A benzothiadiazole-supported *N*-heterocyclic carbene and its rhodium and iridium complexes

Daniela Tapu^{a,*}, Ossie J. Buckner^a, Chance M. Boudreaux^a, Bradley Norvell^a, Monica Vasiliu^b, David A. Dixon^b, and Colin D. McMillen^c

^a *Department of Chemistry and Biochemistry, Kennesaw State University, 1000 Chastain Road, Kennesaw, GA, 30144, USA*

^b *Department of Chemistry, The University of Alabama, Shelby Hall, Tuscaloosa, AL 35487-0336, United States*

^c *Department of Chemistry, Clemson University, Hunter Laboratories, Clemson, SC, 29634, USA*

*Corresponding author. Tel.: 1-470-578-2259; fax: 1-470-578-6744. Email address: dtapu@kennesaw.edu (D. Tapu).

ABSTRACT A new *N*-heterocyclic carbene containing a fused benzothiadiazole (BTD) moiety, 5,7-bis(1,1-dimethylethyl)-5*H*-imidazo[4,5-*f*]-2,1,3-benzothiadiazol-6-ylidene (**1**), was generated by deprotonation of the corresponding tetrafluoroborate salt. The salt precursor was accessed in six steps from the commercially available 1,2-phenylenediamine. This carbene was found to be stable under inert conditions and it was fully characterized by NMR spectroscopy. The sulfur adduct of this carbene was also synthesized and fully characterized. The X-ray structure analysis of the thione revealed that the carbene carbon and the sulfur atom deviate from the plane containing the BTD moiety and the two nitrogen atoms of the imidazole ring by 0.231 and 0.890 Å, respectively. Complexes of type [MCl(COD)(**1**)] (where M =

Rh and Ir) were prepared and characterized using spectroscopic and crystallographic methods. The donor strength of this new carbene was determined by IR spectroscopy (ν_{av}) and cyclic voltammetry ($E_{1/2}$). Preliminary catalytic studies show that the new carbene is a suitable ligand for rhodium and iridium catalysts in the hydrosilylation of acetophenones.

Keywords:

Fused *N*-heterocyclic carbene
5*H*-imidazo[4,5-*f*]-2,1,3-benzothiadiazol
Rhodium
Iridium
Catalytic activity
Hydrosilylation
Annulation

1. Introduction

The use of *N*-heterocyclic carbenes (NHC) as ancillary ligands in organometallic chemistry and homogeneous catalysis is still an area of intense activity 25 years after the isolation and crystallographic characterization of the first stable NHC in early 1991 [1]. NHCs comprise a remarkably varied class of carbon-based ligands with unique electronic and steric properties [2-8]. Many NHC metal complexes are now well recognized as efficient catalysts in a plethora of reactions such as cross-coupling, olefin metathesis, and hydrogenation [4, 6, 9]. To extend the possibilities of ligand tuning and the scope of NHC-based catalysts, structural variations influencing the electronic and steric properties are desirable. One such approach is annulation at the C4-C5 position of the of the typical 5-membered ring parent system (Fig. 1, **I**) with aromatic carbo- or heterocycles. It was observed that this type of annulation has a significant impact on the stability and the electronic nature of NHCs [10-23]. The electron density at the carbene center varies with the π donor or acceptor properties of the annulated rings [10-23]. Despite their proven utility in

catalysis, coordination and polymer chemistry and materials science, only a few monoNHCs that incorporate a fused polycyclic heteroaromatic moiety have been studied so far (Fig. 1, **II-VIII**) [10-18].

Fig. 1. Examples of monoNHCs featuring fused polycyclic heteroaromatic moieties.

This contribution reports our investigation toward the synthesis and reactivity of a new polycyclic heteroaromatic carbene: 5,7-bis(1,1-dimethylethyl)-5*H*-imidazo[4,5-*f*]-2,1,3-benzothiadiazol-6-ylidene (**1**). 2,1,3-Benzothiadiazole (BTD) and its derivatives are a class of aromatic compounds with interesting electronic properties [24]. In recent years, these compounds have attracted significant attention in the area of heterocyclic, coordination, and materials chemistry. For example, they have been used as components of organic-light-emitted diodes and as structural units of low-band gap polymers for photovoltaic applications [24-33]. They have also found applicability as ligands in transition metal complexes [34-40]. Annulation of a BTD moiety to an imidazol-2-ylidene provides a promising framework in which the carbene center is a component of an electron-rich, extended aromatic system. It is expected that the extended π -system should have a significant effect on the donor properties of the carbene center. In addition, carbene **1** displays

several potential coordination sites which could lead to the synthesis of novel heterobimetallic complexes or metal-organic frameworks. The focus of this work is the synthesis and full characterization of this novel carbene. In addition, the synthesis and characterization of its corresponding monometallic complexes $[MCl(COD)(\mathbf{1})]$ (with $M = Rh$ and Ir) are also described. Preliminary studies of the catalytic performance of these metal complexes in the hydrosilylation of acetophenone and its derivatives are reported as well.

2. Results and discussion

2.1. Chemical Synthesis Studies

2.1.1. Synthesis of the Carbene Precursor

Imidazolium salts are the most common precursors used to generate NHCs [1]. Scheme 1 summarizes the six steps necessary to access imidazolium salt **4** from the commercially available 1,2-phenylenediamine. Using published protocols 1,2-phenylenediamine was converted into 5,6-dibromo-2,1,3-benzothiadiazole (**2**) [41]. A Buchwald-Hartwig amination was employed to convert **2** to diamine **3**, which was used without further purification to generate the imidazolium salt precursor **4** by a ring closing reaction with triethylorthoformate and tetrafluoroboric acid. The tetrafluoroborate salt **4** was targeted to avoid potential halide exchange and any subsequent separation problems in reactions involving metal chlorides. The 1H and ^{13}C NMR spectra of **4** are consistent with the proposed structure. In the 1H NMR spectrum, the characteristic imidazolium proton appears at δ 9.02 ppm in d_6 -DMSO, while the ^{13}C NMR signal of NCN carbon appears at δ 146.64 ppm (d_6 -DMSO). Interestingly, this value is the median of the chemical shifts of the NCN carbons of 1,3-bis(1,1-dimethylethyl) benzimidazolium chloride (δ 139.1 ppm in d_6 -DMSO) and the saturated 1,3-bis(1,1-dimethylethyl) imidazolinium chloride (δ 153.5 ppm in d_6 -DMSO) [8]. The unsaturated analogue, 1,3-bis(1,1-dimethylethyl) imidazolium chloride, displays the NCN carbon at δ 132.7 ppm in d_6 -DMSO.

(i) 1) TsCl, Py; 2) Br₂, acetic acid, NaOAc;
 3) H₂SO₄ 4) SOCl₂, Et₃N; (ii) *t*-BuNH₂,
 NaOtBu, Pd catalyst; (iii) HC(OEt)₃, HBF₄.

Scheme 1. Synthesis of imidazolium salt **4**.

2.1.2. Generation of Carbene **1** and its Corresponding Thione **8**

Having isolated **4**, subsequent efforts focused on exploring the synthesis and characterization of the target carbene **1**. The treatment of **4** with potassium *t*-butoxide (KOtBu) or potassium bis(trimethylsilyl)amide (KHMDs) in anhydrous toluene at room temperature afforded the free carbene **1** (Scheme 2), as evidenced by the disappearance of the acidic proton signal at δ 9.02 ppm in the compound's ¹H NMR spectrum. In addition, the ¹³C NMR spectrum of **1** revealed a signal for the carbenic carbon at δ 243.44 ppm (*d*₆-benzene), a 96.8 ppm downfield shift relative to **4**. Surprisingly, this chemical shift is much higher than those displayed by 1,3-bis(1,1-dimethylethyl)imidazol-2-ylidene (**5**) (δ ¹³C2 = 212.58 ppm, *d*₆-benzene) and 1,3-bis(1,1-dimethylethyl)benzimidazol-2-ylidene (**6**) (δ ¹³C2 = 224.7, *d*₆-benzene), its non-annulated and benzannulated counterparts (Table 1) [8]. To our knowledge, this chemical shift is the highest chemical shift reported to date for an annulated imidazol-2-ylidene and it is within the characteristic range observed for saturated imidazolidin-2-ylidenes. For example, the saturated 1,3-bis(1,1-dimethylethyl)imidazolidin-2-ylidene (**7**) displays the chemical shift for the carbenic carbon at δ 238.2 ppm

(*d*₆-benzene) [8]. Overall, this data suggests a decreased π -charge density at the carbenic carbon of **1** in comparison to **5** and **6** and it is consistent with a higher anisotropy at the carbene center due to a lower population of the carbene p_{π} -orbital.

Table 1. Summary of NMR and IR Spectroscopic Data

Carbene	δ C _{carbene} (ppm) (free carbene)	δ C _{carbene} (ppm) in [RhCl(CO) ₂ (NHC)]	ν_{CO}^{av} (cm ⁻¹) for [RhCl(CO) ₂ (NHC)]	TEP (cm ⁻¹) ^c
(5)	212.58 ^a [8]	171.80 ^a	2036	2047
(6)	224.7 ^a [8]	180.95 ^a	2036.5	2047
(7)	238.2 ^a [8]	201.46 ^b	2036.5	2047
1	243.4 ^a	195.73 ^b	2041	2051

^ain *d*₆-benzene. ^bin CDCl₃. ^cThe TEP values were calculated from the corresponding [RhCl(CO)₂(NHC)] complexes using Nolan's method [7].

On a practical note, this carbene was found to be stable in anhydrous benzene and toluene for at least three days. In the solid state, carbene **1** can be stored under a dry nitrogen atmosphere for several weeks without significant decomposition, as determined by NMR spectroscopy. This carbene is soluble in benzene, toluene, and hexane.

The corresponding thione **8** was formed by slow deprotonation of **4** with KO*t*Bu in the presence of excess sulfur (Scheme 2). After column chromatography, the thione was obtained as a bright yellow, air stable solid in 70 % yield (Mp = 149 °C). The molecular structure of **8** was confirmed by ¹H and ¹³C NMR spectroscopy, X-ray crystallography and elemental analysis. In the ¹³C NMR spectrum of thione **8**, the signal for the N₂CS carbon atom appears at a typical chemical shift of δ 177.35 ppm (CDCl₃).

Scheme 2. Synthesis of carbene **1** and its sulfur adduct **8**.

2.1.3. Synthesis of Metal Complexes

Upon characterization of the free carbene and its corresponding thione **8**, subsequent efforts were focused on its coordination to various transition metals. Three different synthetic routes are mainly used to access the metal complexes of NHCs: (i) the direct complexation of the free carbene, (ii) the *in situ* deprotonation of carbene precursors (carbenium ions), and (iii) transmetalation. Rhodium(I) and iridium(I) complexes **9** and **10** were prepared by *in situ* deprotonation of the salt **4** with KHMDS in the presence of rhodium or iridium dimers [MCl(COD)]₂ (M = Rh, Ir) (Scheme 3). Both reactions were conducted at room temperature in inert conditions. Since both complexes are air- and moisture-stable, they were purified by column chromatography on silica gel. These complexes are well soluble in halogenated solvents (CH₂Cl₂, CHCl₃), and they have some solubility in benzene and toluene. The identity of the compounds was confirmed by ¹H and ¹³C-NMR spectroscopy, X-ray crystallography, as well as elemental analysis. As a clear evidence of complex formation, the ¹³C NMR spectra of **9** and **10** show the expected signals for the carbenoid carbon shifted upfield at δ 211.25 and 206.51 ppm in *d*₂-CH₂Cl₂, respectively, if compared to the free carbene **1**. The rhodium complex displays a ¹⁰³Rh-¹³C coupling constant of ¹J_{Rh-C} = 48.3 Hz for the carbenoid carbon.

Scheme 3. Synthesis of rhodium and iridium complexes **9**, **10** and **11**.

Metal-bound carbonyls in compounds such as $[\text{MCl}(\text{CO})_2(\text{NHC})]$ with $\text{M} = \text{Rh}, \text{Ir}$, are valuable spectroscopic handles for measuring the electron density at the coordinated metal centers [7, 42]. A typical way to generate these type of dicarbonyl complexes is to bubble CO gas into a saturated solution of the $[\text{MCl}(\text{COD})(\text{NHC})]$ complex at room temperature. This method failed to produce the desired dicarbonyl complexes starting from **9** or **10**, probably due to steric shielding of the bulky *t*-butyl groups which prevents coordination of the incoming ligand [43]. Fortunately, the deprotonation of **4** in the presence of $[\text{RhCl}(\text{CO})_2]_2$ led to the desired rhodium carbonyl complex **11** in 86% yield (Scheme 3). The ^{13}C NMR spectra of **11** shows the signal for the carbenoid carbon at δ 195.7 ppm in CDCl_3 ($^1J_{\text{Rh-C}} = 41.9$ Hz) (Table 1).

2.2. Assessment of the Ligand Donating Properties of Carbene **1**

Initially, the ligand-donating ability of carbene **1** was investigated by analyzing the carbonyl complex **11** using IR spectroscopy. This method is particularly useful for the evaluation of donor properties of the NHC ligands via CO stretching frequencies of metal carbonyls [7, 42]. The complex **11** exhibited carbonyl stretching frequencies at 2080 cm^{-1} and 2002 cm^{-1} . The average value $\nu_{\text{av}} = 2041\text{ cm}^{-1}$ was used to calculate the Tolman electronic parameter ($\text{TEP} = 2051\text{ cm}^{-1}$) of **1** [44, 45]. To make a direct comparison of

the experimental TEP value of **1** with those of carbenes **5-7**, rhodium complexes [RhCl(CO)₂(NHC)] (NHC = **5**, **6**, and **7**) were also prepared. The average values ν_{av} for these complexes and the TEP values obtained for carbenes **5-7** are summarized in Table 1. The IR spectroscopy data suggest that the annulation with BTM moiety of the 5-membered parent ring resulted in a slightly attenuated ligand donicity relative to those of its non-annulated and benzannulated counterparts. However, the TEP value of **1** is comparable to that displayed by other saturated imidazolidin-2-ylidene (e.g. 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene with a TEP value of 2050.8) [7].

Cyclic voltammetry measurements were also carried out on rhodium and iridium complexes **9** and **10** [46]. Table 2 summarizes the results of the cyclic voltammetry experiments. Complexes **9** and **10** exhibit quasi-reversible redox processes at + 0.683 V ($\Delta E_{1/2} = 79$ mV) and + 0.662 V ($\Delta E_{1/2} = 84$ mV) that are attributed to M^{I/II} couples. These values are within the range reported for other non-annulated NHC-supported [MCl(COD)] complexes ($E_{1/2} = 0.648 - 0.920$ V) [46].

Table 2
Summary of Electrochemical Data^a

	$E_{1/2}$ (V)	ΔE (mV)	E_{pa} (V)	E_{pc} (V)
9	0.683	79	0.723	0.644
10	0.662	84	0.704	0.620

^a The electrochemical data were obtained in CH₂Cl₂ in the presence of 0.1 M [Bu₄N][PF₆] electrolyte with decamethylferrocene (Fc*) as an internal standard (100 mV s⁻¹ scan rate), referenced to SCE.

2.3. Structural studies

X-ray quality crystals of the carbene precursor **4** were obtained by slow evaporation of a saturated acetonitrile solution. Selected bond lengths and angles are given in Table 3. This compound crystallizes in the monoclinic space group $P2_{(1)}/n$. The crystallographic analysis revealed the expected planar framework of **4** as shown in the ORTEP plot in Figure 2. The BTM moiety is in its quinoidic form. The short C2-N bond lengths (1.326(3) and 1.330(3) Å) imply a substantial double-bond character. The N1-C2-N3 angle

measures 112.5(2) degrees which is consistent with the values previously reported for other carbenium salts featuring *tert*-butyl N-substituents [47, 48].

Table 3

Selected bond lengths (Å) and angles (deg) for compounds **4**, **8**, **9** and **10**

	4	8	9	10^a
N3-C2	1.326(3)	1.3909(15)	1.369(6)	1.396(10)
N3-C4	1.401(3)	1.3980(16)	1.405(6)	1.386(11)
C4-C5	1.368(3)	1.3730(18)	1.3689(7)	1.356(13)
C5-C6	1.405(3)	1.4184(18)	1.420(7)	1.424(14)
C6-N7	1.356(3)	1.3506(17)	1.342(6)	1.339(14)
N7-S8	1.603(2)	1.6199(12)	1.611(5)	1.619(10)
S1-C2	-	1.6554(19)	-	-
M-C2	-	-	2.049(5)	2.006(12)
M-Cl1	-	-	2.4391(15)	2.389(4)
M-C21	-	-	2.110(6)	2.121(11)
M-C22	-	-	2.115(6)	2.121(11)
M-C25	-	-	2.174(6)	2.144(10)
M-C26	-	-	2.215(6)	2.144(10)
M-C2-N1	-	-	126.8(3)	128.3(5)
M-C2-N3	-	-	126.2(3)	128.3(5)
N1-C2-N3	112.5(2)	107.21(15)	106.3(4)	102.0(10)
N7-S8-N9	101.76(11)	101.56(9)	100.8(3)	98.8(7)
Cl1-M-C2	-	-	92.25(14)	96.3(4)
Cl1-M-C21	-	-	161.8(2)	160.2(3)
Cl1-M-C22	-	-	160.2(2)	160.2(3)
Cl1-M-C25	-	-	90.4(2)	86.2(4)
Cl1-M-C26	-	-	90.0(3)	86.2(4)

^a Structural data for one of the four unique molecules in the asymmetric unit.

Fig. 2. Molecular structure of salt **4** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

The crystal structure of thiourea **8** is shown in Figure 3. X-ray quality crystals were obtained by slow evaporation of a saturated toluene solution of **8**. Selected bond lengths and angles are given in Table 3. Compound **8** crystallizes in a monoclinic space group $C2/m$ and the quinoidic structure of the BTD core is also retained. The C=S bond of 1.655(19) Å is within the expected range for a C=S double bond [48]. Interestingly however, the carbene carbon and the sulfur atom deviate from the plane defined by the constituting atoms of the BTD moiety and the two nitrogen atoms of the imidazole ring by 0.231 and 0.890 Å, respectively. The C=S bond deviates from the plane of the molecule by 24.6° (Figure 3, bottom). To our knowledge no such large deviation from planarity has been observed before for related thiones. The steric hindrance provided by the bulky *t*-butyl groups is most likely the cause of this structural arrangement.

Fig. 3. (Top) Molecular structure of thione **8** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. The ellipsoids are much smaller since that data was collected at 100 K. (Bottom) Side view of the molecular structure showing the out-of-plane C=S bond.

The rhodium and iridium complexes **9** and **10** crystallizes in the monoclinic space group $P2_1/n$ and $P2_1/m$, respectively. The asymmetric unit of **10** contains four unique half-molecules. Selected bond lengths and angles are shown in Table 3. Rhodium and iridium centers are coordinated in square planar fashion by the carbene, the centers of the two C=C bonds of COD ligand, and the chloride (Figures 4 and 5). The metal coordination planes are quasi-perpendicular with respect to the coordinated carbene plane. The rhodium and iridium centers deviates from the plane defined by the constituting atoms of the BTD moiety and the two nitrogen atoms of the imidazole ring by 0.609 Å and 0.788 Å (average), respectively; a similar deviation was observed for the rhodium complex derived from a *t*-butyl substituted triphenylene-based trisNHC [49]. The deviation of the carbene carbon from the same plane is only 0.122 Å for **9** and 0.136 Å (average) for **10**.

Fig. 4. Molecular structure of **9** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Fig. 5. Molecular structure of **10** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

2.4 Computational studies

The electronic structure of the target carbene **1** was predicted using computational methods. The calculated geometric parameters of **1** and the metal complexes **9** and **10** are in good agreement with the crystallographically determined molecular structures. The structure of thione **8** was also optimized at the same level of theory and a deviation of C=S bond of about 25° from the plane defined by the BTD moiety and the two nitrogen atoms of the imidazole ring was predicted in excellent agreement with the experimental deviation of 25° showing this to be a molecular property and not one due to crystal packing forces. The C=S bond was calculated to be 1.670 Å as compared to an experimental value of 1.655 Å.

The results of density functional calculations performed at the B3LYP/DZVP2 level show that **1** has a HOMO-LUMO gap of 3.50 eV which is considerably smaller than those calculated for **5** and **7** (6.28 and 6.23 eV, respectively); Carbene **6** has an intermediate gap of 4.82 eV. The HOMO of **1** (Figure 6) is mostly localized on the carbene carbon and is in-the-plane sp^2 -like. The LUMO of **1** is a π -type LUMO and is significantly stabilized with a Koopmanns-type electron affinity of 2.5 eV and is mostly localized in the N-S-N region.

The calculated gas phase ^{13}C NMR chemical shifts of the carbene carbon of **1**, **5**, **6**, and **7** and their corresponding metal complexes ($\text{M} = \text{Rh}$ and Ir) are higher by < 20 ppm as compared to the experimental ones, and follow the same trends as observed experimentally (Appendix A). The calculated averaged stretching frequencies are higher by up to 25 cm^{-1} as compared to the corresponding experimental ones, which is good agreement, and show the same basic trends (Appendix A).

Fig. 6. Comparison of frontier molecular orbitals of **1**, **5**, **6**, and **7**.

The gas phase UV-Vis absorption spectra of the carbenes were calculated at the TD-DFT level. The first calculated singlet transition is the HOMO $\rightarrow$ LUMO (σ lone pair $\rightarrow \pi^*$, either on the substituent ring or the π bond in the NHC ring) with essentially no intensity for all the carbenes with the exception of **7** where $f = 0.016$ (Table 4). For **1**, the most intense transition is the HOMO-2 $\rightarrow$ LUMO $\pi \rightarrow \pi^*$ at 302 nm with a significant component of HOMO-2 on the sulfur atom. The next most intense transition is at 394 nm

(HOMO-1 $\rightarrow$ LUMO) with HOMO-1 mostly on the benzene ring. For **6** the most intense transition in the first 3 is at 253 nm and is the HOMO-1 $\rightarrow$ LUMO where HOMO-1 is similar to HOMO-2 of **1**. For **5** and **7**, there are no transitions above 250 nm.

Table 4

Gas phase excitation energies (H= HOMO, L=LUMO)

	Symm.	Transition	eV	nm	f
1					
1	1B_1	H $\rightarrow$ L	441	2.81	0.0
2	1B_2	H-1 $\rightarrow$ L	394	3.15	0.034
3	1A_1	H-2 $\rightarrow$ L	302	4.10	0.372
5					
1	$^1A''$	H $\rightarrow$ L	238	5.20	0.0
2	$^1A'$	H $\rightarrow$ L+1	224	5.54	0.016
3	$^1A''$	H-1 $\rightarrow$ L	190	6.51	0.092
6					
1	1B_1	H $\rightarrow$ L	298	4.15	0.0
2	1A_2	H $\rightarrow$ L+1	253	4.90	0.0
3	1A_1	H-1 $\rightarrow$ L	253	4.91	0.051
7					
1	1A	H $\rightarrow$ L	244	5.08	0.016
2	1A	H-1 $\rightarrow$ L	207	5.98	0.199

2.5. Catalytic studies

The catalytic hydrosilylation of acetophenone and acetophenone derivatives with diphenylsilane was chosen as a model reaction to evaluate the catalytic potential of complexes **9** and **10**. All catalytic experiments were carried out in d_6 -benzene in the presence of 3 equivalents of Ph_2SiH_2 and 0.96 M initial concentration of **12**. As opposed to rhodium and iridium complexes of other annulated monoNHC reported to date (*e.g.* $[MCl(COD)(V)]$ where $M = Rh, Ir$) which work at room temperature, **9** and **10** catalyze the reaction only at temperatures above 65 °C, likely a result of higher steric hindrance provided by the *t*-butyl groups [10]. All reactions were conducted with a 0.25 mol% catalyst loading. The reactions were monitored by 1H NMR spectroscopy until all of the starting material **12** was consumed. The yield of silyl

ether **13** was calculated by comparing the integration values of the CH₃ doublet and the CH quartet with that of the OCH₃ singlet of the internal standard, 1,3,5-trimethoxybenzene. Similarly, the yield of **14** was calculated by comparing the integration values of the two vinylic CH doublets with that of the OCH₃ singlet of the internal standard. The results are summarized in Table 5. The data shows that both complexes are active catalysts in this reaction. The reaction works with both electron rich and electron poor substrates. The data suggests that the more sterically hindered groups react slower. In addition, it was observed that the identity of the metal proved to have a significant effect on the outcome of the reaction. The rhodium complex **9** catalyzed the reaction much faster than its iridium counterpart **10**; however, the rhodium catalyst is less selective than iridium and forms more of the side product **13**.

Table 5
Hydrosilylation of acetophenone derivatives **12** with complexes **9** and **10**^a

Entry	Catalyst	R	Time (h)	NMR yield 13	NMR yield 14
1	9	H	1.3	65%	31%
2	10	H	12.3	89%	5%
3	9	4-OMe	1.3	75%	18%
4	10	4-OMe	6.3	98%	2%
5	9	4-F	1.0	71%	25%
6	10	4-F	9.0	90%	5%
7	9	4-CH ₃	0.6	62%	27%
8	10	4-CH ₃	9.7	94%	3%
9	9	4-Cl	1.4	60%	34%
10	10	4-Cl	9.8	92%	7%
11	9	4-Br	1.9	56%	31%
12	10	4-Br	8.3	87%	7%
13	9	2-OMe	0.5	51%	37%
14	10	2-OMe	16.0	93%	2%
15	9	2-Cl	2.2	30%	52%
16	10	2-Cl	22.5	74%	20%

17	9	2-NH ₂	1.4	79%	9%
18	10	2-NH ₂	22.0	92%	0%

^aInitial concentration: 0.96 M of **12** in *d*₆-benzene. Yields calculated by ¹H NMR spectroscopy as averages of two runs using 1,3,5-trimethoxybenzene as internal standard.

3. Conclusion

In summary, a novel benzothiadiazole-fused imidazol-2-ylidene **1** was generated by deprotonation at room temperature of the corresponding BTD-fused imidazolium tetrafluoroborate **4**. This salt precursor was obtained by a six-step synthesis from commercial available 1,2-phenylenediamine. The corresponding thione was prepared by deprotonation of **4** in the presence of excess sulfur. The thione **8** was fully characterized by NMR spectroscopy, elemental analysis and X-ray crystallography. The X-ray structure analysis of **8** revealed that the carbene carbon and the sulfur atom deviate from the plane containing the BTD moiety and the two nitrogen atoms of the imidazole ring. Details on the chemistry of this ligand with respect to its ability to support catalytically relevant metal complexes were provided. A series of metal complexes of type [MCl(COD)(**1**)] (M = Rh, Ir) and [MCl(CO)₂(**1**)] (M = Rh) have been synthesized and fully characterized. The solid state molecular structures of both COD complexes have been determined by X-ray diffraction studies. Using the data provided by the IR spectroscopic analysis of complex **11**, a TEP value of 2051 cm⁻¹ was determined for carbene **1**. To make a direct comparison of the experimental TEP value of **1** with those of **5**, **6**, and **7**, rhodium complexes [RhCl(CO)₂(NHC)] (NHC = **5**, **6**, and **7**) were also prepared and analyzed by IR spectroscopy. The data suggest that the annulation with BTD moiety of the 5-membered parent ring resulted in a slightly attenuated ligand donicity relative to those of its non-annulated and benzannulated counterparts. However, its TEP value is comparable to that displayed by other saturated imidazolidin-2-ylidenes (*e.g.* 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene has a TEP = 2050.8 cm⁻¹). Preliminary catalytic studies show that this BTD-fused NHC is a suitable ligand for rhodium and iridium catalysts in the hydrosilylation of acetophenones. The facile synthesis of **1** and its unique

topological properties renders this new system a promising scaffold well suited to function as a building block in the synthesis of homo- and heterometallic complexes and metal–organic frameworks. These studies are underway in our laboratory.

4. Experimental section

4.1. General procedures

Reagents were purchased from commercial sources and used as supplied. Dry toluene was purchased from Alfa Aesar and used as received. Reactions with air- or moisture-sensitive compounds were conducted under a nitrogen atmosphere using a glove box or Schlenk techniques. Glassware was dried at 100 °C in an oven for at least 12 hours. Column chromatography was performed using the solvent systems indicated on silica gel (63-200 μm). NMR spectra were recorded on a Bruker DPX 300 (^1H , 300 MHz; ^{13}C , 75.5 MHz). Chemical shifts are described in parts per million downfield shifted from SiMe_4 . IR spectra of the metal carbonyls were recorded on a PerkinElmer FT-IR spectrometer Frontier in CH_2Cl_2 solution as films between KBr plates. The resolution of the IR experiments was 1 cm^{-1} . Electrochemical experiments were conducted on an Epsilon Electrochemical Workstation from BASi using a three electrode cell in air at room temperature. The cell was equipped with platinum working and counter-electrodes, as well as a Ag/AgCl reference electrode containing aqueous 3 M KCl. Measurements were performed in CH_2Cl_2 with 0.1 M [tetra-*n*-butylammonium][PF₆] as the electrolyte and decamethylferrocene [Fc*] as the internal standard. All potentials were determined at a 100 mV s^{-1} scan-rate and referenced to SCE by shifting [Fc*]^{0/+} to -0.057 V [50]. Single crystal X-ray diffraction measurements were made using two different diffractometers, both equipped with Mo K α ($\lambda = 0.71073\text{ \AA}$) radiation. A Bruker D8 Venture diffractometer with an Incoatec microfocus source and a Photon 100 CMOS detector was used to measure

diffraction data at 100 K for compound **8**. Room temperature data were obtained for **4**, **9**, and **10** using a Rigaku AFC8S diffractometer with a sealed glass X-ray tube and a Mercury CCD detector.

4.2. Synthesis

4.2.1. Synthesis of **3**

To a mixture of N,N'-1,3-bis(2,6-diisopropylphenyl)imidazolium chloride [51] (0.45 g, 1.06 mmol) and Pd(OAc)₂ (0.13 g, 0.59 mmol) in toluene (4 mL), a suspension of NaO*t*-Bu (0.16 g, 1.66 mmol) in dry toluene (3 mL) was added under inert conditions. The solution was heated at 88 °C for 30 minutes. This mixture was cooled to room temperature and added to a pressure tube containing **2** [41] (2.00 g, 6.8 mmol) in toluene (70 mL). To this mixture, *tert*-butylamine (1.5 mL, 14.27 mmol) was added followed by NaO-*t*Bu (1.60 g, 16.65 mmol). The pressure tube was sealed and heated for 16 h at 130 °C. After cooling, the reaction mixture was filtered through Celite. The filtrate was collected and evaporated to yield **3** as a light brown solid (1.941 g, crude yield). The crude product was engaged in the following reaction with no further purification. ¹H NMR (CDCl₃, 300 MHz): δ 7.14 (s, 2H, Ar*H*), 3.40 (br, 2H, NH), 1.41 (s, 18H, CH₃).

4.2.2. Synthesis of **4**

A flask was charged under inert conditions with **3** (5.68 g, 15.09 mmol), triethyl orthoformate (180 mL, 1.08 mol), and aqueous HBF₄ (2.7 mL, 48 wt. %, 20.66 mmol). The reaction mixture was heated at 50 °C for 24 h. The reaction was cooled to room temperature and poured into 150 mL of diethyl ether affording the product as a tan precipitate. The solid was collected and washed with diethyl ether (3 x 40 mL). The solid was purified by trituration in hot ethanol to give after filtration a tan solid (6.83 g, 89% yield). ¹H NMR (*d*₆-DMSO, 300 MHz) δ 9.14 (s, 2H, Ar*H*), 9.02 (s, 1H, N₂CH), 1.90 (s, 18H, CH₃). ¹³C NMR (*d*₆-DMSO, 75.5 MHz): δ 151.40 (ArC), 146.64 (NCN), 134.17 (ArC), 107.19 (ArC), 62.13 [C(CH₃)₃], 28.11

(CH₃). Anal. Calcd. for C₁₅H₂₁BF₄N₄S (376.22): C, 47.89; H, 5.63; N, 14.89. Found: C, 47.98; H, 5.76; N, 14.66. Crystals suitable for X-ray diffraction analysis were grown by slow evaporation a saturated solution of **4** in acetonitrile.

4.2.3. Synthesis of **1**

To imidazolium salt **4** (30 mg, 0.08 mmol) in anhydrous toluene (2 mL), a suspension of KO*t*-Bu (9 mg, 0.08 mmol) in toluene (2 mL) was added dropwise under inert conditions. The reaction mixture was stirred at room temperature for 2 h. The mixture was filtered through Celite and the solvent was removed *in vacuo* to yield **1** as a yellow solid in quantitative yield. ¹H NMR (C₆D₆, 300 MHz): δ 7.86 (s, 2H, ArH), 1.58 (s, 18H, CH₃). ¹³C NMR (C₆D₆, 75.5 MHz): δ 243.44 (NCN), 151.79 (ArC), 139.53 (ArC), 101.22 (ArC), 58.19 [C(CH₃)₃], 30.3 (CH₃).

4.2.4. Synthesis of **8**

To a mixture of **4** (100 mg, 0.27 mmol) and excess sulfur (86 mg, 2.7 mmol) in anhydrous toluene (4 mL), a suspension of potassium KO*t*-Bu (30 mg, 0.27 mmol) in toluene (4 mL) was added slowly under inert conditions. The reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered through Celite and the solvent was evaporated. The residue was purified by flash chromatography (silica, 1:1.5:12.5 v/v diethyl ether/hexanes/petroleum ether mixture) to give **8** as a yellow solid (60 mg, 70% yield). ¹H NMR (CDCl₃, 300 MHz): δ 8.05 (s, 2H, ArH), 2.11 (s, 18H, CH₃). ¹³C NMR (CDCl₃, 75.5 MHz): δ 177.35 (NCN), 150.56 (ArC), 138.13 (ArC), 99.55 (ArC), 63.25 [C(CH₃)₃], 30.44 (CH₃). Anal. Calcd. For C₁₅H₂₀N₄S₂ (320.48): C, 56.22; H, 6.29; N, 17.48. Found: C, 56.24; H, 6.20; N, 17.59. . X-ray quality crystals were obtained by slow evaporation of a saturated toluene solution of **8**.

4.2.5. Synthesis of **9**

To imidazolium salt **4** (500 mg, 1.33 mmol) in anhydrous toluene (15 mL), a solution of KHMDS (263 mg, 1.32 mmol) in toluene (8 mL) was added slowly under inert condition. The reaction mixture was stirred at room temperature for 25 minutes. Chloro(1,5-cyclooctadiene)rhodium(I) dimer (325 mg, 0.65 mmol) in toluene (5 mL) was added to the reaction dropwise. After 12 h, the reaction mixture was filtered through Celite. The mixture was evaporated and the residue was purified by flash chromatography (silica, 3:1:4 methylene chloride:ethyl ether:hexanes as eluent) to give **9** as an orange solid (400 mg, 53% yield). ¹H NMR (C₆D₆, 300 MHz): δ 7.82 (s, 2H, ArH), 5.48 (br, 2H, CH_{COD}), 2.82 (br, 2H, CH_{COD}), 2.31-2.21 [m, 4H, (CH₂)_{COD}], 2.11 (s, 18H, CH₃), 1.67-1.46 [m, 4H, (CH₂)_{COD}]. ¹³C NMR (C₆D₆, 75.5 MHz): δ 212.3 (d, $J_{\text{Rh-C}} = 45$ Hz, NCN), 150.42 (ArC), 138.10 (ArC), 102.21 (ArC), 94.49 (d, $J_{\text{Rh-C}} = 7.6$ Hz, CH_{COD}), 67.54 (d, $J_{\text{Rh-C}} = 14.4$ Hz, CH_{COD}), 60.95 [C(CH₃)₃], 32.19 [(CH₂)_{COD}], 31.56 (CH₃), 28.63 [(CH₂)_{COD}]. ¹³C NMR (d₂-CH₂Cl₂, 75.5 MHz): δ 211.25 (d, $J_{\text{Rh-C}} = 48.3$ Hz, NCN), 150.15 (ArC), 138.38 (ArC), 102.12 (ArC), 94.72 (d, $J_{\text{Rh-C}} = 7.64$ Hz, CH_{COD}), 68.30 (d, $J_{\text{Rh-C}} = 15.27$ Hz, CH_{COD}), 61.17 [C(CH₃)₃], 32.12 [(CH₂)_{COD}], 31.75 (CH₃), 28.47 [(CH₂)_{COD}]. Anal. Calcd. for C₂₅H₃₉ClN₄RhS·0.5 CHCl₃ (625.72): C, 47.46; H, 5.50; N, 9.42. Found: C, 47.69; H, 5.68; N, 9.43. A single crystal suitable for X-ray crystallographic measurements was grown by slow evaporation of a saturated dichloromethane solution of **9**.

4.2.6. Synthesis of **10**

To imidazolium salt **4** (100 mg, 0.27 mmol) in anhydrous toluene (2 mL), a solution of KHMDS (65 mg, 0.33 mmol) in toluene (2 mL) was added slowly under inert conditions. The reaction mixture was stirred at room temperature for 25 minutes. Chloro(1,5-cyclooctadiene)iridium(I) dimer (89 mg, 0.13 mmol) in toluene (2 mL) was then added dropwise. After 24 h, the reaction was filtered through Celite. The mixture was evaporated and the residue was purified by flash chromatography (silica, 3:1:4 methylene

chloride:ethyl ether:hexanes as eluent) to give **10** as a red solid (72 mg, 43% yield). ^1H NMR (C_6D_6 , 300 MHz): δ 7.81 (s, 2H, ArH), 5.11 (br, 2H, CH_{COD}), 2.39 (br, 2H, CH_{COD}), 2.05-2.25 [m, 4H, $(\text{CH}_2)_{\text{COD}}$], 1.97 (s, 18H, CH_3), 1.46-1.58 [m, 2H, $(\text{CH}_2)_{\text{COD}}$], 1.21-1.36 [m, 2H, $(\text{CH}_2)_{\text{COD}}$]. ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 206.71 (NCN), 150.11 (ArC), 138.75 (ArC), 102.20 (ArC), 81.78 (CH_{COD}), 61.14 [$\text{C}(\text{CH}_3)_3$], 51.94 (CH_{COD}), 32.68 (CH_3), 32.68 [$(\text{CH}_2)_{\text{COD}}$], 28.80 [$(\text{CH}_2)_{\text{COD}}$]. ^{13}C NMR ($d_2\text{-CH}_2\text{Cl}_2$, 75.5 MHz): δ 206.51 (NCN), 150.18 (ArC), 138.85 (ArC), 102.18 (ArC), 81.26 (CH_{COD}), 61.04 [$\text{C}(\text{CH}_3)_3$], 51.90 (CH_{COD}), 32.61 [$(\text{CH}_2)_{\text{COD}}$], 32.49 (CH_3), 28.73 [$(\text{CH}_2)_{\text{COD}}$]. Anal. Calcd. for $\text{C}_{25}\text{H}_{39}\text{ClIrN}_4\text{S}\cdot\text{CH}_2\text{Cl}_2$ (740.27): C, 40.64; H, 4.83; N, 7.9. Found: C, 40.69; H, 4.83; N, 8.28. Slow diffusion of diethyl ether into a saturated dichloromethane solution of **10** led to X-ray quality crystals.

4.2.7. Synthesis of **11**

Under inert conditions, to a stirring solution of **4** (65 mg, 0.17 mmol) in anhydrous toluene (2 mL) a solution of KHMDS (38 mg, 0.19 mmol) in toluene (2 mL) was added slowly. After stirring for 15 minutes, the carbene solution was added dropwise to a stirring solution of di- μ -chlorotetracarbonyldirhodium(I) (34 mg, 0.087 mmol) in toluene (3 mL). After 24 h, the reaction was filtered through Celite and the solvent was evaporated. The product was purified by precipitation from dichloromethane with hexanes (72 mg, 86% yield). ^1H NMR (CDCl_3 , 300 MHz): δ 8.38 (s, 2H, ArH), 2.26 (s, 18H, CH_3). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 195.7 (d, $J_{\text{Rh-C}} = 41.90$ Hz, NCN), 185.5 (d, $J_{\text{Rh-C}} = 57.09$, CO), 182.14 (d, $J_{\text{Rh-C}} = 76.95$, CO), 150.1 (ArC), 137.7 (ArC), 104.0 (ArC), 61.4 [$\text{C}(\text{CH}_3)_3$], 32.0 (CH_3). IR ν_{CO} (cm^{-1}): 2080, 2002. HRMS-EI m/z : calcd. for $\text{C}_{17}\text{H}_{20}\text{N}_4\text{O}_2\text{SClRh}$: 482.0051; found: 482.0040. Slow decomposition of the compound prevented a correct elemental analysis.

4.2.8. Synthesis of $[\text{RhCl}(\text{CO})_2]$ (**5**)

Under inert conditions, to a mixture of 1,3-bis(1,1-dimethylethyl)imidazol-2-ylidene (0.030 g, 0.17 mmol) and di- μ -chloro-tetracarbonyldirhodium(I) (0.032 g, 0.085 mmol) THF (3 mL) was added and the solution was stirred for 3 h. The reaction mixture was evaporated to yield the product as a dark red solid (63 mg, quantitative yield). ^1H NMR (C_6D_6 , 300 MHz): δ 6.49 (s, 2H, CH), 1.58 (s, 18H, CH_3). ^{13}C NMR (C_6D_6 , 75.5 MHz): δ 186.9 (d, $J_{\text{Rh-C}} = 55.5$ Hz, CO), 184.1 (d, $J_{\text{Rh-C}} = 75.0$, CO), 171.8 (d, $J_{\text{Rh-C}} = 43.1$, NCN), 118.7 (CH), 59.0 [$\text{C}(\text{CH}_3)$], 32.2 (CH_3). IR ν_{CO} (cm^{-1}): 2076, 1996. HRMS-EI m/z : calcd. for $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_2\text{ClRh}$: 374.0268; found: 374.0258. Slow decomposition of the compound prevented a correct elemental analysis.

4.2.9. Synthesis of $[\text{RhCl}(\text{CO})_2]$ (6)

Under inert conditions, to a stirring suspension of 1,3-bis(1,1-dimethylethyl)benzimidazolium chloride (47 mg, 0.18 mmol) in anhydrous THF (2 mL) a solution of $\text{KO}t\text{-Bu}$ (25 mg, 0.22 mmol) in THF (2 mL) was added slowly. After stirring for 16 minutes, the carbene solution was added dropwise to a stirring solution of di- μ -chloro-tetracarbonyldirhodium(I) (34 mg, 0.087 mmol) in THF (2 mL). After 24 h, the reaction was filtered through Celite and the solvent was evaporated. The crude solid was extracted using diethyl ether (3 mL) to give the product as a yellow solid after drying (25 mg, 34% yield). ^1H NMR (CDCl_3 , 300 MHz): δ 7.77 (m, 2H, ArH), 7.20 (m, 2H, ArH), 2.09 (s, 18H, CH_3). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 185.9 (d, $J_{\text{Rh-C}} = 56.6$ Hz, CO), 182.5 (d, $J_{\text{Rh-C}} = 77.6$, CO), 180.9 (d, $J_{\text{Rh-C}} = 41.9$, NCN), 135.1 (ArC), 121.9 (ArC), 115.7 (ArC), 60.5 [$\text{C}(\text{CH}_3)$], 32.4 (CH_3). IR ν_{CO} (cm^{-1}): 2076, 1997. HRMS-EI m/z : calcd. for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2\text{ClRh}$: 424.0425; found: 424.0424. Slow decomposition of the compound prevented a correct elemental analysis.

4.2.10. Synthesis of $[\text{RhCl}(\text{CO})_2]$ (7)

Under inert conditions, to a stirring suspension of 1,3-bis(1,1-dimethylethyl)imidazolinium chloride (0.041

g, 0.19 mmol) in anhydrous THF (2 mL) a solution of KO^t-Bu (26 mg, 0.23 mmol) in THF (2 mL) was added slowly. After stirring for 15 minutes, the carbene solution was added dropwise to a stirring solution of di-μ- chloro-tetracarbonyldirrhodium(I) (0.030 g, 0.09 mmol) in THF (2 mL). After 24 h, the reaction was filtered through Celite and the solvent was evaporated. The crude reaction mixture was triturated with anhydrous hexanes (2 mL) to give the product as an air sensitive yellow solid (40 mg, 57% yield). ¹H NMR (C₆D₆, 300 MHz): δ 2.80 (m, 4H, CH₂), 1.48 (s, 18H, CH₃). ¹³C NMR (C₆D₆, 75.5 MHz): δ 201.4 (d, *J*_{Rh-C} = 39.07 Hz, NCN), 187.2 (d, *J*_{Rh-C} = 54.7, CO), 184.2 (d, *J*_{Rh-C} = 75.8, CO), 56.6 [C(CH₃)], 45.6 (CH₂), 31.0 (CH₃). IR ν_{CO} (cm⁻¹): 2077, 1996. HRMS-EI m/z: calcd. for C₁₃H₂₂N₂O₂ClRh: 376.0425; found: 376.0426. Slow decomposition of the compound prevented a correct elemental analysis.

4.3. Catalytic studies (Table 5)

Stock solutions of the catalysts and the internal standard were prepared by dissolving **9** or **10** (0.0242 mmols) and 1,3,5-trimethoxybenzene (internal standard, 0.32 g, 1.9 mmols) in *d*₆-benzene in a 10 mL volumetric flask. For each catalytic experiment, 0.5 mL of these stock solutions were added to an NMR tube. To each NMR tube, one of the acetophenone derivatives (0.48 mmols) and diphenylsilane (0.26 mL, 1.48 mmol) were added. The reaction was monitored by ¹H NMR spectroscopy. The yield of **13** was calculated by comparing the integration values of the CH₃ doublet and the CH quartet with that of the OCH₃ singlet of the internal standard, 1,3,5-trimethoxybenzene. The yield of **14** was calculated by comparing the integration values of the two vinylic CH doublets with that of the OCH₃ singlet of the internal standard.

Acknowledgements

This work was supported by from National Science Foundation (grant number CHE-1464281, 2015) and the Donors of the American Chemical Society Petroleum Research Fund (Grant # 50126-UNI1). DT and

BN thank Aditya Birla Carbon for their generous donation to support the Birla Carbon Scholars Program at Kennesaw State University. We thank the National Science Foundation (CHE-1058984, 2011) for financial support of the computational work (DAD). DAD also thanks the Robert Ramsay Chair Fund of The University of Alabama for support.

Appendix A. Supplementary data

A complete description of the X-ray crystallographic determination on **4**, **8**, **9** and **10** including tables of fractional coordinates, isotopic and anisotropic thermal parameters, and bond distances and angles (PDF and CIF), electrochemical data of **9** and **10**, as well as details on the computational studies (including frontier molecular orbitals, CO stretching Frequencies, and optimized XYZ coordinates) can be found in the online version, at doi: XXXX.

Appendix B. Supplementary data

CCDC ID: 1496885-1496888 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

- [1] A.J. Arduengo, III, R.L. Harlow, M.J. Kline, A stable crystalline carbene, *J. Am. Chem. Soc.*, 113 (1991) 361–363.
- [2] D. Bourissou, O. Guerret, F.P. Gabbar, G. Bertrand, Stable carbenes, *Chem. Rev.*, 100 (2000) 39–92.
- [3] R.H. Crabtree, Recent developments in the organometallic chemistry of N-heterocyclic carbenes, *Coord. Chem. Rev.*, 251 (2007) 595–896.
- [4] S. Diez-González, N-Heterocyclic carbenes: From laboratory curiosities to efficient synthetic tools, Royal Society of Chemistry, Cambridge, 2011.

- [5] S. Diez-González, N. Marion, S.P. Nolan, N-Heterocyclic carbenes in late transition metal catalysis, *Chem. Rev.*, 109 (2009) 3612–3676.
- [6] F. Glorius, N-Heterocyclic carbenes in transition metal catalysis, Springer, Berlin/Heidelberg, 2007.
- [7] D.J. Nelson, S.P. Nolan, Quantifying and understanding the electronic properties of N-heterocyclic carbenes, *Chem. Soc. Rev.*, 42 (2013) 6723–6753.
- [8] D. Tapu, D.A. Dixon, C. Roe, ¹³C NMR spectroscopy of “Arduengo-type” carbenes and their derivatives, *Chem. Rev.*, 109 (2009) 3385–3407.
- [9] S.P. Nolan, N-Heterocyclic carbenes in synthesis, Wiley-VCH, Weinheim, Germany, 2006.
- [10] D. Tapu, Z. McCarty, L. Hutchinson, C. Ghattas, M. Chowdhury, J. Salerno, D. VanDerveer, A Dibenz[a,c]phenazine-supported N-heterocyclic carbene and its rhodium and iridium complexes, *J. Organomet. Chem.*, 749 (2014) 134–141.
- [11] A.A. Webster, S.K.K. Prasad, J.M. Hodgkiss, J.O. Hoberg, An N-heterocyclic carbene phenanthroline ligand: synthesis, multi-metal coordination and spectroscopic studies, *Dalton Trans.*, 44 (2015) 3728–3736.
- [12] M. Dangalov, M. Stoyanova, P. Petrov, M. Putala, N.G. Vassilev, Fluxional Pd(II) NHC complexes - Synthesis, structure elucidation and catalytic studies, *J. Organomet. Chem.*, 817 (2016) 1–14.
- [13] H. Valdes, M. Poyatos, E. Peris, Postmodification of the electronic properties by addition of π -stacking additives in N-heterocyclic carbene complexes with extended polyaromatic systems, *Inorg. Chem.*, 54 (2015) 3654–3659.
- [14] K. Peuntinger, T.D. Pilz, R. Staehle, M. Schaub, S. Kaufhold, L. Petermann, M. Wunderlin, H. Görls, F.W. Heinemann, J. Jing Li, T. Drewello, J.G. Vos, D.M. Guldi, S. Rau, Carbene based photochemical molecular assemblies for solar driven hydrogen generation, *Dalton Trans.*, 43 (2014) 13683–13695.
- [15] H.J. Park, K. Kim, Y.K. Chung, ReI-IrI bimetallic complexes based on a bis(chelating) ligand composed of 1,10-phenanthroline and N-heterocyclic carbene: Coordination chemistry and their application for optical indicator of CO gas, *Inorg. Chim. Acta*, 410 (2014) 214–220.
- [16] H.J. Park, Y.K. Chung, Ru(II)-M(I) (M = Rh and Ir) bimetallic complexes based on a bridging ligand composed of 1,10-phenanthroline and N-heterocyclic carbene: Coordination chemistry and detection property of carbon monoxide, *Inorg. Chim. Acta*, 391 (2012) 105–113.
- [17] J.T. Price, N.D. Jones, P.J. Ragnogna, An N-Heterocyclic carbene containing a bithiophene backbone: Synthesis and coordination chemistry, *Inorg. Chem.*, 51 (2012) 6776–6783.
- [18] P. Murer, T. Gessner, C. Eickhoff, J. Birnstock, F. May, K. Kahle, Electroluminescent imidazo-quinoxaline carbene metal complexes, *PCT Int. Appl. WO 2016020516 A1*, 2016.
- [19] D.M. Khranov, V.M. Lynch, C.W. Bielawski, N-Heterocyclic carbene–transition metal complexes: Spectroscopic and crystallographic analyses of π -back-bonding interactions, *Organometallics*, 26 (2007) 6042–6049.
- [20] M.D. Sanderson, J.W. Kamplain, C.W. Bielawski, Quinone-annulated N-heterocyclic carbene–transition-metal complexes: Observation of π -backbonding using FT-IR spectroscopy and cyclic voltammetry, *J. Am. Chem. Soc.*, 128 (2006) 16514–16515.
- [21] L. Pause, M. Robert, J. Heinike, O. Köhl, Radical anions of carbenes and carbene homologues. DFT study and preliminary experimental results, *J. Chem. Soc., Perkin Trans. 2*, 2001 (2001) 1383–1388.
- [22] S. Saravanakumar, A.I. Oprea, M.K. Kindermann, P.G. Jones, J. Heinicke, Anellated N-heterocyclic carbenes: 1,3-Dineopentyl-naphtho[2,3-d]imidazol-2-ylidene: Synthesis, KOH addition product, transition-metal complexes, and annellation effects, *Chem. Eur. J.*, 12 (2006) 3143–3154.
- [23] D. Tapu, C. Owens, D. Donald VanDerveer, K. Gwaltney, The first phenanthrene-fused imidazol-2-ylidene and its transition-metal complexes, *Organometallics*, 28 (2009) 270–276.
- [24] R.T. Boéré, T.L. Roemmele, Electrochemistry of redox-active group 15/16 heterocycles, *Coord. Chem. Rev.*, 210 (2000) 369–445.

- [25] F.S. Mancilha, L. Barloy, F.S. Rodembusch, J. Dupontb, M. Pfeffera, Cyclopalladated complexes of 4-aryl-2,1,3-benzothiadiazoles: new emitters in solution at room temperature, *Dalton Trans.*, 40 (2011) 10535–10544.
- [26] P.-L.T. Boudreault, A. Najari, M. Leclerc, Processable low-bandgap polymers for photovoltaic applications, *Chem. Mater.*, 23 (2011) 456–469.
- [27] T. Linder, E. Badiola, T. Baumgartner, T.C. Sutherland, Synthesis of π -extended thiadiazole (oxides) and their electronic properties, *Org. Lett.*, 12 (2010) 4520–4523.
- [28] S. Ellinger, K.R. Graham, P. Shi, R.T. Farley, T.T. Stekler, R.N. Brookins, T. Taranekar, J. Mei, L.A. Padilha, T.R. Ensley, H. Hu, S. Webster, D. Hagan, E.W. Van Stryland, K.S. Schanze, J.R. Reynolds, Donor–acceptor–donor-based π -conjugated oligomers for nonlinear optics and near-IR emission, *Chem. Mater.*, 23 (2011) 3805–3817.
- [29] K.R.J. Thomas, J.T. Lin, M. Velusamy, Y.T. Tao, C.H. Chuen, Color tuning in benzo[1,2,5]thiadiazole-based small molecules by amino conjugation/deconjugation: Bright red-light-emitting diodes, *Adv. Funct. Mater.*, 14 (2004) 83–90.
- [30] X. Zhang, H. Gorohmaru, M. Kadowaki, T. Kobayashi, T. Ischii, T. Thiemann, S. Mataka, Benzo-2,1,3-thiadiazole-based, highly dichroic fluorescent dyes for fluorescent host–guest liquid crystal displays, *J. Mater. Chem.*, 14 (2004) 1901–1904.
- [31] Q. Hou, Q. Zhou, Y. Zhang, W. Yang, R. Yang, Y. Cao, Synthesis and electroluminescent properties of high-efficiency saturated red emitter based on copolymers from fluorene and 4,7-di(4-hexylthien-2-yl)-2,1,3-benzothiadiazole, *Macromolecules*, 37 (2004) 6299–6305.
- [32] J. Liu, Q. Zhou, Y. Cheng, Y. Geng, L. Wang, D. Ma, X. Jing, F. Wang, White electroluminescence from a single-polymer system with simultaneous two-color emission: Polyfluorene as the blue host and a 2,1,3-benzothiadiazole derivative as the orange dopant, *Adv. Funct. Mater.*, 16 (2006) 957–965.
- [33] B.A.D. Neto, A.A.M. Lapis, E.N. da Silva Júnior, J. Dupont, 2,1,3-Benzothiadiazole and derivatives: Synthesis, properties, reactions, and applications in light technology of small molecules, *Eur. J. Org. Chem.*, 2013 (2013) 228–255.
- [34] D.A. Bashirov, T.S. Sukhikh, N.V. Kuratieva, E.A. Chulanova, I.V. Yushina, N.P. Gritsan, S.N. Konchenko, A.V. Zibarev, Novel applications of functionalized 2,1,3-benzothiadiazoles for coordination chemistry and crystal engineering, *RSC Adv.*, 4 (2014) 28309–28316.
- [35] D.A. Bashirov, T.S. Sukhikh, N.V. Kuratieva, D.Y. Naumov, S.N. Konchenko, N.A. Semenov, A.V. Zibarev, Iridium complexes with 2,1,3-benzothiadiazole and related ligands, *Polyhedron*, 42 (2012) 168–174.
- [36] V.V. Davydov, I.N. Marov, V.K. Belyaeva, A.S. Katugin, B.E. Zaitsev, A.K. Molodkin, Study of coordination compounds of copper(II) with 2,1,3-benzothiadiazole derivatives, *Russ. J. Inorg. Chem.*, 26 (1981) 969–973.
- [37] M. Herberhold, A.F. Hill, The coordination chemistry of 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole. Complexes of ruthenium, osmium and iridium, *J. Organomet. Chem.*, 377 (1989) 151–156.
- [38] M. Munakata, H. He, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, Dicopper complexes derived from 4-amino-2,1,3-benzothiadiazole with versatile co-ordination number and geometry, *Chem. Soc., Dalton Trans.*, (1998) 1499–1502.
- [39] G.S. Papaefstathiou, S.P. Perlepesa, A. Escuerb, R. Vicente, A. Gantisc, C.P. Raptopoulouc, A. Tsohosc, V. Psycharisc, A. Terzisc, E.G. Bakalbassis, Topological control in two-dimensional cobalt(II) coordination polymers by π – π stacking interactions: Synthesis, spectroscopic characterization, crystal structure, and magnetic properties, *J. Solid State*, 159 (2001) 371–378.

- [40] N.A. Semenov, I.Y. Bagryanskaya, A.V. Alekseev, Y.V. Gatilov, E. Lork, R. Mews, G.V. Roeschentaler, A.V. Zibarev, New molecular complexes of trimeric perfluoro-ortho-phenylene mercury with heterocyclic compounds, *J. Struct. Chem.*, 51 (2010) 552–557.
- [41] J. Shao, J. Chang, C. Chi, Linear and star-shaped pyrazine-containing acene dicarboximides with high electron-affinity, *Org. Biomol. Chem.*, 10 (2012) 7045–7052.
- [42] T. Dröge, F. Glorius, The measure of all rings—N-Heterocyclic carbenes, *Angew. Chem., Int. Ed.*, 49 (2010) 6940–6952.
- [43] J.A.V. Er, A.G. Tennyson, J.W. Kamplain, M.V. Lynch, C.W. Bielawski, Synthesis and study of 5,5'-bibenzimidazolyliidenes and their bimetallic complexes, *Eur. J. Inorg. Chem.*, 2009 (2009) 1729–1738.
- [44] R.A.I. Kelly, H. Clavier, S. Giudice, N. Scott, E.D. Stevens, J. Bordner, I. Samardjiev, C.D. Hoff, L. Cavallo, S.P. Nolan, Determination of N-heterocyclic carbene (NHC) steric and electronic parameters using the [(NHC)Ir(CO)₂Cl] system, *Organometallics*, 27 (2008) 202–210.
- [45] C.A. Tolman, Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis, *Chem. Rev.*, 77 (1977) 313–348.
- [46] S. Leuthäuser, D. Schwarz, H. Plenio, Tuning the electronic properties of N-heterocyclic carbenes, *Chem. Eur. J.*, 13 (2007) 7195–7203.
- [47] K.A. Williams, C.W. Bielawski, Cerberus-type N-heterocyclic carbenes: synthesis and study of the first tritopic carbenes with D_{3h}-symmetry, *Chem. Commun.*, 46 (2010) 5166–5168.
- [48] K.M. Denk, S. Gupta, J. Brownie, S. Tajammul, A.J. Lough, C-H activation with elemental sulfur: synthesis of cyclic thioureas from formaldehyde amins and S₈, *Chem. Eur. J.*, 7 (2001) 4477–4486.
- [49] S. Gonell, R.G. Alabau, M. Poyatos, E. Peris, Unveiling the stereoelectronic properties of a triphenylene-based tris N-heterocyclic carbene, *Chem. Commun.*, 49 (2013) 7126–7128.
- [50] I. Noviadri, K.N. Brown, D.S. Fleming, P.T. Gulyas, P.A. Lay, A.F. Masters, L. Phillips, The Decamethylferrocenium/Decamethylferrocene Redox Couple: A superior redox standard to the ferrocenium/ferrocene redox couple for studying solvent effects on the thermodynamics of electron transfer, *J. Phys. Chem. B*, 103 (1999) 6713–6722.
- [51] P. Tang, W. Wang, T. Ritter, Deoxyfluorination of phenols, *J. Am. Chem. Soc.*, 133 (2011) 11482–11484.

Figure and Scheme Captions

Fig. 1. Examples of monoNHCs featuring fused polycyclic heteroaromatic moieties.

Fig. 2. Molecular structure of salt **4** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Fig. 3. (Top) Molecular structure of thione **8** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. The ellipsoids are much smaller since that data was collected at 100 K. (Bottom) Side view of the molecular structure showing the out-of-plane C=S bond.

Fig. 4. Molecular structure of **9** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Fig. 5. Molecular structure of **10** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Fig. 6. Comparison of frontier molecular orbitals of **1**, **5**, **6**, and **7**.

Scheme 1. Synthesis of imidazolium salt **4**.

Scheme 2. Synthesis of carbene **1** and its sulfur adduct **8**.

Scheme 3. Synthesis of rhodium and iridium complexes **9**, **10** and **11**.

A new polycyclic *N*-heterocyclic carbene featuring a fused 2,1,3-benzothiadiazol moiety was generated and characterized by ^1H and ^{13}C NMR spectroscopy. Complexes of type $[\text{MCl}(\text{COD})]$ and $[\text{MCl}(\text{CO})_2]$ ($\text{M}=\text{Rh}$ and Ir) incorporating this carbene were prepared and characterized using spectroscopic and crystallographic methods. These new metal complexes show catalytic activity in hydrosilylation of acetophenone derivatives.