H, Ar−H), 4.69 (s, 2H, cod−CH), 3.24 (s, 2H, cod−CH), 2.32 (s, 4H, cod−CH_2), 1.62 (s, 2H, cod−CH_2), 1.45 (s, 2H, cod−CH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 153.7 (NCS), 149.6 (Ar−C$_{ipso,N}$), 127.3 (Ar−C$_{meta,N}$ and Ar−C$_{meta,S}$), 124.9 (Ar−C$_{ortho,N}$), 124.6 (Ar−C$_{ipso,S}$), 122.3 (Ar−C$_{ortho,S}$), 70.1 (cod−CH *trans* to benzothiazole), 60.0 (cod−CH *trans* to bromide), 31.3, 31.1 (cod−CH_2). MS (MALDI-TOF): *m*/*z* 435 [M − Br]$^+$. Anal. Calcd for $C_{15}H_{17}NBrIrS$: C, 34.95; H, 3.32; N, 2.72. Found: C, 34.61; H, 3.12; N, 2.41.

1,5-Cyclooctadiene(3-propylbenzothiazolin-2-ylidene)iridium Bromide (4). A sample of [Ir(μ-Cl)cod]$_2$ (336 mg, 0.5 mmol) and $AgBF_4$ (195 mg, 1.0 mmol) are dissolved in acetonitrile (20 mL) and stirred for 30 min at ambient temperature. The precipitated silver chloride is removed by filtration over Celite, 3-(2-propenyl)-benzothiazolium bromide, (H-**1**)Br (256 mg, 1.0 mmol), is added to the filtrate, and the mixture is stirred for 5 min. After this, NaH (24 mg, 1.0 mmol) is added and the reaction mixture is stirred overnight in a sealed flask. After removal of the solvent in vacuo, the crude product is purified by column chromatography (SiO_2, CH_2Cl_2) to give **3** as colorless crystals. Yield: 342 mg (61%). ^{1}H NMR (200.1 MHz, CD_2Cl_2,): δ 7.72, 7.57 (d, 2H, Ar−H$_{ortho}$), 7.45, 7.33 (t, 2H, Ar−H$_{meta}$), 5.14−4.62 (m, 4H, NCH_2 and cod−CH *trans* to carbene), 3.22−2.84 (m, 2H, cod−CH *trans* to bromide), 2.38−2.17 (m, 4H, cod−CH_2), 2.05−1.81 (m, 2H, NCH_2CH_2), 1.75−1.58 (m, 4H, cod−CH_2), 1.12 (t, 3H, CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2,): δ 218.9 (NCS), 144.4, 135.9 (Ar−C$_{ipso}$), 126.5, 124.3 (Ar−C$_{meta}$), 122.0, 113.6 (Ar−C$_{ortho}$), 89.2 (cod−CH *trans* to carbene), 60.1 (cod−CH *trans* to bromide), 56.5 ($N-CH_2$), 33.6, 29.9 (cod−CH_2), 22.3 ($NCH_2CH_2CH_3$), 11.6 (CH_3). MS (MALDI-TOF): *m*/*z* 478 [M − Br]$^+$. Anal. Calcd for $C_{18}H_{23}NBrIrS$: C, 38.77; H, 4.16; N, 2.51. Found: C, 39.21; H, 4.18; N, 2.56.

1,5-Cyclooctadiene)[3-(2-propenyl)benzothiazolin-2-ylidene]-iridium(I) Bromide (5). A sample of [Ir(μ-Cl)(cod)]$_2$ (336 mg, 0.5 mmol) and $AgBF_4$ (195 mg, 1.0 mmol) are dissolved in acetonitrile (20 mL) and stirred for 30 min at ambient temperature. The precipitated silver chloride is removed by filtration over Celite. Under an argon atmosphere 3-(2-propenyl)benzothiazolium bromide, (H-**1**)Br (256 mg, 1.0 mmol), is added and the reaction mixture is stirred for 5 min. Subsequently, KO^{t}Bu (112 mg, 1.0 mmol) is added and the reaction mixture is stirred overnight. The solvent is removed by filtration and the solid obtained is extracted

with CH_2Cl_2. Removal of the solvent gives crude **5**, which is recrystallized from CH_2Cl_2 to yield colorless crystals of **5**. Yield: 247 mg (42%). ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 7.73 (d, 1H, Ar−$H_{ortho,S}$), 7.52 (d, 1H, Ar−$H_{ortho,N}$), 7.46 (t, 1H, Ar−$H_{meta,N}$), 7.36 (t, 1H, Ar−$H_{meta,S}$), 4.98 (t, 1H, cod−CH), 4.53 (dd, 1H, $^2J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 5.7 Hz NC*H*′H), 4.30 (m, 1H, NCH_2CH=CH_2), 4.17 (dd, 1H, $^2J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 1.1 Hz, NCH′*H*), 3.54, 3.52, 3.44 (3 × t, 3H, cod−CH), 3.06, 2.67, 2.64, 2.40, 2.33, 2.23 (6 × m, 7H, cod−CH_2), 1.99 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^2J_{HH}$ = 2.2 Hz, NCH_2CH=CH*H*$_{cis}$), 1.90 (m, 1H, cod−CH_2), 1.86 (dd, 1H, $^3J_{HH}$ = 8.9 Hz, $^2J_{HH}$ = 2.2 Hz, NCH_2CH=CH*H*$_{trans}$). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 202.1 (NCS), 142.5 (Ar−$C_{ipso,N}$), 135.6 (Ar−$C_{ipso,S}$), 127.2 (Ar−$C_{meta,N}$), 124.9 (Ar−$C_{meta,S}$), 123.0 (Ar−$C_{ortho,S}$), 114.3 (Ar−$C_{ortho,N}$), 99.6 (cod−CH), 95.8 (cod−CH), 68.2 (cod−CH), 59.0 (cod−CH), 55.5 (NCH_2), 43.0 (NCH_2*C*H=CH_2), 38.5 (cod−CH_2), 33.4 (cod−CH_2), 31.3 (NCH_2CH=*C*H_2), 30.3 (cod−CH_2) 28.6 (cod−CH_2). MS (MALDI-TOF): *m*/*z* 476 [M − Br]$^+$. Anal. Calcd for $C_{18}H_{21}NBrIrS$: C, 38.92; H, 3.81; N, 2.52. Found: C, 38.74; H, 3.71; N, 2.49.

(3-Propylbenzothiazolin-2-ylidene)dicarbonyliridium(I) Bromide (6). CO is bubbled through a solution of **4** (200 mg, 0.40 mmol) in dichloromethane (10 mL) for 20 min. After removing the solvent in vacuo, complex **6** is isolated as a yellow solid in quantitative yield. ^{1}H NMR (200.1 MHz, CD_2Cl_2,): δ 7.93, 7.78 (2 × d, 2H, Ar−H_{ortho}), 7.64, 7.55 (2 × t, 2H, Ar−H_{meta}), 4.87 (t, 2H, NCH_2), 2.07 (m, 2H, NCH_2C*H*$_2$), 1.10 (t, 3H, CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ 209.2 (NCS), 181.5 (CO), 168.5 (CO), 143.8, 136.0 (Ar−C_{ipso}), 127.8, 126.2 (Ar−C_{meta}), 122.8, 115.0 (Ar−C_{ortho}), 57.4 (NCH_2), 22.5 (NCH_2*C*H$_2$), 11.5 (CH_3). IR (CH_2Cl_2): ν(CO): 2071, 1992 cm^{-1} (similar intensities). MS (EI): *m*/*z* (%) 505 (57.4) [M]$^+$, 477 (32.9) [M − CO]$^+$, 449 (52.20) [M − 2CO]$^+$. Anal. Calcd for $C_{12}H_{11}NBrIrO_2S$: C, 28.52; H, 2.19; N, 2.77. Found: C, 28.66; H, 2.21; N, 2.71.

X-ray Diffraction Studies. Diffraction data for (H-**1**)Br and **2**−**5** were collected with a Bruker APEX CCD diffractometer equipped with a rotating anode at 153(2) K using graphite-monochromated Mo Kα radiation. Data were collected over the full sphere and were corrrected for absorption. Structure solutions were found by direct methods (for (H-**1**)Br) or by the Patterson method. Structure refinement was carried out by full-matrix least squares on F^2 using SHELXL-97[19] using first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. The asymmetric unit of **5** contains two almost identical molecules. Hydrogen atom positions were calculated and refined riding on carbon atoms. The highest electronic residuals for the iridium complexes were found in close vicinity to the iridium atoms and make no chemical sense. Additional data collection and refinement parameters can be found in Table 1.

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Supporting Information Available: X-ray crystallographic file for the complexes (H-**1**)Br and **2**−**5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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