# Click chemistry

# Comparing Isomeric Tridentate Carbazole-Based Click Ligands: Metal Complexes and Redox Chemistry

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**Abstract:** Two novel bis(triazolyl)carbazole ligands Hbtc1 (3,6-di(*tert*-butyl)-1,8-bis[(1-(3,5-di(*tert*-butyl)phenyl)-1,2,3-triazol-4-yl)]-9*H*-carbazole) and Hbtc2 (3,6-di(*tert*-butyl)-1,8-bis[(4-(3,5-di(*tert*-butyl)phenyl)-1,2,3-triazol-1-yl)]-9*H*-carbazole), differing in the regiochemistry of triazole attachment, have been synthesized by Cu-catalyzed azide-alkyne cyclo-addition, the so-called "click-reactions". Metalation with Ru, Zn, and Ni precursors led to the formation of M(btc)<sub>2</sub> complexes (M = Ru, Zn, Ni), with two deprotonated ligands coordinating to the metal center in tridentate fashion, forming almost perfectly octahedral coordination spheres. The redox properties of M(btc)<sub>2</sub> complexes have been investigated by

cyclic voltammetry, UV/Vis spectroscopy, spectroelectrochemistry, and chemically. The CV of the ruthenium complexes revealed three quasi-reversible one-electron oxidation processes, one assigned as the Ru<sup>II/III</sup> couple and two originating from ligand-based oxidations. The CVs of both Zn and Ni complexes contained only two oxidation waves corresponding to the oxidation of the two ligands. The oxidation potentials of complexes derived from Hbtc1 ligands were found to be 300–400 mV lower than those of the corresponding complexes derived from Hbtc2, reflecting the significant difference in donation through the N(2) or N(3) atom of the triazole moiety.

# Introduction

Since the discovery that the Huisgen 1,3-dipolar cycloaddition between terminal azides and alkynes can be catalyzed by copper salts (CuAAC), and then proceeds with exquisite conversion and regioselectivity as a "click reaction"," it has emerged as one of the most powerful synthetic tools to create covalent linkages in (bio)materials. However, the resulting 1,4disubstituted 1,2,3-triazoles are of interest beyond serving as a link between two entities, and in fact many applications of CuAAC nowadays aim at exploiting specific features of the generated triazole moieties.<sup>[2]</sup> The fact that 1,2,3-triazoles are remarkably stable and readily tunable had soon suggested their utilization as a coordination site to engage in the formation of transition metal complexes and thus triggered ligand design based on CuAAC.<sup>[3]</sup> Within the last ten years a plethora of such "click ligands" with different denticities and numbers of triazole donors has been reported.<sup>[2c]</sup> We have contributed to this field with the first "clickates" based on 2,6-bis(1-aryl-1,2,3-triazol-4-yl)pyridines (btps, Scheme 1) as a versatile motif

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**Scheme 1.** Previously reported bis(1,2,3-triazolyl)pyridine (btp),<sup>[4,5]</sup> where  $R^1 = CO_2Tg$ , OTg ( $Tg = -(CH_2CH_2O)_3CH_3$ ),  $R^2 = CH_3$ , I,  $NO_2$ ,  $N(CH_3)_2$ ,  $CO_2Et$ ,  $OCH_3$ ,  $nC_{10}H_{21}$ , and bis(1,2,3-triazolyl)carbazole (Hbtc) ligands studied in this work.

for coordination and supramolecular chemistry.<sup>[4]</sup> Btps with a wide range of substitution patterns were prepared in a modular fashion, and the redox properties as well as thermodynamic stabilities of their transition-metal complexes, in particular with Fe<sup>II</sup> and Ru<sup>II</sup>, display an excellent correlation with the electronic properties of the ligands.<sup>[5]</sup> Moreover it turned out that the btp motif has very similar binding properties as compared to terpyridine (terpy), with similar bond angles and lengths determined for Ru<sup>II</sup> complexes. Due to such structural observations, 1,2,3-triazoles are often regarded as easy-to-modify pyridine surrogates, but one has to bear in mind, that compared to pyridine they are somewhat weaker  $\sigma$ - and  $\pi$ -donors, as well as  $\pi$ acceptors.<sup>[2c]</sup> Hence, replacement of the peripheral pyridyl units in terpy by 1,2,3-triazole residues in btp leads to a destabilization of the LUMO ( $\pi^*$ ) and thus increases the energy of the <sup>3</sup>MLCT for low-spin d<sup>6</sup>-metal complexes.<sup>[2c, 5, 6]</sup>

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Based on our experience with btps, we considered exploiting the respective modular approach for the construction of new, electronically different ligands to extend the scope of our tridentate systems. In particular, we envisioned to replace the central pyridyl unit by a carbazole entity giving rise to a bis(1,2,3-triazolyl)carbazole (Hbtc, Scheme 1) ligand, for which we anticipated significantly altered properties and coordination chemistry as exemplarily detailed below for ruthenium:

1) In contrast to the charge-neutral btp, the deprotonated btc<sup>-</sup> is an anionic ligand, which would allow to access rare examples of overall neutral bis(tridentate) Ru<sup>II</sup> complexes,<sup>[7]</sup> which could be purified and vacuum-processed by evaporation/sublimation.

2) It is known for bis(tridentate) Ru<sup>II</sup> complexes that the bite angle of the ligand (158.8° for terpy, 156.7° for btp)<sup>[3a]</sup> has a strong influence on the electronic structure, as it determines the distortion from the ideal octahedron (z compression/xy elongation)–this in turn determines the relative positioning of the <sup>3</sup>MC and <sup>3</sup>MLCT states.<sup>[8]</sup> Changing from a pyridyl to a carbazole unit can be expected to enlarge the bite angle significantly, which will increase the donor strength of the triazole units.

3) Likewise, the negatively charged amido N atom of the carbazole is a much stronger donor than the pyridyl N atom in btp, which will increase the ligand field strength in z direction.

Typically, the two neighboring N atoms of a triazole differ in their donor strengths, with the N(2) being weaker than the N(3), and hence we sought to compare the two possible variants of Hbtc (Scheme 1): Hbtc1, where the terminal triazoles are connected to the carbazole through their C(4) atoms and thus the coordination involves the N(3) atoms, and Hbtc2, where the connection is inverted and involves the N(3) leading to coordination through the N(2) atoms.

Whilst Hbtc2 represents a completely new type of ligand, it should be noted that one derivative of Hbtc1 (with benzyl instead of aryl residues at the triazole N atoms) has been reported as a ligand of an in situ generated Cu complex used for cyanide sensing.<sup>[9]</sup> Very recently corresponding Co complexes have been investigated as well.<sup>[12]</sup> Another recently published compound formally belongs to the family of Hbtc ligands and was used as a precursor for bis(carbene) CNC pincer ligands; however, note that NNN tridentate coordination is not possible as the N(3) atom is alkylated.<sup>[10]</sup>

Here, we present a comparative study of the two Hbtc ligands (Scheme 1) based on first investigations on the coordination behavior of the btc2 anion and an extension of the scarce knowledge on btc1 complexes. Both ligands proved redox active, and through detailed examination of corresponding Ru, Zn, and Ni complexes we were able to reveal common properties and differences of the two isomeric ligand systems.

## **Results and Discussion**

**Ligand synthesis**: Synthesis of both ligands involved facile two-fold click reactions of the corresponding terminal building blocks to the carbazole core (Scheme 2). On the one hand, Hbtc1 was synthesized by CuAAC of the in situ generated bis-





Scheme 2. Synthetic routes to the Hbtc ligand precursors.

(*tert*-butyl)phenyl azide with the complementary 1,8-diethynylcarbazole.<sup>[9]</sup> Hbtc2, on the other hand, was obtained by starting from the 1,8-diamino-carbazole derivative,<sup>[13]</sup> which was converted to the corresponding 1,8-bisazide, followed by CuAAC with the bis(*tert*-butyl)phenyl acetylene.<sup>[14]</sup>

**Complex synthesis and structures**: All initial attempts to deprotonate the carbazole NH unit, applying various different bases, prior to a subsequent reaction with a ruthenium precursor provided the desired products only in very low yields, due to incomplete deprotonation, reprotonation by the environment, ligand decomposition, and nonuniform complexation.

Finally, the Ru(btc)<sub>2</sub> products were obtained in satisfactory yields through a route in analogy to one established for a tridentate pyrrole ligand,<sup>[7c]</sup> that is, in one step, by reaction of the Hbtc with RuCl<sub>2</sub>(DMSO)<sub>4</sub> in the presence of NEt<sub>3</sub> as a base and hot EtOH/THF as the solvent. After reflux for 24 h under anaerobic conditions, the desired complexes Ru(btc1)<sub>2</sub> and Ru(btc2)<sub>2</sub> precipitated from the reaction mixture in good yields as dark red powders. Interestingly, formation of the homoleptic complexes with a metal to ligand ratio of 1:2 was always observed, irrespective of the precursor ratio used in the reaction.

Successful metalation was indicated by the absence of a sharp band for the v(NH) stretching vibration at 3379 cm<sup>-1</sup> in the IR spectra of the crude products, and the absence of a singlet peak at 12.2 ppm in the <sup>1</sup>H NMR spectra, which are caused by the N–H unit of the free carbazole. The compositions of the Ru(btc)<sub>2</sub> compounds were further verified by ESI-MS and in the case of Ru(btc2)<sub>2</sub>, also by NMR spectroscopy. <sup>1</sup>H NMR spectra recorded for Ru(btc1)<sub>2</sub> were never interpretable (independently of the treatment or the way of workup), presumably as the complex is rather sensitive towards oxidation. Consistently, even crystals of Ru(btc1)<sub>2</sub> showed an EPR signal, as they obviously also contained the oxidized version.

Both Ru(btc1)<sub>2</sub> and Ru(btc2)<sub>2</sub> are almost insoluble in most organic solvents, but readily dissolve in chlorinated or fluorinated solvents (CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>F, etc.). Therefore, methylene chloride has been selected as the solvent for crystallization. Single crystals suitable for X-ray diffraction could be grown through slow evaporation of the volatiles from saturated solutions of the complexes. From the fact that those of Ru(btc1)<sub>2</sub> showed an EPR signal, indicating the presence of Ru(btc1)<sub>2</sub><sup>+</sup> cations, which, however, could not be further elucidated, it had to be

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concluded that there may be some ambiguity about the determined bond lengths and angles. These data are thus not discussed, whereas the principal structure is shown in the Supporting Information (Figure S5). The molecular structure of Ru(btc2)<sub>2</sub> is however reliable, and shown in Figure 1. In both cases the btc ligands are bound to the ruthenium center in tridentate modes, forming almost perfectly octahedral coordination geometries around the Ru<sup>II</sup> ions (average angle N-Ru-N in Ru(btc2)<sub>2</sub> equals 89.94(12)°). Comparison of the bond lengths in the carbazole backbone of Hbtc2 and coordinated btc2- ligands suggests that the ligands are bound as monoanions. The average Ru-N(carbazole) bond length equals 2.007(3) Å, which is, as expected, slightly shorter than typical N(pyridine) bonds found in ruthenium complexes of btps (2.02 Å). Due to the favorable positioning of the donors, the Ru-N<sub>trz</sub> bonds found in Ru(btc2)<sub>2</sub> are also slightly shorter than corresponding bond lengths observed for Ru-btp complexes (2.06 Å), with minimal differences observed within one and the same ligand: The distance Ru–N(1) (2.014(3) Å) is slightly shorter than Ru– N(5) (2.027(3) Å). The bite angles found in Ru(btc2)<sub>2</sub> are significantly larger (177.43(13) and 178.89(11)°), than corresponding angles in Ru-btp complexes (156.7°) and enable the almost perfect octahedral arrangement of the donors.



**Figure 1.** a) View of the crystal structure of Ru(btc2)<sub>2</sub>; all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru–N3 2.008(3), Ru–N10 2.006(3), Ru–N1 2.014(3), Ru–N5 2.027(3), Ru–N8 2.024(3), Ru–N12 2.016(3), N1–N2 1.378(4), N1–N7 1.317(4), N4–N5 1.369(4), N5–N6 1.305(4), N8–N14 1.314(4), N8–N9 1.371(4), N11–N12 1.370(4), N12–N13 1.313(5), N8-Ru-N12 177.43(13), N5-Ru-N1 178.89(11), N3-Ru-N10 179.75(15); b) Packing diagram of the unit cell for complex Ru(btc2)<sub>2</sub>; c) Fragment of the crystal structure showing nitrogen atom numbering scheme in Ru(btc2)<sub>2</sub>.

For comparing the redox properties of Ru(btc1)<sub>2</sub> and Ru(btc2)<sub>2</sub> (see below) we have prepared the analogous zinc(II) complexes Zn(btc1)<sub>2</sub> and Zn(btc2)<sub>2</sub> by treating Hbtc with ZnEt<sub>2</sub>, as well as the high-spin complexes Ni(btc1)<sub>2</sub> and Ni(btc2)<sub>2</sub> (an Evans measurement revealed two unpaired electrons per Ni center) by reacting NiBr<sub>2</sub>-DME (DME = 1,2-dimethoxyethane) with Hbtc in the presence of NEt<sub>3</sub>. Both Hbtc1 derived complexes, Zn(btc1)<sub>2</sub> and Ni(btc1)<sub>2</sub>, have been crystallized successfully. While the data obtained for Zn(btc1)<sub>2</sub> were not sufficient to allow for a structure discussion, the molecular structure of Ni(btc1)<sub>2</sub> is depicted, with selected bond lengths and angles, in Figure 2, as an example of a complex that contains the btc1 ligand.



**Figure 2.** a) View of the crystal structure of Ni(btc1)<sub>2</sub>·4 (acetone) all hydrogen atoms and solvent molecules omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–N1 2.032(5), Ni–N2 2.071(4), N2–N3 1.318(7), N3–N4 1.338(7), N1-Ni-N1' 180.0, N2-Ni-N2' 175.1(3); b) Fragment of the crystal structure showing nitrogen atom numbering scheme in complex Ni(btc1)<sub>2</sub>.

As expected, the Ni(btc1)<sub>2</sub> complex exhibits the same structure as its ruthenium analogs. The nickel center is located in an almost ideal octahedral coordination sphere with an average N-Ni-N bond angle of 90.03(15)°. A large bite angle, similar to the one found in Ru(btc2)<sub>2</sub>, is observed (175.1° in Ni(btc1)<sub>2</sub> vs. 178.89° in Ru(btc2)<sub>2</sub>), imposed by the steric constraint provided by the ligand. Notably, the average Ni–N(carbazole) bond in Ni(btc1)<sub>2</sub> is found to be slightly longer (2.032(5) Å) than the corresponding Ru–N(carbazole) bond in Ru(btc2)<sub>2</sub> (2.007 Å). Similarly, the Ni–N(triazole) bond was found to be much longer than the analogous Co–N(triazole) bonds in a Co(btc)<sub>2</sub>(BF<sub>4</sub>) complex (2.07 Å and 1.94 Å, respectively).<sup>[12]</sup>

**Cyclic voltammetry (CV)**: The redox properties of the Ru complexes have been examined by cyclic voltammetry, at a platinum working electrode for  $CH_2CI_2$  solutions, containing  $[NBu_4][PF_6]$  as supporting electrolyte. The peak potentials determined for the observed electron transfers are summarized

Table 1. Summary of electrochemical data.			
	$Ep_a^1$ [V] M <sup>II</sup> $\rightarrow$ M <sup>III</sup>	Ep <sub>a</sub> <sup>2</sup> [V] btc <sub>ox1</sub>	<i>E</i> p <sub>a</sub> <sup>3</sup> [V] btc <sub>ox2</sub>
Hbtc1 <sup>[a]</sup>		0.735	
Me-btc1 <sup>[a]</sup>		0.741	
[btc1] <sup>-</sup> Bu <sub>4</sub> N <sup>+[a]</sup>		-0.311	0.722
Ru(btc1) <sub>2</sub> <sup>[b]</sup>	-0.879	-0.062	0.739
Zn(btc1) <sub>2</sub> <sup>[b]</sup>		-0.104	0.106
Ni(btc1) <sub>2</sub> <sup>[b]</sup>		-0.230	0.009
Hbtc2 <sup>[a]</sup>		0.975 (irr)	
Me-btc2 <sup>[a]</sup>		1.056	
[btc2] <sup>-</sup> Bu <sub>4</sub> N <sup>+[a]</sup>		-0.069	0.984 (qr)
Ru(btc2) <sub>2</sub> <sup>[b]</sup>	-0.454	0.297	1.150
Zn(btc2) <sub>2</sub> <sup>[b]</sup>		0.338	0.574
Ni(btc2) <sub>2</sub> <sup>[b]</sup>		0.212	0.447
Me-carbazole <sup>[a]</sup>		0.768 (qr)	
3,6-(tBu) <sub>2</sub> -9-Me-carbazole <sup>[a]</sup>		0.671	
[a] Experiment performed in MeCN; [b] Experiment performed in $CH_2CI_2$ .			

in Table 1 and referenced versus the ferrocene/ferrocenium potential.

The cyclic voltammogram of Ru(btc2)<sub>2</sub> ( $-1.15 V \rightarrow 1.25 V$ , see Figure 3) exhibits three quasi-reversible redox waves centered at -0.45, 0.29, and 1.15 V versus Fc/Fc<sup>+</sup>, which all belong to oxidations. One of these events certainly belongs to the  $Ru^{II} \rightarrow$ Ru<sup>III</sup> transition and related compounds are compared for the assignment.  $[Ru(btp)_2]^{2+}$  compounds were found to show these transitions between 0.58 and 1.19 V, dependent on the substituents at the triazole unit,<sup>[5]</sup> which already demonstrates the significant influence of even subtle changes within one and the same ligand class. For [Ru(terpy)<sub>2</sub>]<sup>2+</sup> this redox event was found at +0.86 V<sup>[11]</sup>, which is in the range observed for the btp complexes. However, these are dicationic complexes, which are not as appropriate for comparison as neutral [L<sub>2</sub>Ru] compounds, where—as in Ru(btc1)<sub>2</sub> and Ru(btc2)<sub>2</sub>—the negative charge is localized at the ruthenium centers. A neutral bis(2,5-di(2-pyridyl)pyrrolato)-ruthenium(II) complex was found to be oxidized at a potential as negative as -0.36 V, which was attributed to both the effect of overall charge and to the stabilization of the harder Ru<sup>III</sup> state by the harder, charged pyrrola-





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to donor.<sup>[7c]</sup> The same is the case here and therefore we assign the first transition to the Ru<sup>II</sup>/Ru<sup>III</sup> couple. This means that the next two oxidation events involve either both ligands, or only one of them, whereas the second one corresponds to a Ru<sup>III</sup>/Ru<sup>IV</sup> couple.

To support these assignments and further decipher the redox behavior, the electrochemical behavior of  $Zn(btc2)_2$  was studied, since the CV measurements should exclusively reflect the behavior of the ligand, due to the presence of the redoxinert metal center. The cyclic voltammogram of  $Zn(btc2)_2$  (Figure 4) exhibits two quasi-reversible waves at positive po-



Figure 4. Cyclic voltammograms of Zn(btc)<sub>2</sub> complexes in CH<sub>2</sub>Cl<sub>2</sub>.

tentials, namely at 0.34 and 0.57 V versus Fc/Fc<sup>+</sup>, which supports assignment of the two redox events at positive potentials in the CV of Ru(btc2)<sub>2</sub> as ligand-centered oxidations, and at the same time that the first one at negative potential (-0.45 V) corresponds to oxidation of Ru<sup>III</sup> to Ru<sup>III</sup>. Location of the second redox wave representing ligand oxidation in Zn(btc2)<sub>2</sub> at much lower potential than in the analogous Rucomplex (Ru(btc2)<sub>2</sub>) may be attributed to the fact that the Zn center with completely filled d-orbitals, does not mediate electronic communication between the ligands to the same extent as the Ru<sup>II</sup> ion, so that the first oxidation does not affect the second one significantly. Location of the first one also at more negative potential on moving from Zn to Ru is attributed to the oxidation state + III.

A solution of Ru(btc1)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> displays three quasi-reversible redox waves at -0.87, -0.06, and 0.74 V. By analogy with Ru(btc2)<sub>2</sub> two waves at higher potential can be assigned to ligand oxidation and the one at -0.87 V originates from Ru<sup>II</sup> to Ru<sup>III</sup> oxidation (Scheme 3). This assignment is consistent with the presence of two quasi-reversible waves, originating from ligands oxidation processes, in a CV of the corresponding zinc complex (Zn(btc1)<sub>2</sub>) at -0.104 and 0.106 V. Also, for the homoleptic octahedral cobalt complexes of a btc1 derivative, three redox events (-0.79, 0.38, and 0.59 V vs. Ag/AgNO<sub>3</sub>) have been recently reported.<sup>[12]</sup>

The CVs of the corresponding Ni complexes look very similar as compared to those of the Zn complexes, but appear at yet more negative potentials (see Table 1). A conceivable explana-

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 $R = -C_6H_3(t-Bu)_2$ 

Scheme 3. Electron transfer processes occurring in Ru(btc1)<sub>2</sub> complexes.

tion would be a more ionic character of the Ni–N(carbazole) bonds as compared to the corresponding Zn–N(carbazole) bonds.

The CVs of the ligands Hbtc1 and Hbtc2 were also measured for comparison. Whereas, Hbtc1 revealed a reversible one-electron oxidation wave at 0.73 V corresponding to the formation of the radical cation Hbtc1/Hbtc1<sup>-+</sup>, Hbtc2 only exhibited an irreversible oxidation at 0.97 V.

To provide a better stability to the one-electron oxidized form of the Hbtc1 and Hbtc2 ligands, their methylated forms (Me-btc1 and Me-btc2) were also synthesized and studied by CV. Indeed, both Me-btc1 and Me-btc2 reveal a single oneelectron reversible redox event at 0.741 and 1.056 V, respectively. Notably, these values compare well with the second one-electron oxidation events of Ru(btc1)<sub>2</sub> and Ru(btc2)<sub>2</sub> (Table 1) at 0.739 and 1.150 V, respectively, which supports their assignment as a predominantly ligand-based process. The CVs of the in situ generated anionic forms (btc1<sup>-</sup> and btc2<sup>-</sup>) (using addition of Bu<sub>4</sub>NOH to a solution of Hbtc in an electrochemical cell) were also determined for comparison purposes (Table 1, Figure S25 and S26 in Supporting Information).

Comparison of the redox properties of metal complexes with btc1 and btc2 reveals the significant difference in redox stability of the complexes, depending on the connection mode of the triazoles to the carbazole moiety, that is, either through C(4) in btc1 or through N(3) in btc2, and the resulting distinctly different coordination to the metal center. The oxidation events in the ruthenium, zinc, and nickel complexes of btc1 are located at significantly lower potentials (between 300–400 mV) than in the corresponding btc2 complexes. Hence, the electron density at the carbazole N atom of btc1 is significantly higher than in case of btc2. The rather negative potential of the  $Ru^{II} \rightarrow Ru^{III}$  transition in  $Ru(btc1)_2$  explains the difficulties that we encountered when attempting to isolate this compound in its fully reduced form in bulk, since it is rather easily oxidized.

**UV/Vis Spectroscopy**: Optical spectra of the Hbtcs and their metal complexes have been measured in CH<sub>2</sub>Cl<sub>2</sub> over the range 200–1000 nm. The spectra of both Hbtcs show intense bands in the UV-region, originating from intra-ligand  $\pi \rightarrow \pi^*$ 

transitions, typical for unsaturated hydrocarbons. For the ruthenium complexes–apart from intense bands in the UV region representing ligand-based transitions–additional bands in the visible and infrared region of the spectrum are also observed. Figure 5 shows the spectra of free ligand Hbtc2, as well as Ru(btc2)<sub>2</sub>. The bands at 446, 546, and 582 nm are presumably transitions with MLCT character, as evident from their high absorption coefficients (Table 2). For comparison, corresponding btp complexes show 2–3 bands in the region between 320–480 nm, in dependence of the residues attached.



Figure 5. UV/Vis absorption spectra of Hbtc2 and Ru(btc2)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>.

**Redox chemistry**: While studying the UV/Vis properties of Ru(btc2)<sub>2</sub> we noted that, in contrast to Hbtc2, Ru(btc2)<sub>2</sub> is sensitive to UV-light and is oxidized in chlorinated solvents. Irradiation of CH<sub>2</sub>Cl<sub>2</sub> (or CHCl<sub>3</sub>) solutions of both Ru-complexes with UV-light (190–370 nm) leads to a color change from red to brown, and the NMR spectra recorded afterwards clearly indicated formation of a paramagnetic species. This was accompanied also by significant changes in spectral features within the UV/Vis spectrum. As shown in Figure 6, two new bands are developing in the visible region of the spectrum at 406 and 490 nm and two in the near infrared region at 755 and 845 nm, originating from LMCT or LLCT. At the same time the three bands in the visible region of the spectrum of Ru(btc2)<sub>2</sub>,

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<b>Table 2.</b> UV/Vis spectral data of the Hbtc ligands and their Ru complexes in $CH_2Cl_2$ solution.					
	$\lambda_{\max}$ [nm]	( $\varepsilon$ [dm <sup>3</sup> mol <sup>-</sup>	<sup>1</sup> cm <sup>-1</sup> ])		
Hbtc1	318 (23 500)	361 (17 200)	377 (18 100)		
Ru(btc1) <sub>2</sub>	413 (32 300)	530 (7 100)	570 (5 800)		
[Ru(btc1) <sub>2</sub> ] <sup>+</sup>	432 (59 500)	587 (40 400)	750 (5 200)	890 (9 100)	
Ru(btc1) <sub>2</sub> ] <sup>2+</sup>	318 (71 400)	522 (8000)	638 (8000)	696 (11 500)	900 (15000)
Hbtc2	307 (58 500)	353 (22 000)	367 (25 500)		
Ru(btc2) <sub>2</sub>	446 (29 000)	546 (11 800)	582 (11 000)		
[Ru(btc2) <sub>2</sub> ] <sup>+</sup>	406 (36 500)	490 (26 800)	755 (9 500)	844 (16000)	
Ru(btc2) <sub>2</sub> ] <sup>2+</sup>	369 (14 800)	429 (13 400)	682 (8 200)	813 (13000)	



**Figure 6.** Evolution of UV/Vis spectra upon irradiating a solution of  $Ru(btc2)_2$  in  $CH_2CI_2$  (0.1 mM) with UV-light (190 to 400 nm) over 300 s. Spectra collected at the intervals of 2 s.

at 446, 546, and 582 nm (see above), are decreasing. No such changes are observed upon irradiation with visible light. Iso-sbestic points indicate a unimolecular conversion.

An ESI/MS of the solution after UV-irradiation revealed the presence of only one species with a value of m/z 1678.97, and isotopic distribution consistent with the formulation [Ru(btc2)<sub>2</sub>]<sup>+</sup>, which, however, is also found in the ESI/MS spectrum of Ru(btc2)<sub>2</sub>. It is known that certain dyes reductively cleave dichloromethane upon photolysis, thereby generating a radical cation of the dye. The same is conceivable in our case, that is, UV-light populates an excited state with a ligand-centered reducing electron, which after being transferred to the chlorinated solvent leaves behind an oxidized ruthenium complex. Indeed, the complex proved photostable in fluorobenzene, but treating a fluorobenzene solution of Ru(btc2)<sub>2</sub> under anaerobic conditions with chemical oxidants such as ferrocenium tetrafluoroborate ( $E^{\circ\prime} = 0.0 \text{ V}$ ), [N(C<sub>6</sub>H<sub>4</sub>Br-4)<sub>3</sub>]SbCl<sub>6</sub> ( $E^{\circ\prime} =$ 0.70 V vs. Fc), cerium ammonium nitrate (CAN), or bulk electrolysis (1.2 V) led to the disappearance of the bands typically observed for Ru(btc2)<sub>2</sub>, and the formation of four new intense bands at 400, 485, 752, and 836 nm, and hence to formation of a product displaying basically the same UV/Vis spectrum as the one obtained after irradiation, which we assign as  $[Ru(btc2)_2]^+$ .

Accordingly, chemical oxidation under all conditions tested stopped after the first oxidation event seen in the CV, although some reagents should have also been capable of realizing the second oxidation. As in the CV, the first redox event is also chemically reversible: upon addition of one equivalent of  $[CoCp_2]$  ( $E^{\circ} = -1.33$  V vs. Fc) to the oxidized complexes, rapid regeneration of the bands at 446, 546, and 582 nm could be observed.

Consistently, spectroelectrochemical studies showed that the UV/Vis spectroscopic changes noted above are associated with the first redox event ( $Ru^{II} \rightarrow Ru^{III}$ , Figure 7) and passing the second one leads to further increasing absorption in the area where the most redshifted bands appear, as well as evolution of a band at even longer wavelengths (Figure 8). Importantly, the spectra belonging to  $Ru(btc2)_2$ ,  $[Ru(btc2)_2]^+$ , and  $[Ru(btc2)_2]^{2+}$  can reversibly be generated while moving along the CV.



**Figure 7.** Changes in the UV/Vis spectra of Ru(btc2)<sub>2</sub> during cyclic voltammetry. Difference spectrum of Ru(btc2)<sub>2</sub> while moving through the first oxidation wave in 0.1  $mmm Bu_4NPF_6/CH_2Cl_2$ , Pt-mesh,  $dE/dt = 10 \text{ mV s}^{-1}$ ,  $c = 5 \times 10^{-4} \text{ mol} \text{I}^{-1}$ , cuvette d = 0.5 mm.



**Figure 8.** Changes in the UV/Vis spectra during cyclic voltammetry. Mathematically subtracted difference spectrum of Ru(btc2)<sub>2</sub> while moving through the second oxidation wave in 0.1  $\times$  Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub>, Pt-mesh, d*E*/dt = 10 mV s<sup>-1</sup>,  $c = 5 \times 10^{-4}$  mol l<sup>-1</sup>, cuvette d = 0.5 mm.

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Investigation of a solution of Ru(btc2)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> before and after exposure to UV-light using electron paramagnetic resonance (EPR) furthermore confirmed that the oxidation to [Ru(btc2)<sub>2</sub>]<sup>+</sup> is metal-centered. The X-band EPR spectrum of Ru(btc2)<sub>2</sub> at 77 K (Figure S38 in Supporting Information) was found to be predominantly silent, typical for Ru<sup>II</sup>, with minor species having the characteristic rhombic  $S = \frac{1}{2}$  EPR signal. Exposure of the sample to UV-light gives rise to a strong signal of rhombic lineshape with  $g_1 = 2.28$ ,  $g_2 = 2.12$ ,  $g_3 = 1.98$ , characteristic of a Ru<sup>III</sup> low-spin species with octahedral metal configuration. Significant *g* anisotropy  $\Delta g = g_1 - g_3 = 0.3$  clearly demonstrates a large contribution from the metal center to the paramagnetism of this species.

Analogous studies for Ru(btc1)<sub>2</sub> reflected great similarity with the properties of Ru(btc2)<sub>2</sub>. Exposition of DCM solutions to UV-light triggered disappearance of the three bands in the visible region (413, 530, and 570 nm) characteristic for Ru(btc1)<sub>2</sub> and appearance of new bands at 432, 587, 750, and 890 nm. Several isosbestic points indicated the temporary presence of only two species, with ultimate formation of the singly oxidized complex, as also confirmed by spectroelectrochemical studies (see Figure S29). The same features were observed in the spectra recorded after reaction of Ru(btc1)<sub>2</sub> with various chemical oxidizing agents (Figure S27), and similarly to complex Ru(btc2)<sub>2</sub>, the redox process occurring in the presence of chemical oxidants is fully reversible: Reduction of one-electron oxidized species by one equivalent of [CoCp<sub>2</sub>] recreates the original spectrum of complex Ru(btc1)<sub>2</sub>.

# Conclusion

We report here two new ligand systems, namely bis(triazole)carbazoles btc1 and btc2, that were accessed by "click reactions". Although they are isomeric and differ only in the position of one N atom in the triazole units, the properties of their metal complexes  $M(btc)_2$  (M = Ru, Zn, Ni) are remarkably different. Each of the complexes undergoes two reversible ligand centered oxidation events (at the carbazole N atoms). The corresponding oxidation waves appear at 300-400 mV lower potentials for the btc1 complexes indicating a significantly higher electron density at the carbazole N atoms. For a given btc ligand, the potentials decrease on going from  $Ru \rightarrow Zn \rightarrow Ni$ . The ruthenium complexes are oxidized at the metal centers first, though, before ligand oxidation occurs. With their redox activities that can readily be tuned by the regiochemistry of triazole attachment, these pincers are anticipated to be valuable supporting ligands in heteroleptic complexes, to be employed in catalysis.

## **Experimental Section**

#### Ligand syntheses

Synthesis of Hbtc1: 1-Bromo-3,5-di-tert-butyl-benzene (2.340 g, 8.690 mmol) was added to a suspension of ascorbic acid (172 mg, 0.869 mmol), Cul (331 mg, 1.738 mmol), N,N'-dimethylethylenediamine (153 mg, 1.738 mmol), and NaN<sub>3</sub> (1.13 g, 17.38 mmol) in EtOH/H<sub>2</sub>O (7:1, 120 mL). The mixture was refluxed for 2 h. After cooling to room temperature, the mixture was extracted with petroleum ether (5 $\times$ 50 mL), and the combined organic layers were washed with aqueous ethylenediaminetetraacetic acid (EDTA) solution (2×100 mL) and brine (1×100 mL). After evaporation of the solvent, 3,5-di-tert-butylphenyl azide (2.07 g, 8.97 mmol, 100% crude) was obtained as an oil, which was used without further purification. The crude azide (2.070 g, 8.97 mmol), 3,6-di-tert-butyl-1,8-diethynyl-9H-carbazole<sup>[9]</sup> (1.277 g, 3.90 mmol), ascorbic acid (77 mg, 0.390 mmol), CuSO<sub>4</sub> (97 mg, 0.390 mmol), and tris(benzyltriazolylmethyl)amine (TBTA, 207 mg, 0.390 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>/tertBuOH/H<sub>2</sub>O (4:4:1, 50 mL) and stirred at room temperature overnight. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (200 mL), the organic layer was separated, washed with EDTA solution (3  $\times$ 200 mL), and dried over MgSO<sub>4</sub>. After evaporation of the solvent under reduced pressure, the residue obtained was subjected to column chromatography (petroleum ether/ethyl acetate = 20:1) to obtain Hbtc1 as a colorless powder (1.08 g, 35%); <sup>1</sup>H NMR (500.130 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 1.45$  (s, 36 H), 1.56 (s, 18 H), 7.60 (s, 2 H), 7.79 (s, 2H), 7.89 (s, 4H), 8.22 (s, 2H), 8.56 (s, 2H), 12.17 (s, 1 H) ppm (for assignment see Figure S7); <sup>13</sup>C NMR (125.758 MHz,  $CD_2CI_2$ ):  $\delta = 31.5$ , 32.3, 35.1, 35.6, 112.9, 115.7, 117.1, 118.0, 120.6, 123.4, 124.3, 136.1, 137.3, 142.6, 148.4, 153.4 ppm (Figure S8); elemental analysis calcd (%) for  $C_{52}H_{67}N_7$  C 79.04, H 8.55, N 12.41; found: C 78.69, H 8.56, N 12.41.

Synthesis of Hbtc2: NaNO<sub>2</sub> (1.338 g, 19.389 mmol) in H<sub>2</sub>O (10 mL) was added to a solution of 1,8-diamino-3,6-di-tert-butyl-9H-carbazole<sup>[13]</sup> (2.00 g, 6.463 mmol), in EtOH/H<sub>2</sub>O (4:1, 50 mL) over 30 min at 0°C and subsequently stirred at this temperature for 1 h. NaN<sub>3</sub> (1.260 g, 19.389 mmol) in H<sub>2</sub>O (10 mL) was added to the reaction mixture at 0 °C within 30 min and subsequently stirred at ambient temperature for 1 h. The mixture was extracted with ethyl acetate  $(3 \times 50 \text{ mL})$  and the combined organic phases were dried with MgSO<sub>4</sub>. After column chromatography (petroleum ether/ethyl acetate = 20:1) 1,8-diazido-3,6-di-tert-butyl-9H-carbazole (0.896 g, 38% crude) was obtained, which was used without further purification. The crude azide (1.230 g, 3.403 mmol), 3,5-di-tert-butylphenyl acetylene<sup>[14]</sup> (2.188 g, 10.209 mmol), ascorbic acid (67 mg, 0.340 mmol), 1 м aqueous CuSO<sub>4</sub> (0.25 mL, 0.340 mmol), and TBTA (180 mg, 0.340 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/tertBuOH/H<sub>2</sub>O (4:4:1, 35 mL) were stirred at ambient temperature overnight. The mixture was diluted with  $CH_2CI_2$  (200 mL), the organic phase was separated, washed with aqueous EDTA solution (3×200 mL), and dried over MgSO<sub>4</sub>. After evaporation of the solvent under reduced pressure the residue obtained was subjected to column chromatography (petroleum ether/ethyl acetate = 20:1) to obtain Hbtc2 as a colorless powder (1.30 g, 48%). <sup>1</sup>H NMR (500.130 MHz,  $CD_2CI_2$ ):  $\delta = 1.45$  (s, 36H), 1.57  $(s,\ 18\,H),\ 7.52\ (s,\ 2\,H),\ 7.80\ (s,\ 2\,H),\ 7.92\ (s,\ 4\,H),\ 8.27\ (s,\ 2\,H),\ 8.57\ (s,\ 4\,H),\ 8.57\ (s,\ 4\,H)$ 2H), 11.37 (s, 1H) ppm (for assignment see Figure S9); <sup>13</sup>C NMR (125.758 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=31.2, 31.7, 34.9, 113.7, 116.7, 117.0, 120.3, 121.2, 122.8, 125.7, 129.4, 129.9, 143.5, 148.3, 151.6 ppm (Figure S10); elemental analysis calcd (%) for  $C_{52}H_{67}N_7$  C 79.04, H 8.55, N 12.41; found: C 78.44, H 8.67, N 11.89.

Synthesis of Me-btc1 and Me-btc2: NaH (15 mg, 0.375 mmol) was added at 0 °C to a solution of Hbtc1 and Hbtc2, respectively, (198 mg, 0.25 mmol) in DMF (2 mL). The mixture was allowed to stir at ambient temperature for 2 h, followed by dropwise addition of iodomethane (23  $\mu$ L, 0.375 mmol). After stirring overnight, H<sub>2</sub>O (5 mL) was added. The precipitated solid was isolated by filtration, washed with H<sub>2</sub>O and subjected to column chromatography (petroleum ether/ethyl acetate = 10:1) to obtain Me-btc1 and Mebtc2, respectively, as colorless powder.

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*Me-btc1*: 160 mg (88%); mp=316.1-316.8 °C; <sup>1</sup>H NMR (500.130 MHz, CDCl<sub>3</sub>):  $\delta$ =8.13 (s, 2 H), 8.11 (d, *J*=1.95 Hz, 2 H), 7.58 (d, *J*=1.80 Hz, 4 H), 7.35 (d, *J*=1.80 Hz, 2 H), 7.28 (t, *J*=1.80 Hz, 2 H), 2.48 (s, 3 H), 1.33 (s, 18 H), 1.21 (s, 36 H) ppm (for assignment see Figure S11); <sup>13</sup>C NMR (125.758 MHz, CDCl<sub>3</sub>):  $\delta$ =152.9, 147.2, 142.4, 139.9, 136.8, 127.0, 125.0, 123.1, 121.0, 116.9, 115.4, 113.8, 37.0, 35.2, 34.7, 32.0, 31.4 ppm (Figure S12). HRMS-ESI<sup>+</sup>: calcd. for [C<sub>53</sub>H<sub>70</sub>N<sub>7</sub><sup>+</sup>]: *m/z* 804.5639; found: *m/z* 804.5703.

*Me-btc2*: 145 mg (79%); mp = 323.6–324.1 °C; <sup>1</sup>H NMR (500.130 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.13 (d, *J* = 1.85 Hz, 2 H), 7.99 (s, 2 H), 7.54 (d, *J* = 1.75 Hz, 4 H), 7.53 (d, *J* = 1.95 Hz, 2 H), 7.45 (t, *J* = 1.70 Hz, 2 H), 3.18 (s, 3 H), 1.42 (s, 18 H), 1.32 (s, 36 H) ppm (for assignment see Figure S13); <sup>13</sup>C NMR (125.758 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.5, 148.9, 143.3, 134.9, 129.1, 125.5, 123.9, 123.3, 122.8, 120.8, 120.3, 118.6, 60.4, 35.0, 34.8, 31.9, 31.5 ppm (Figure S14); HRMS-ESI<sup>+</sup> calcd. for [C<sub>53</sub>H<sub>70</sub>N<sub>7</sub><sup>+</sup>]: *m/z* 804.5639; found: *m/z* 804.5726.

#### Syntheses of metal complexes

Synthesis of Ru(btc1)<sub>2</sub>: RuCl<sub>2</sub>(DMSO)<sub>4</sub> (30 mg, 0.06 mmol), Hbtc1 (100 mg, 0.12 mmol), and triethylamine (ca. 0.3 mL) were refluxed overnight in a mixture of degassed ethanol (10 mL) and THF (5 mL) with stirring under an inert atmosphere. The reaction mixture was cooled to  $-15\,^\circ\text{C}$  and the precipitated solid collected by filtration to afford the title compound as dark red precipitate. The resulting product was dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and filtered through Celite. Slow removal of CH<sub>2</sub>Cl<sub>2</sub> under a stream of dinitrogen caused the crystallization of the product as red plates. The red microcrystals were collected by filtration and washed with pentane (70 mg, 68%); ESI-MS: calcd. for [Ru(btc1)<sub>2</sub>]<sup>+</sup>: *m/z* 1679.99; found: m/z 1678.97; elemental analysis calcd (%) for RuC<sub>104</sub>H<sub>132</sub>N<sub>14</sub> C 74.38, H 7.92, N 11.68; found: C 72.34, H 7.91, N 11.28. For all btc complexes correct H and N values were found, whereas the C values were (for unknown reasons) too low, despite many attempts for different samples. For the following compounds: Ru(btc2)<sub>2</sub>,  $Zn(btc1)_2$  and  $Zn(btc2)_2$  purity has been demonstrated by NMR spectroscopy.

Synthesis of Ru(btc2): The product was synthesized following the procedure described for [Ru(btc1)<sub>2</sub>] but employing Hbtc2. It was obtained as a dark red solid. Single crystals of Ru(btc2)<sub>2</sub> were grown by slow evaporation of DCM under an inert atmosphere (65 mg, 63%); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =8.61 (s, 4H), 8.49 (s, 4H), 7.74 (br, 4H), 7.19 (t, *J*=1.85 Hz, 4H), 7.04 (d, *J*=1.88 Hz, 8H), 1.59 (s, 36H), 1.16 ppm (s, 72H) (for assignment see Figure S15); <sup>13</sup>C{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =151.0, 146.9, 128.5, 122.2, 119.4, 117.0, 34.6, 31.0 ppm (Figure S16); ESI-MS calcd. for [Ru(btc1)<sub>2</sub>]<sup>+</sup>: *m/z* 1679.99; found: *m/z* 1678.98; elemental analysis calcd (%) for RuC<sub>104</sub>H<sub>132</sub>N<sub>14</sub> C 74.38, H 7.92, N 11.68; found: C 72.08, H 7.85, N 11.26; for the C deviation see comment for Ru(btc1)<sub>2</sub>.

*Synthesis of Zn*(*btc1*)<sub>2</sub>: Zn(Et)<sub>2</sub> as a 1 μ solution in hexane (0.15 mL, 0.15 mmol) was added to a solution of Hbtc1 (100 mg, 0.126 mmol) in THF (2 mL). Stirring the reaction mixture at ambient temperature overnight led to the formation of a yellow precipitate. After filtration the precipitate was washed with THF (3 mL) and hexane (3 mL) and dried under vacuum to obtain Zn(btc1)<sub>2</sub> in 76% yield (25 mg); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.32 (d, *J* = 1.98 Hz, 4H), 8.16 (s, 4H) 7.68 (d, *J* = 1.91 Hz, 4H), 7.29 (t, *J* = 1.74 Hz, 4H), 7.00 (d, *J* = 1.71 Hz, 8H), 1.54 (s, 36H), 1.19 ppm (s, 72H) (for assignment see Figure S17); <sup>13</sup>C[<sup>1</sup>H] (CD<sub>2</sub>Cl<sub>2</sub>): 152.8, 149.5, 147.1, 136.7, 136.7, 126.8, 122.9, 119.7, 117.2, 116.5, 112.4, 68.1, 35.2, 34.7, 32.5, 31.4, 25.9 ppm (Figure S18); ESI-MS calcd. for [Zn(btc1)<sub>2</sub>H<sup>+</sup>]: *m/z* 1644.01; found: *m/z* 1644.08.

Synthesis of  $Zn(btc2)_2$ : The product was synthesized following the procedure described for  $[Zn(btc1)_2]$ . After drying of the yellow solid in vacuum  $[Zn(btc1)_2]$  could be obtained in pure form in 79% yield (26 mg); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.45 (d, *J* = 1.72 Hz, 4H), 8.25 (s, 4H), 7.62 (d, *J* = 1.72 Hz, 4H), 7.25 (t, *J* = 1.81 Hz, 4H), 7.10 (d, *J* = 1.81 Hz, 8H), 1.56 (s, 36H), 1.21 ppm (s, 72 H) (for assignment see Figure S19); <sup>13</sup>C{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 151.3, 147.8, 140.4, 138.8, 129.2, 129.0, 122.6, 122.0, 120.0, 117.7, 117.3, 113.3, 35.0, 35.0, 32.3, 31.6 ppm (Figure S20); ESI-MS calcd. for  $[Zn(btc2)_2H^+]$ : *m/z* 1644.01; found: *m/z* 1644.06.

Synthesis of Ni(btc1)<sub>2</sub>: Triethylamine (0.2 mL) was added to a solution of NiBr<sub>2</sub>·DME (11.7 mg, 38 µmol) and Hbtc1 (60 mg, 76 µmol) in degassed THF (10 mL). An immediate color change of the solution from orange to red was observed. The reaction mixture was further stirred at room temperature overnight, and the precipitated yellow solid was collected by filtration. This crude product was washed with small portions of THF, followed by extraction with Et<sub>2</sub>O. Evaporation of the solvent and drying under vacuum provided Ni(btc1)<sub>2</sub> as an orange solid in 82% yield (51 mg). Single crystals of Ni(btc1)<sub>2</sub> can be grown by slow evaporation of the solvent from a DCM/acetone solution under an inert atmosphere. ESI-MS calcd. for [Ni(btc1)<sub>2+</sub>H]<sup>+</sup>: *m/z* 1636.02; found: *m/z* 1636.02; calcd. for  $[Ni(btc1)_2 + Na]^+$ : m/z 1658.00; found: m/z 1658.00; elemental analysis calcd (%) for NiC<sub>104</sub>H<sub>132</sub>N<sub>14</sub>: C 76.31, H 8.13, N 11.98; found C 75.47, H 8.32, N 11.60; for the C deviation see comment for Ru(btc1)<sub>2</sub>; magnetic moment (in C<sub>6</sub>D<sub>6</sub>, 300 MHz)  $\mu_{eff} = 2.63 \mu_B$  (2 unpaired electrons per Ni).

Synthesis of Ni(btc2)<sub>2</sub>: The product was synthesized following the procedure described for [Ni(btc1)<sub>2</sub>] but employing Hbtc2. Yield: 41% (34.2 mg); ESI-MS calcd. for [Ni(btc2)<sub>2</sub>+H]<sup>+</sup>: *m/z* 1636.02; found: *m/z* 1636.02; calcd. for [Ni(btc2)<sub>2</sub> + Na]<sup>+</sup>: *m/z* 1658.00; found: *m/z* 1658.00; elemental analysis calcd (%) for NiC<sub>104</sub>H<sub>132</sub>N<sub>14</sub>: C 76.31, H 8.13, N 11.98; found C 75.61, H 8.35, N 11.74; for the C deviation see comment for Ru(btc1)<sub>2</sub>; magnetic moment (in C<sub>6</sub>D<sub>6</sub>, 300 MHz)  $\mu_{eff}$  = 2.84  $\mu_{B}$  (2 unpaired electrons per Ni).

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# **Conflict of interest**

The authors declare no conflict of interest.

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- H. C. Kolb, M. G. Finn, K. B. Sharpless, Angew. Chem. Int. Ed. 2001, 40, 2004–2021; Angew. Chem. 2001, 113, 2056–2075.
- [2] a) Click Triazoles, *Topics in Heterocyclic Chemistry*, Vol. 28 (Ed.: J. Košmrlj), Springer, **2012**; b) Z.-J. Zheng, D. Wang, Z. Xu, L.-W. Xu, *Beilstein J. Org. Chem.* **2015**, *11*, 2557–2576; c) B. Schulze, U. S. Schubert, *Chem. Soc. Rev.* **2014**, *43*, 2522–2571.
- [3] a) J. P. Byrne, J. A. Kitchen, T. Gunnlaugsson, Chem. Soc. Rev. 2014, 43, 5302–5325; b) G. Aromí, L. A. Barrios, O. Roubeau, P. Gamez, Coord. Chem. Rev. 2011, 255, 485–546; c) J. D. Crowley, D. A. McMorran, "Click-Triazole" Coordination Chemistry: Exploiting 1,4-Disubstituted-1,2,3-Triazoles as Ligands in Click Triazoles. Topics in Heterocyclic Chemistry (Ed.: J.

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8





Kosmrlj), Springer, Berlin, 2012; d) D. Schweinfurth, L. Hettmanczyk, L. Suntrup, B. Sarkar, Z. Anorg. Allg. Chem. 2017, 643, 554–584.

- [4] R. M. Meudtner, M. Ostermeier, R. Goddard, C. Limberg, S. Hecht, Chem. Eur. J. 2007, 13, 9834–9840.
- [5] M. Ostermeier, M.-A. Berlin, R. Meudtner, S. Demeshko, F. Meyer, C. Limberg, S. Hecht, *Chem. Eur. J.* 2010, *16*, 10202–10213.
- [6] Y. Li, J. C. Huffman, A. H. Flood, Chem. Commun. 2007, 2692–2694.
- [7] a) M. Duati, S. Tasca, F. C. Lynch, H. Bohlen, J. G. Vos, S. Stagni, M. D. Ward, *Inorg. Chem.* 2003, 42, 8377–8384; b) B. A. Frazier, E. R. Bartholomew, P. T. Wolczanski, S. DeBeer, M. Santiago-Berrios, H. D. Abruña, E. B. Lobkovsky, S. C. Bart, S. Mossin, K. Meyer, T. R. Cundari, *Inorg. Chem.* 2011, 50, 12414–12436; c) A. McSkimming, V. Diachenko, R. London, K. Olrich, C. J. Onie, M. M. Bhadbhade, M. P. Bucknall, R. W. Read, S. B. Colbran, *Chem. Eur. J.* 2014, 20, 11445–11456.
- [8] L. Hammarström, O. Johansson, Coord. Chem. Rev. 2010, 254, 2546-2559.

- [9] H.-C. Gee, C.-H. Lee, Y.-H Jeong, W.-D. Jang, Chem. Commun. 2011, 47, 11963–11965.
- [10] D. I. Bezuidenhout, G. Kleinhans, G. Guisado-Barrios, G. C. Liles, G. Ung, G. Bertrand, Chem. Commun. 2014, 50, 2431 – 2433.
- [11] A. B. P. Lever, Inorg. Chem. **1990**, 29, 1271-1285.
- [12] M. S. Bennington, H. L. C. Feltham, Z. J. Buxton, N. G. White, S. Brooker, Dalton Trans. 2017, 46, 4696–4710.
- [13] G. Sanchez, A. Espinosa, D. Curiel, A. Tarraga, P. Molina, J. Org. Chem. 2013, 78, 9725.
- [14] R. S. Stoll, M. V. Peters, A. Kühn, S. Heiles, R. Goddard, M. Bühl, C. M. Thiele, S. Hecht, J. Am. Chem. Soc. 2009, 131, 357–367.

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# **FULL PAPER**

## Click chemistry

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Comparing Isomeric Tridentate Carbazole-Based Click Ligands: Metal Complexes and Redox Chemistry



Two isomers with a click: After complexation of isomeric bis(triazolyl)carbazoles, differing only in the triazole linkage, they represent redox active ligands, and the triazole positioning sensitively influences the redox properties of the complexes. These novel pincers are thus anticipated to be valuable supporting ligands in heteroleptic complexes for catalytic applications.

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**Full Paper** 

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