

Copper(I) halide complexes of the new 4,4'-bridged heteroaromatic biscarbenes of the 1,2,4-triazole series

Arthur V. Knishevitsky^a, Nikolai I. Korotkikh^a, Alan H. Cowley^{b,*}, Jennifer A. Moore^b, Tatyana M. Pekhtereva^a, Oles P. Shvaika^a, Gregor Reeske^b

^a The L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, Ukrainian Academy of Sciences, 70, R. Luxemburg, Donetsk 83114, Ukraine

^b The University of Texas at Austin, Department of Chemistry and Biochemistry, 1 University Station A5300, Austin, TX 78712-0165, USA

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Abstract

The stable biscarbenes, 1,4- and 1,3-bis[1-(1-adamantyl)-3-phenyl-1,2,4-triazol-5-yliden-4-yl]benzenes (**4a,b**) have been prepared. Treatment of **4b** with copper(I) chloride and copper(I) iodide in acetonitrile or acetonitrile/toluene solution afforded the biscarbene copper(I) complexes **5a** and **5b**, respectively. The reactions of **4a** and **4b** with diphenyldiazomethane and sulfur resulted in the novel bisazine (**6**) and bsthione (**7**) derivatives, respectively. The X-ray crystal structures of **4a** and **5b** were determined.

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1. Introduction

Following the syntheses of the first stable carbenes [1–4], interest began to develop in the possibility of synthesizing polyfunctional carbenes. It was recognized [5] that carbene dimerization might render this objective somewhat difficult. However, it was not long before Dias et al. [6] reported the synthesis of the first triscarbene ligand of the imidazole series in which the electronically isolated carbenes are linked by a mesitylene moiety. The first syntheses of biscarbenes of the imidazole series were reported by Herrmann and co-workers [7]. In these biscarbenes, the imidazole rings are connected by ethylene bridges at the nitrogen atoms. However, these carbenes were obtained *in situ* and characterized spectroscopically prior to their use for the synthesis of metal carbene complexes. More recently, new stable biscarbenes of the 1,2,4-triazole series have been isolated and characterized [8], as have some related biscarbenes of the imidazole series [9,10]. Crabtree et al. [11] have also shown that the reaction of [(nbd)RhCl]₂

with a chelating bis-[1,2,4]-triazolium salt gives a norticycyl Rh complex.

In the present contribution we describe (i) the synthesis of two stable heteroaromatic biscarbenes of the 1,2,4-triazole series in which triazole rings are connected by phenylene bridges to the nitrogen atoms in the 4 positions; (ii) the synthesis of two biscarbene complexes of copper(I) halides; (iii) the synthesis of two new organic derivatives by treatment of the new carbenes with diphenyldiazomethane and elemental sulfur; and (iv) the X-ray crystal structures of the *m*-phenylene-bridged bistriazolylidene and its complex with copper(I) iodide. In conceiving of this study, it was assumed that, akin to the 3,3'-bonded bistriazolylidenes [8], conjugation between the 4,4'-bonded biscarbenes would afford some degree of electronic interaction between the triazole rings and hence between the two carbene centers of the molecule.

2. Results and discussion

The ring transformations of 2-phenyl-1,3,4-oxadiazole (**1**) into triazoles were effected by treatment of *p*-phenylenediamine dihydrochloride or *m*-phenylenediamine with

* Corresponding author. Tel.: +1 5124717484; fax: +1 5124716822.

E-mail address: cowley@mail.utexas.edu (A.H. Cowley).

equimolar amounts of trifluoroacetic acid at 180 °C in *o*-dichlorobenzene. The solvent choice was dictated by the high polarity of *o*-dichlorobenzene (μ 2.50 D) and its lack of reactivity toward oxadiazole **1**. Bistriazoles **2a,b** were prepared in isolated yields of 54–56%. The syntheses, spectral data and other characteristics of triazoles **2a,b** have been described by us earlier [12].

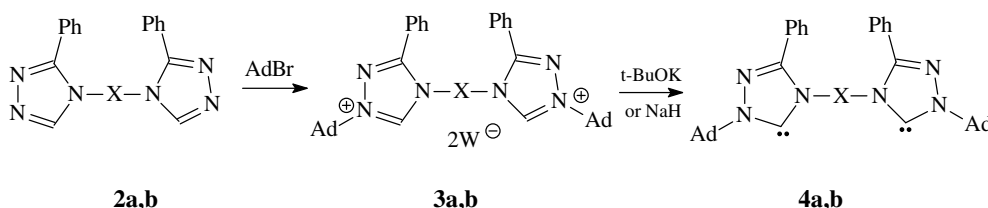
The quaternization of triazoles **2a,b** to the corresponding bistriazolium salts **3a,b** was effected *via* thermal reaction with 1-bromoadamantane in acetic acid or DMF solution (Scheme 1). In the case of triazole **2b**, the reaction of 1-bromoadamantane in acetic acid afforded 96–100% yields of **3b** after 12–14 h. Under analogous conditions, triazole **2a** forms a sparingly soluble bistriazolium acetate which inhibits the desired quaternization process and restricts the yields of **3a** to 20% even in the presence of a large excess of 1-bromoadamantane. On the other hand, if the aprotic polar solvent DMF is employed in the presence of a 20–30% excess of 1-bromoadamantane, these side reactions are avoided and almost quantitative yields of **3a** are realized. The bistriazolium bromides **3a,b** produced by the above methods were purified by crystallization from water, followed by treatment with sodium perchlorate to precipitate the perchlorate salts. If necessary, perchlorates **3a,b** can be recrystallized from 40% aqueous DMF or acetic acid.

The compositions and structures of bistriazolium salts **3a,b** were established on the basis of elemental analyses and NMR spectral data. Thus, the ¹H NMR spectra of salts **3a,b** are indicative of the presence of two carbenoid protons on the triazolium rings and occur in the range δ 10.60–10.67 ppm, which is downfield relative to those for triazoles **2a,b** by 1.77 ppm [12] (the atom numbering system is based on the chemical names of compounds). The resonances for the adamantyl protons are evident at δ 1.6–2.3 ppm.

The preparation of biscarbenes **4a,b** was carried out by deprotonation of the respective bistriazolium perchlorates **3a,b** by means of sodium hydride in acetonitrile solution or potassium *tert*-butoxide in a toluene/*t*-butanol mixed solvent as summarized in Scheme 1. This method of synthesis for carbenes **4a,b** proved to be very successful. In particular, the use of acetonitrile as solvent [13,14] permits rapid, high yield reactions due to the high solubility of the initial salt and one of the products (sodium perchlorate). Moreover, the solubilities of the biscarbenes in acetonitrile is low hence they are precipitated from the reaction mixture

in a pure state. In the case of **4a**, the reaction was complete in 40–50 min at room temperature in a yield of 88%. Interestingly, the method employed for the conversion of **3b** to **4b** is unsuitable for the synthesis of **4b**. Even at low temperatures the deprotonation of salt **3b** is accompanied by unidentified side reactions that presumably involve carbene insertion into a C–H bond of acetonitrile to form cyanomethyl derivatives of the respective bistriazolium [14,15] and H-complexes of the carbene and the initial salt similar to those reported by Arduengo and co-workers [16]. However, biscarbene **4b** was prepared in quantitative yield *via* the reaction of triazolium salt **3b** with an equimolar quantity of sodium *tert*-butoxide in a 5:1 mixture of toluene and *tert*-butanol. The presence of *tert*-butanol in the reaction mixture permits complete solubility of the initially formed triazolium *tert*-butoxide, thereby facilitating its decomposition to the biscarbene and *tert*-butanol by slow solvent evaporation. Moreover, the *tert*-butoxide anion is a strong base ($pK_a \sim 19$) with a basicity close to that of triazolylidene. Furthermore, the *tert*-butyl substituent is a good sterically protecting group and this facilitates the elimination of the C(5)H proton from the bistriazolium salt and prevents the H-interaction of the biscarbene with unreacted salt as discussed in reference [16]. Experiments conducted in the presence of other alcohols (isopropanol, methanol) showed that, along with carbene **4b**, from 40 to 60% of the relatively stable (to 120–130 °C) triazolium alkoxides accumulate, thereby preventing isolation of the pure biscarbenes. It should be noted that 1,4-bis[1-(1-adamantyl-4-phenyl-1,2,4-triazol-5-ylidene-3-yl)benzene] [9], which is isomeric with biscarbenes **4a,b**, was obtained in 85% yield by deprotonation of the precursor salt with potassium methylate in a 1:1 toluene/methanol mixture. In this case, it was reported that the corresponding bistriazolium methoxide decomposed to form the biscarbene at 70–80 °C.

Biscarbenes **4a** and **4b** can be purified easily by recrystallization from toluene and cyclohexane, respectively. Compounds **4a,b** were characterized by means of elemental analysis, ¹H and ¹³C NMR spectroscopy, and in the case of **4a** also by single-crystal X-ray diffraction. The salient feature that distinguishes the ¹H NMR spectra of carbenes **4a,b** from those of their precursors **3a,b** is the absence of carbenoid signals in the range δ 10.6–10.7 ppm. The adamantyl protons are observed as three multiplets with chemical shifts of δ 1.6–1.8, 2.1–2.3 and 2.6–2.8 ppm. As noted for the monocarbene analogues [9,14], there is a significant deshielding of the adamantyl protons closest to the triazole



Scheme 1. **3a,b**: W = ClO₄, Br; **2–4**: X = 1,4-C₆H₄ (a) and 1,3-C₆H₄ (b)

rings that is not evident in the precursor bistriazolium salts. The ^{13}C NMR spectra of biscarbenes **4a,b** exhibit a signal for the carbenic carbon in the range δ 206.3–209.2 ppm. Comparable chemical shifts have been reported for mono-1,2,4-triazol-5-ylidenes (δ 207–214 ppm). These chemical shift values imply a small degree of conjugation between the triazole rings and phenylene bridge.

Crystals of biscarbene **4a** suitable for X-ray diffraction study were grown as colorless prisms by slow cooling of a hot saturated toluene solution. Biscarbene **4a** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$; there are no unusually short contacts between individual molecules. Crystal data collection and refinement details are summarized in Table 1 and selected metrical parameters are listed in Table 2. As illustrated in Fig. 1, the phenyl substituents at the C(2)-carbon atoms of biscarbene **4a** are arranged in a mutually *trans* fashion and the metrical parameters for the triazole rings are similar to those for adamantyl-substituted monocarbenes of the 1,2,4-triazole series [14]. The aromatic rings at the C(2) and N(1) positions are twisted by $31.1(3)^\circ$ and $123.5(2)^\circ$, respectively, in relation to the plane of each triazole ring. The molecule is characterized by significant delocalization reminiscent of that found for monotriazolylidenes thus confirming the aromatic character of the biscarbene. As in the case of monocarbenes, a significant feature of the structure of **4a** is a noticeable inequality of the bond orders in each triazole ring. Thus, the C(1)–N(2) bond has a particularly high multiplicity (the Penny–Dirac bond order, $p = 1.782$ vs. 1.736 for the monocarbenes described in Ref. [14]), thus implying a considerable contribution of an ylidic structure both in **4a** and also in its monocarbene analogues. It should also be noted that the Penny–Dirac bond order is $p = 1.983$ for the C=N double bond of compound **4a** while for the related mono-

Table 1
Crystal data for **4a** and **5b**

	4a	5b
Formula	$\text{C}_{42}\text{H}_{44}\text{Cl}_3\text{N}_6$	$\text{C}_{45}\text{H}_{51}\text{Cu}_2\text{I}_2\text{N}_7\text{O}$
Formula weight	632.83	1086.81
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a/\text{\AA}$	6.365(5)	13.922(3)
$b/\text{\AA}$	9.952(5)	14.203(3)
$c/\text{\AA}$	16.149(5)	14.221(3)
$\alpha/^\circ$	102.899(5)	66.66(3)
$\beta/^\circ$	98.185(5)	64.70(3)
$\gamma/^\circ$	95.948(5)	61.32(3)
$V/\text{\AA}^3$	977.2(10)	2164.6(11)
Z	1	2
$D_x/\text{g cm}^{-3}$	1.075	1.667
Crystal size/mm	$0.13 \times 0.10 \times 0.05$	$0.30 \times 0.21 \times 0.21$
θ Max/ $^\circ$	2.12–27.49	2.72–27.47
Number of reflections collected	7417	15,020
Number of independent reflections [R_{int}]	4442 [0.251]	9675 [0.0263]
R_1 [$I > 2\sigma(I)$]	0.0584	0.0338
wR_2 [$I > 2\sigma(I)$]	0.1482	0.0750
Peak and hole/ $e \text{\AA}^{-3}$	0.369 and -0.305	0.893 and -0.851

Table 2
Selected bond distances and angles for **4a** and **5b**

4a		5b	
<i>Bond lengths</i> (\AA)			
C(1)–N(1)	1.390(2)	Cu(1)–I(1)	2.5799(8)
C(1)–N(2)	1.338(2)	Cu(1)–I(2)	2.6100(9)
C(2)–N(1)	1.390(2)	Cu(2)–I(1)	2.5058(7)
C(2)–N(3)	1.303(2)	Cu(2)–I(2)	2.8268(10)
N(2)–N(3)	1.394(2)	Cu(1)–Cu(2)	2.6631(12)
N(2)–N(3)	1.436(2)	Cu(1)–C(1)	1.928(3)
		Cu(2)–C(25)	1.918(3)
		C(1)–N(1)	1.342(4)
		C(1)–N(2)	1.378(4)
		N(1)–N(3)	1.383(3)
		N(3)–C(2)	1.297(4)
		C(2)–N(2)	1.385(4)
		N(2)–C(19)	1.443(4)
<i>Bond angles/dihedral angles</i> ($^\circ$)			
N(1)–C(1)–N(2)	100.19(3)	I(1)–Cu(1)–I(2)	107.68(3)
C(1)–N(1)–C(2)	110.58(13)	Cu(1)–I(1)–Cu(2)	63.10(3)
N(1)–C(2)–N(3)	109.73(13)	I(1)–Cu(2)–I(2)	103.35(3)
C(2)–N(3)–N(2)	103.26(12)	Cu(1)–I(2)–Cu(2)	58.49(3)
N(3)–N(2)–C(1)	116.24(13)	N(1)–C(1)–N(2)	101.8(2)
N(1)–C(2)–C(3)–C(4)	31.1(3)	C(1)–N(1)–N(3)	114.2(2)
C(1)–N(1)–C(9)–C(10)	$-123.52(17)$	N(1)–N(3)–C(2)	104.5(2)
		N(3)–C(2)–N(2)	109.8(2)
		C(2)–N(2)–C(1)	109.7(2)

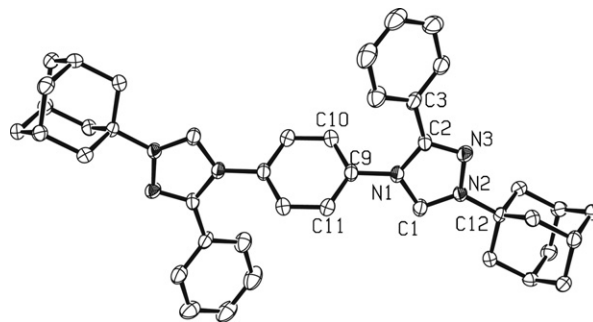


Fig. 1. X-ray structure of biscarbene **4a** showing the atom numbering scheme.

carbenes the value is 1.994. The other endocyclic bonds in biscarbene **4a** show less or equal multiplicities (C(1)–N(1) 1.483, C(1)–N(1) 1.483, N(2)–N(3) 1.293), than those for monocarbenes (C(1)–N(1) 1.506, C(2)–N(1) 1.517, N(2)–N(3) 1.293). The multiplicity of the C(Ar)–C(2) bond ($p = 1.305$) is somewhat larger than that for the C(Ar)–N(1) bond ($p = 1.218$). This is due to the smaller twist angle of the C(2)-aromatic ring relative to the triazole ring than to the N(1)-ring. The bond angle at the carbene carbon atom C(1) is almost the same as that for the related monocarbenes ($100.2(1)^\circ$) according to the X-ray diffraction study.

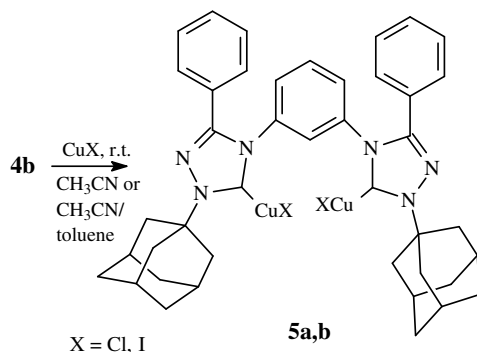
Biscarbenes **4a,b** are among the most stable carbenic structures. Thus crystalline **4a** reacts very slowly with water and oxygen in a moist atmosphere. However, in order to explore the reactivities of **4a** and **4b** somewhat further, **4a** was treated with diphenyldiazomethane, and **4b** was

allowed to react with copper(I) chloride, copper(I) iodide, and elemental sulfur. The synthesis of copper complexes **5a,b** was effected in one step by treatment of biscarbene **4b** with copper(I) halides in acetonitrile (CuCl) or an acetonitrile–toluene mixture (CuI) under an inert atmosphere (Scheme 2). The reaction of biscarbene **4b** with CuI proceeds at room temperature and complex **5b** precipitates as a white powder in good yield (72%) after 5–10 min. The interaction of carbene **4b** with CuCl is complicated by the formation of unidentified side products and is accompanied by intense coloration of the reaction mixture. As a result, the yield is reduced to 50%. Complexes **5a,b** were characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy and, in the case of **5b**, by single-crystal X-ray diffraction. Thus, the elemental analysis data indicate that the overall compositions of **5a** and **5b** correspond to the formula (biscarbene) Cu_2X_2 , where O = Cl, I. The ^1H NMR resonances for the adamantyl groups are observed in the ranges δ 1.76–1.84; 2.27–2.36; 2.51–2.53 ppm. The resonances for the protons in the 2 position of the phenylene bridge for **5a** and **5b** (δ 8.21 and 8.94 ppm, respectively) are the most diagnostic.

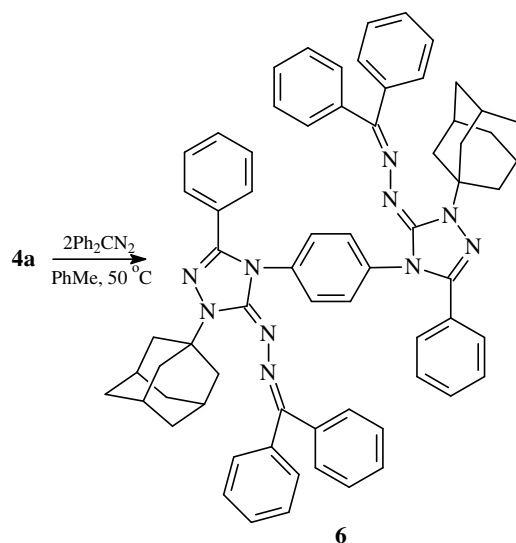
In the ^{13}C NMR spectra the carbenoid signals (C5) for complexes **5a,b** are observed at δ 176.6 and 184.4 ppm for $\text{Cu}_2\text{Cl}_2\text{L}_2$ and $\text{Cu}_2\text{I}_2\text{L}_2$, respectively (L_2 = biscarbene ligand). These signals for **5a,b** are 24.6–32.4 ppm upfield in comparison with those for biscarbenes **4a** and **4b** and 36–44 ppm downfield in comparison with those of the 1,2,4-triazolium salts.

The reaction of carbene **4a** with diphenyldiazomethane in toluene solution takes place at 50 °C and results in a good yield (70%) of the yellow-colored azine **6** (Scheme 3). Carbene **4b** reacts readily with elemental sulfur to form the bithione **7** in 77% yield (Scheme 4). Note, however, that a short heating period is required for complete decomposition of the intermediate hypervalent compounds as described in Ref. [14b].

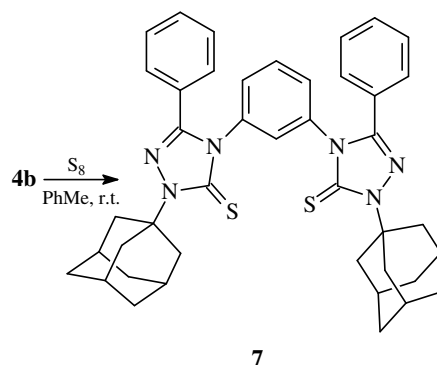
The most characteristic resonances in the ^{13}C NMR spectrum of azine **6** are those for the cyclic carbon atoms C(3) and C(5) which appear at δ 149.4 and 155.2 ppm, respectively. The signal for the C(5) atom of dithione **7** is



Scheme 2.



Scheme 3.



Scheme 4.

downfield with respect to that for azine **6** (e.g., C(3) and C(5) appear at δ 147.7 and 166.2 ppm, respectively).

Crystals of complex **5b** suitable for X-ray diffraction study, were grown from DMF solution. The complex crystallizes in the space group $P\bar{1}$ with $Z = 2$ and there are no close intermolecular contacts. There is one molecule of DMF per formula unit present in the crystal structure. Crystal data collection and refinement details are summarized in Table 1 and selected metrical parameters are listed in Table 2.

Individual molecules of **5b** (Fig. 2) feature a Cu_2I_2 core which is chelated by the biscarbene ligand **4b**. However, there is significant asymmetry in the Cu–I–Cu bridges. Thus, the Cu(2)–I(2) bond distance (2.827(1) Å) is notably longer than that for the bond Cu(1)–I(1) (2.580(1) Å). Nevertheless, both values are considerably less than the sum of ionic radii for copper and iodine (3.15–3.20 Å) and closer to the sum of covalent radii for these atoms (2.60–2.65 Å). The Cu–C(1) bond distance (1.928(3) Å) is also closer to the sum of atomic radii for the indicated atoms (2.05 Å) than to the sum of ionic radii for copper and car-

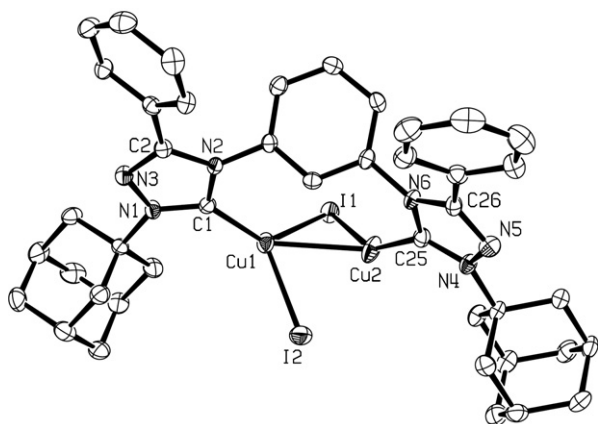


Fig. 2. X-ray structure of the DMF solvate of copper iodide biscarbene complex **5b** showing the atom numbering scheme.

bon atom (1.72 Å). On the other hand, the Cu(1)–Cu(2) distance (2.663(1) Å) exceeds the sum of atomic radii (2.56 Å) and is significantly larger than the sum of ionic radii for two copper atoms (1.90 Å). Clearly, there is no direct bonding interaction between the two copper centers. The metrical parameters for the triazole rings are similar to those for the monocarbenes [13,14]. The multiplicity of the C(Ar)–C(2) bond (Penney–Dirac order $p = 1.345$) calculated using the linear dependence of p on bond length is notably larger than that for the C(Ar)–N(2) bond ($p = 1.178$). This is probably due to the larger twist angle of aromatic ring at nitrogen N(2) than at carbon atom C(2).

In summary, we have synthesized representatives of a new class of stable biscarbenes of the 1,2,4-triazole series, namely the 4,4'-arylene-bis-1,2,4-triazol-5-ylidenes **4a,b**. Two copper(I) halide complexes have been prepared along with two new organic derivatives, **6** and **7**.

3. Experimental

3.1. General

All experiments with biscarbenes **4a,b** were carried out under an argon atmosphere. All solvents were dried by standard methods prior to use. ^1H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane (TMS, $\delta = 0.00$) as internal standard. IR spectra were measured as Nujol mulls and thin-layer chromatography was performed on silica gel with chloroform or a 10:1 mixture of chloroform and methanol as eluent, followed by development with iodine. Elemental analyses were carried out at the Analytical Laboratory of the Litvinenko Institute of Physical Organic and Coal Chemistry. Triazoles **2a,b** were obtained by the ring transformation of the respective oxadiazole **1** with *p*-phenylenediamine dihydrochloride or *m*-phenylenediamine in the presence of trifluoroacetic acid. Both reactions were carried out in *o*-dichlorobenzene at 180 °C according to the literature method [12].

3.1.1. 4,4'-*p(m)*-Phenylene-bis-[1-(1-adamantyl)-3-phenyl-1,2,4-triazolium] bromides (**3a,b**)

A mixture of (1,3-) or (1,4-)bis-(3-phenyl-1,2,4-triazole-4-yl)benzene **2a,b** (1.5 g, 4.12 mmol) and 1-bromoadamantane (2.12 g, 9.9 mmol) in acetic acid (4 mL) or dimethylformamide (6 mL) was refluxed for 6 h, followed by the addition of 1-bromoadamantane (0.27 g, 1.26 mmol) and heating for 8 h. After the reaction was complete, the mixture was treated with 10–15 mL of diethyl ether and the resulting precipitate was filtered off, washed with small amounts of hexane and diethyl ether, then dried. Each bromide salt was converted into the corresponding perchlorate by treatment with an excess of sodium perchlorate (2.02 g, 16.5 mmol) in aqueous solution.

Perchlorate **3a**: yield 96%, m.p. 285–287 °C (DMF–water, 2:3). ^1H NMR (DMSO- d_6 , 200 MHz): 1.70–1.90 (m, 12H), 2.05–2.55 (m, 18H, Ad), 7.46–7.82 (m, 14H, Ar), 10.67 (s, 2H, CHN). ^{13}C NMR (DMSO- d_6 , 50.3 MHz): 28.2; 34.6; 40.3; 62.6 (Ad); 127.8; 128.6; 128.8; 131.6 (Ar); 122.1 (*ipso*-CC); 133.4 (*ipso*-CN); 141.8 (C5); 152.0 (C3). Anal. Calc. for $\text{C}_{42}\text{H}_{46}\text{Cl}_2\text{N}_6\text{O}_8$: C, 60.50; H, 5.56; Cl, 8.50; N, 10.08. Found: C, 60.60; H, 5.49; Cl, 8.37; N, 10.01%.

Perchlorate **3b**: yield 100%, m.p. 266–267 °C (acetic acid–water, 2:1); ^1H NMR (DMSO- d_6 , 200 MHz): 1.59–1.97 (m, 12H), 2.02–2.44 (m, 18H, Ad), 7.39–7.93 (m, 14H, Ar), 10.59 (s, 2H, CHN). ^{13}C NMR (DMSO- d_6 , 50.3 MHz): 28.7; 35.0; 40.9; 63.2 (Ad); 125.6; 129.2 (enhanced int.); 130.0; 131.7; 132.2 (Ar); 122.3 (*ipso*-CC); 133.0 (*ipso*-CN); 142.3 (C5); 152.6 (C3). Anal. Calc. for $\text{C}_{42}\text{H}_{46}\text{Cl}_2\text{N}_6\text{O}_8$: C, 60.50; H, 5.56; Cl, 8.50; N, 10.08. Found: C, 60.72; H, 5.37; Cl, 8.52; N, 10.18%.

3.1.2. 1,4-Bis[1-(1-adamantyl)-3-phenyl-1,2,4-triazol-5-yliden-4-yl]benzene (**4a**)

Sodium hydride (0.31 g, 0.72 mmol) in a 55% mineral oil suspension was added to a solution of 0.3 g (0.36 mmol) of 4,4'-*p*-phenylene-bis-[1-(1-adamantyl)-3-phenyl-1,2,4-triazolium] perchlorate in 6 mL of acetonitrile at –78 °C and the resulting reaction mixture was stirred for 40–50 min, during which time the temperature rose gradually to 25 °C. The progress of the reaction was monitored by the volume of hydrogen evolved (8.1 mL). When the reaction was complete, the precipitate was filtered off, washed 2–3 times with small quantities of acetonitrile, and vacuum dried at 80 °C for 1 h. Yield 0.2 g (88%), m.p. 186–188 °C (toluene). ^1H NMR spectrum (Py- d_5 , 200 MHz): 1.55–1.92 (m, 12H), 2.04–2.25 (m, 6H), 2.43–2.62 (m, 12H, Ad); 7.15–7.55 (m, Ar). ^1H NMR (benzene- d_6): 1.70–1.92 (m, 12H), 2.00–2.10 (m, 6H), 2.40–2.82 (m, 12H, Ad); 6.50–8.12 (m, 14H, Ar). ^{13}C NMR (Py- d_5 , 50.3 MHz): 30.6; 37.0; 44.3; 60.2 (Ad); 125.8; 127.9; 128.7; 129.2; 129.8 (Ar); 130.0 (*ipso*-CC); 141.2 (*ipso*-CN); 151.4 (C3); 206.2 (C5). Anal. Calc. for $\text{C}_{42}\text{H}_{44}\text{N}_6$: C, 79.71; H, 7.01; N, 13.28. Found: C, 79.89; H, 7.21; N, 13.54%.

3.1.3. 1,3-Bis[1-(1-adamantyl)-3-phenyl-1,2,4-triazol-5-yliden-4-yl]benzene (**4b**)

A mixture of 4,4'-*m*-phenylene-bis-[1-(1-adamantyl)-3-phenyl-1,2,4-triazolium] perchlorate (0.6 g, 0.72 mmol) and 99% potassium *tert*-butoxide (0.16 g, 1.44 mmol) in 6 mL of toluene and 1.5 mL of *tert*-butanol was stirred at room temperature for 15 min. The reaction mixture was filtered and the resulting precipitate was washed with small quantities of toluene, following which the mother liquor was vacuum evaporated. The crude carbene was dried under vacuum at 50–60 °C for 30–40 min, triturated with 4 mL of hexane, then filtered off and dried. Yield 0.41 g (90%), m.p. 140 °C (cyclohexane). ¹H NMR (benzene-*d*₆, 200 MHz): 1.72–1.95 (m, 12H), 2.08–2.37 (m, 6H), 2.51–2.96 (m, 12H, Ad); 6.96–7.83 (m, 14H, Ar). ¹³C NMR (benzene-*d*₆, 50.3 MHz): 30.0; 36.6; 43.9; 59.7 (Ad); 101.9; 125.3; 127.90; 128.7; 129.2; 129.8 (Ar); 130.0 (*ipso*-CC); 140.9 (*ipso*-CN); 150.8 (C3); 209.2 (C5). Anal. Calc. for C₄₂H₄₄N₆: C, 79.71; H, 7.01; N, 13.28. Found: C, 79.78; H, 7.06; N, 13.44%.

3.1.4. Complex of 1,3-bis[1-(1-adamantyl)-3-phenyl-1,2,4-triazol-5-yliden-4-yl]benzene with copper(I) chloride (**5a**)

A mixture of carbene **4b** (0.15 g, 0.24 mmol) and copper(I) chloride (0.047 g, 0.48 mmol) in 3 mL of acetonitrile was stirred for 1.5 h. The solvent was evaporated and the resulting precipitate was triturated with diethyl ether. Following filtration, the isolated product was purified by flash chromatography on silica gel (the eluent is chloroform). The solvent was evaporated and the residue was triturated with hexane, filtered off and dried. The resulting complex was crystallized from DMF. Yield 0.1 g (50%), m.p. 271–273 °C (DMF). ¹H NMR (CDCl₃, 200 MHz): 1.76–2.00 (m, 12H), 2.30–2.48 (m, 6H), 2.53 (m, 12H, Ad); 7.07–7.68 (m, 13H), 8.21 (s, 1H, Ar). ¹³C NMR (CDCl₃, 50.3 MHz): 29.7; 35.8; 43.8; 62.0 (Ad); 124.0; 125.6; 128.2; 129.3; 129.4; 130.7 (Ar); 131.0 (*ipso*-CC); 138.8 (*ipso*-CN); 151.9 (C3); 178.6 (C5). Anal. Calc. for C₄₂H₄₄Cl₂Cu₂N₆: C, 60.72; H, 5.34; Cl, 8.53; Cu, 15.30; N, 10.11. Found: C, 60.51; H, 5.28; Cl, 8.42; Cu, 15.10; N, 10.16%.

3.1.5. Complex of 1,3-bis[1-(1-adamantyl)-3-phenyl-1,2,4-triazol-5-ylidene-4-yl]benzene with copper(I) iodide (**5b**)

A mixture of carbene **4b** (0.13 g, 0.21 mmol) and copper(I) iodide (0.078 g, 0.41 mmol), in 3 mL of acetonitrile and 1.5 mL of toluene was stirred for 1.5 h. The precipitated complex **5b** was filtered off, washed with small amounts of acetonitrile and diethyl ether, then dried. The isolated product was purified by flash chromatography on silica gel (chloroform eluent). Yield 0.15 g (72%), m.p. 263–265 °C (DMF). ¹H NMR (CDCl₃, 200 MHz): 1.61–1.88 (m, 12H), 2.05–2.41 (m, 6H), 2.41–2.72 (m, 12H, Ad); 6.76–7.54 (m, 13H), 8.94 (s, 1H, Ar). ¹³C NMR (CDCl₃, 50.3 MHz): 29.9; 36.1; 42.9; 62.0 (Ad); 122.8; 126.5; 128.4; 129.1; 129.5; 130.8 (Ar); 125.6 (*ipso*-CC); 138.4 (*ipso*-CN); 150.5 (C3); 184.5 (C5). Anal. Calc. for

C₄₂H₄₄Cu₂I₂N₆: C 49.76; H 4.37; Cu 12.54; I 25.04; N 8.29. Found: C 49.67; H 4.41; Cu 12.29; I 24.78; N 8.51%.

3.1.6. 1,4-Bis[1-(1-adamantyl)-3-phenyl-1,2,4-triazol-5-(2,2-diphenylazin)-4-yl]benzene (**6**)

A mixture of carbene **4a** (0.15 g, 0.24 mmol), diphenyldiazomethane (0.092 g, 0.48 mmol) and toluene (1.5 mL) was heated at 50 °C for 10 h. The reaction mixture was stirred with hexane (5 mL), the precipitate formed was filtered off, washed with small amounts of hexane and dried. Yield 0.17 g (70%), m.p. 268–270 °C (DMF). ¹H NMR (CDCl₃, 200 MHz): 1.43–1.77 (m, 12H), 2.03–2.36 (m, 18H, Ad); 6.90–7.55 (m, 14H, Ar). ¹³C NMR (CDCl₃, 50.3 MHz): 29.7; 36.1; 39.4; 60.1 (Ad); 126.5; 127.4; 127.6; 128.1; 128.2; 129.0; 129.3; 129.7 (Ar); 126.7; 137.2; 139.2; 145.3 (*ipso*-C); 149.4 (C3); 155.2 (C5). Anal. Calc. for C₆₈H₆₄N₁₀: C, 79.97; H, 6.32; N, 13.71. Found: C, 80.21; H, 6.18; N, 13.66%.

3.1.7. 1,3-Bis[1-(1-adamantyl)-3-phenyl-1,2,4-triazol-5-thion-4-yl]benzene (**7**)

A mixture of carbene **4b** (0.2 g, 0.32 mmol), elemental sulfur (0.04 g, 1.26 mmol) and toluene (2 mL) was stirred at room temperature for 8 h. A further 0.03 g (0.94 mmol) of sulfur was then added and the reaction mixture was refluxed for a short time. Then hexane (5 mL) was added to the cooled reaction mixture, and the resulting precipitate was filtered off, washed with small amounts of hexane, and dried. Yield 0.17 g (77%), m.p. >310 °C (DMF). ¹H NMR (CDCl₃, 200 MHz): 1.60–1.96 (m, 12H), 2.07–2.43 (m, 6H), 2.56–2.90 (m, 12H, Ad); 7.00–7.64 (m, 13H), 7.85 (s, 1H, Ar). ¹³C NMR (CDCl₃, 50.3 MHz): 29.6; 35.8; 39.1; 63.5 (Ad); 125.0; 128.3; 128.5; 128.9; 130.1; 130.4 (Ar); 131.8; 135.6 (*ipso*-C); 147.7 (C3); 166.2 (C5). Anal. Calc. for C₄₂H₄₄N₆S₂: C, 72.38; H, 6.36; S, 9.20; N, 12.06. Found: C, 72.54; H, 6.40; S, 9.09; N, 12.22%.

3.2. X-ray crystallography

Crystals of **4a** and **4b** were removed from sealed vials, placed on glass slides, covered with degassed hydrocarbon oil, and mounted on thin nylon loops. The X-ray diffraction data were collected at 153(2) K on a Nonius Kappa CCD area detector diffractometer equipped with an Oxford Cryostream low-temperature device and a graphite-monochromated Mo K α radiation source ($\lambda = 0.71073$ Å). Corrections were applied for Lorentz and polarization effects. Both structures were solved by direct methods and refined by full-matrix least-squares cycles on F^2 [17]. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were placed in fixed, calculated positions using a riding model (C–H 0.96 Å). Pertinent experimental data are listed in Table 1 and selected metrical parameters are compiled in Table 2.

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Appendix A. Supplementary material

CCDC 623045 and 623046 contain the supplementary crystallographic data for **4a** and **5b**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.07.056](https://doi.org/10.1016/j.jorganchem.2007.07.056).

References

- [1] A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* 110 (1988) 6463–6466.
- [2] G.R. Gillette, A. Baceiredo, G. Bertrand, *Angew. Chem., Int. Ed. Engl.* 102 (1990) 1486–1488.
- [3] A.J. Arduengo III, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* 113 (1991) 361–363.
- [4] A.J. Arduengo III, H.V.R. Dias, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* 114 (1992) 5530–5534.
- [5] I.P. Shvaika, N.I. Korotkikh, A.F. Aslanov, *Chem. Heterocycl. Comp. (Latvia)* (1992) 1155–1170.
- [6] H.V.R. Dias, W. Jin, *Tetrahedron Lett.* 35 (1994) 1365–1366.
- [7] W.A. Herrmann, M. Elison, J. Fischer, K. Kocher, G.R.J. Artus, *Chem. Eur. J.* (1996) 1627–1636.
- [8] N.I. Korotkikh, A.V. Kiselyov, G.F. Rayenko, N.M. Olyinik, O.P. Shvaika, *Rep. Ukr. Acad. Sci.* 6 (2002) 142–146.
- [9] M. Albrecht, R.H. Crabtree, J. Mata, E. Peris, *Chem. Commun.* (2002) 32–33.
- [10] V.C. Vargas, R.J. Rubio, T.K. Hollis, M.E. Salcido, *Org. Lett.* 5 (2003) 4847–4849.
- [11] J.A. Mata, C. Incarvito, R.H. Crabtree, *Chem. Commun.* (2003) 184–185.
- [12] N.I. Korotkikh, A.V. Kiselyov, A.V. Knishevitsky, G.F. Rayenko, O.M. Pekhtereva, I.P. Shvaika, *Chem. Heterocycl. Comp. (Latvia)* 7 (2005) 1026–1032.
- [13] N.I. Korotkikh, G.F. Rayenko, O.P. Shvaika, *Rep. Ukr. Acad. Sci.* 2 (2000) 135–140.
- [14] (a) N.I. Korotkikh, G.F. Rayenko, O.P. Shvaika, T.M. Pekhtereva, A.H. Cowley, J.N. Jones, C.L.B. Macdonald, *J. Org. Chem.* 68 (2003) 5762–5765;
(b) N.I. Korotkikh, O.P. Shvaika, G.F. Rayenko, A.V. Kiselyov, A.V. Knishevitsky, A.H. Cowley, J.N. Jones, C.L.B. Macdonald, *ARKIVOC* 8 (2005) 10–43.
- [15] N.I. Korotkikh, G.F. Rayenko, T.M. Pekhtereva, O.P. Shvaika, *Rep. Ukr. Acad. Sci.* 6 (1998) 149–152.
- [16] A.J. Arduengo, S.F. Gamper, M. Tamm, J.C. Calabrese, F. Davidson, H.A. Craig, *J. Am. Chem. Soc.* 117 (1995) 572–573.
- [17] G.M. Sheldrick, SHELL-PC Version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, USA, 1994.