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1,3-Dipolar cycloaddition of diaryldiazomethanes across *N*-ethoxy-carbonyl-*N*-(2,2,2-trichloroethylidene)amine and reactivity of the resulting 2-azabutadienes towards thiolates and cyclic amides

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Dedicated to the memory of
Prof. Bernard Laude, deceased in 2015

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ABSTRACT

1,3-dipolar cycloaddition of diaryldiazomethanes $Ar_2C{=}N_2$ across $Cl_3C{-}CH{=}N{-}CO_2Et$ **1** yields Δ^3-1,2,4-triazolines **2**. Thermolysis of **2** leads, *via* transient azomethine ylides **3**, to diaryldichloroazabutadienes $[Ar(Ar')C{=}N{-}CH{=}CCl_2]$ **4**. Treatment of **4a** (Ar = Ar' = C_6H_5) and **4c** (Ar = Ar' = *p*-ClC_6H_4) with NaSR in DMF yields 2-azabutadienes $[Ar_2C{=}N{-}C(H){=}C(SR)_2]$ **5**. In contrast, nucleophilic attack of NaS*t*Bu on **4** affords azadienic dithioethers $[Ar_2C{=}N{-}C(S^tBu){=}C(H)(S^tBu)]$ (**7a** Ar = C_6H_5; **7b** Ar' = *p*-ClC_6H_4). The reaction of **4a** with NaSEt conducted in neat EtSH produces $[Ph_2C{=}N{-}C(H)(SEt){-}CCl_2H]$ **8**, which after dehydrochloration by NaOMe and subsequent addition of NaSEt is converted to $[Ph_2C{=}N{-}C(SEt){=}C(H)(SEt)]$ **7c**. Upon the reaction of **4c** with NaS^iPr, the intermediate dithioether $[(p\text{-}ClC_6H_4)_2C{=}N{-}CH{=}C(S^iPr)_2]$ **5k** is converted to tetrakisthioether $[(p\text{-}^iPrSC_6H_4)_2C{=}N{-}CH{=}C(S^iPr)_2]$ **6**. Treatment of **4a** with the sodium salt of piperidine leads to $[Ph_2C{=}N{-}CH{=}C(NC_5H_{10})_2]$ **10**. The coordination of **6** on CuBr affords the macrocyclic dinuclear Cu(I) complex **11**. The crystal structures of **5i**, **7a**,**b**, **10** and **11** have been determined by X-ray diffraction.

1. Introduction

The reactive imine ethoxycarbonyl-*N*-(2,2,2-trichloroethylidene)amine (**1**) (also named anhydrochloral-urethane), first described by Feist and Ulrich *et al.* [1,2], has been used in the past by several groups as a versatile starting material for a number of transformations. For example, treatment of $Cl_3C{-}CH{=}N{-}CO_2Et$ (**1**) with Grignard reagents gives $Cl_3C{-}CHRNHCO_2Et$ (R = Me, Et, Pr, Bu, $PhCH_2$, $CH_2{=}CHCH_2$), which after hydrolysis and decarboxylation leads to α-amino acids [3]. Hetero-Michael addition of pyrazolinones to $Cl_3CCH{=}NCO_2R$ is reported to yield novel 1,3,4-substituted 2-pyrazolin-5-ones [4]. The synthesis of 5,6,7-substituted 1,2,4-triazolo[1,5-*a*]pyrimidines was achieved by the treatment of triazolopyrimidinols with **1** [5]. Several papers deal also with the utilisation of this imine as a heterodienophile for [4 + 2] Diels-Alder cycloadditions [6–9].

Our laboratory investigated in the late 90s the potential of the title compound as a reagent for the synthesis of heterocycles via 1,3-dipolar cycloaddition [10–12]. In this

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context we have described and discussed the unexpected formation of 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene [$Ph_2C{=}N{-}CH{=}CCl_2$] (**4a**) by cycloaddition of diphenyldiazomethane across the imine function of **1** at 65 °C in toluene [12]. We have demonstrated that the first step of the process consists of a dipolar 1,3-cycloaddition of the diazo-compound across the imine, leading to the Δ^3-1,2,4-triazoline **2a**. Then, extrusion of dinitrogen gives the transient azomethine ylide **3a**. Subsequent elimination of ethyl chloroformate produces the 2-azadiene **4a** in 70% yield (Scheme 1). Investigating the electronic structure and chemical properties of **4a**, we have found that it presents an interesting reactivity towards various nucleophiles, such as alkoxides, thiolates, and the sodium salt of pyrrole or the cyanide anion [13–17]. More recently, some of these compounds were reacted as *S,N*-chelators with transition metal derivatives and allowed us to access new organometallic products *via* oxidative addition and cyclometallation reaction [18,19].

In order to modulate the electronic properties of this reactive 2-azadienic array, we now have investigated two different strategies to prepare functionalized derivatives of **4a** to have a feedstock for further organic or organometallic transformations:

(i) introduction of electron-pushing or withdrawing substituents at the *para*-positions of the phenyl rings.
(ii) systematic investigation of the reactivity towards a wide series of thiolates SR^- and amides NR_2^- to obtain functional ligands possessing both *S,N* or *N,N* donor sites for complexation studies.

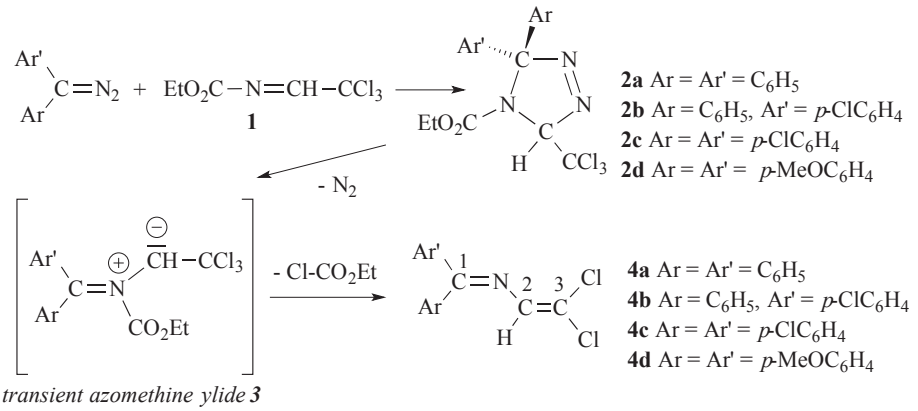
We report herein the preparation of some new functionalized 1,1-diaryl-4,4-dichloro-2-azabutadienes and the rich reactivity of these π-conjugated compounds [20] towards various thiolate nucleophiles of the type NaSR. The molecular structures of some azadienic dithioethers resulting from the unpredictable attack of thiolates have been determined by means of X-ray diffraction studies. This investigation includes also a reactivity study of **4a** toward the sodium salt of piperidine and the structural characterization of the resulting substitution product.

2. Results and discussion

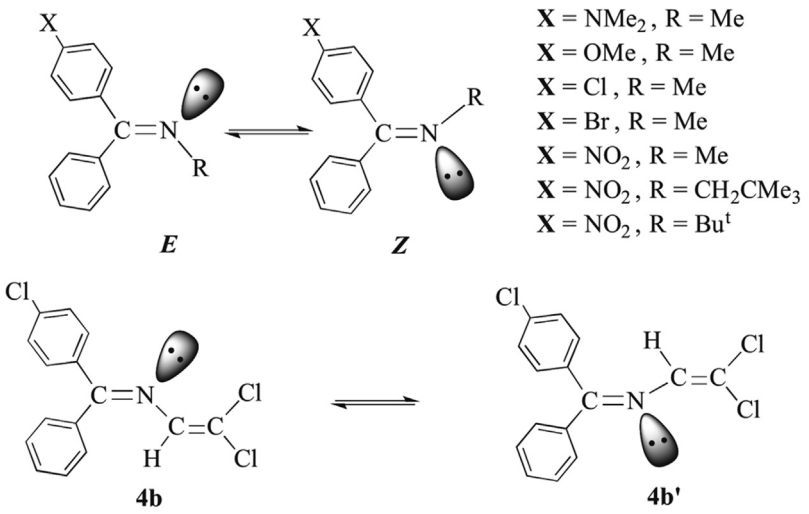
2.1. Cycloaddition of diaryldiazomethanes $Ar_2C{=}N_2$ across $Cl_3C{-}CH{=}N{-}CO_2Et$

In analogy to the protocol using diphenyldiazomethane as a dipole, the cyloaddition of di(*p*-chlorophenyl)diazomethane, (*p*-chlorophenyl)phenyldiazomethane and di(*p*-methoxyphenyl)-diazomethane produces at 20 °C in toluene as solvent, the expected Δ^3-1,2,4-triazolines **2b–d** as colourless powders (see Scheme 1). Subsequent thermolysis of these heterocyclic compounds in toluene at 60° leads to (most probably *via* the transient azomethine ylides **3** [21]) the corresponding 1,1-diaryl-4,4-dichloro-2-azabutadienes **4b–d** as pale-yellow stable solids. However, it is not necessary to isolate first the heterocyclic intermediates **2**. If the imine **1** is treated with $Ar_2C{=}N_2$ in warm toluene, *in situ* transformation affords straightforwardly the 2-azadienes **4**. The crude residue of **4c** is contaminated by 10–15% of tetrakis(*p*-chlorophenyl)diazine (p-$ClC_6H_4)_2C{=}N{-}N{=}C(p$-$ClC_6H_4)_2$ as a minor product, which can be separated by fractional crystallisation from hot ethanol [22].

As observed in the proton NMR spectrum of **4a**, the vinylic hydrogen resonances of **4c** and **4d** are quite low-field shifted and appear as singlets at δ 7.07. Furthermore, two distinct singlets due to the methoxy groups are found at δ 3.83 and δ 3.87 in the spectrum of **4d**. In the case of **4b**, two singlets in a 2:1 ratio are detected at δ 7.03 and δ 7.01 in $CDCl_3$ solution, respectively. Two singlets, attributed to the C=N resonance, are also observed in the $^{13}C\{^1H\}$ spectrum at δ 167.0 and 166.9 in an approximate 2:1 ratio. Initially, we rationalized this finding by formation of two stereoisomers resulting from different approaches of the dissymmetric diaryldiazoalkane across the C=N bond of imine **1** in the transition state. A careful examination under an optical microscope confirmed that the morphology of all crystals of **4b** within this batch was quite homogenous, the melting point being sharp between 64–66 °C. Surprisingly, dissolving a single crystal in $CDCl_3$ again gave rise to two sets of signals in the 2:1 ratio. A survey of the literature revealed that this phenomenon is most probably due to a hindered inversion at the imine nitrogen. For example,



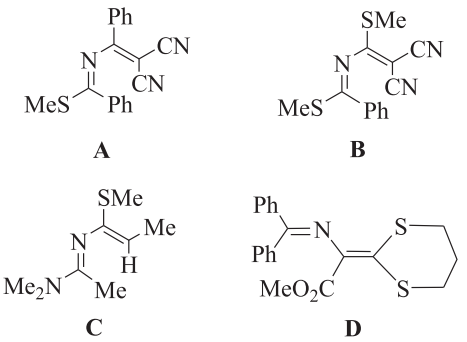
Scheme 1. Reaction of diaryldiazomethanes with imine **1**.



Scheme 2. Invertomers resulting from N-inversion of the imine.

Jennings *et al.* investigated in detail a series of Schiff bases of type *p*-$XC_6H_4(C_6H_5)C{=}NR$ reminiscent to **4b**, illustrated in Scheme 2 [23].

The activation barrier for this imine inversion has been estimated by means of dynamic NMR spectroscopy to be of some 30 kcal/mol, the value varying in function of substituent X. We suppose, that in the case of **4b**, a similar inversion process may operate giving rise to a co-existence of *E* and *Z* invertomers in solution. Since this phenomenon is beyond the topic of this article, we did not undertake NMR studies at variable temperature.



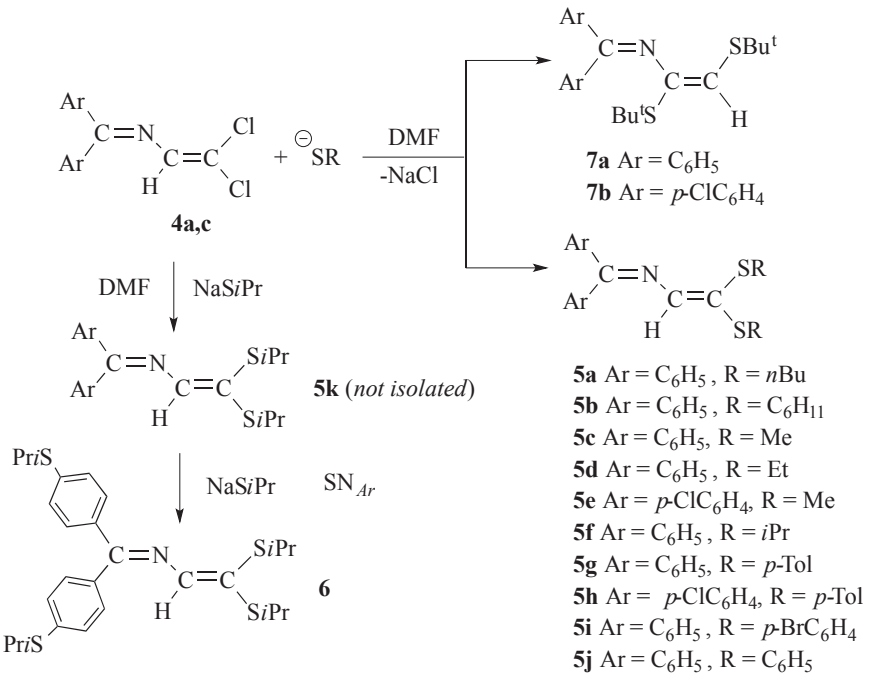
2.2. Reactivity of **4a** and **4c** towards NaSAr, $NaSC_6H_{11}$, NaSMe and NaS^nBu

Three strategies have been developed in the past to synthesise 2-azabuta-1,3-dienes with thioether substituents: (*E*)-1-methylthio-2-azabuta-1-3-diene-4-carbonitriles like **A** and **B** were prepared by the addition of thioamides to methoxymethylene compounds or ketene dithioacetals and subsequent methylation, [24] whilst 3-aza-2-(dimethylamino-4-(methylthio)-2,4-hexadiene (**C**) was obtained from treatment of *N*-(thiopropionyl)acetamidine with CH_3I and subsequent deprotonation of the resulting *N*-ylidene amidinium salt [25]. The crystallographically characterized dithioether **D** and related compounds were obtained by alkylation of the dithiolates $Na_2[S_2C{=}C(R){-}N{=}CPh_2]$ (R = CO_2Me, CN) with CH_3I or $Br(CH_2)_nBr$ (n = 2, 3) [26].

In precedent papers we have demonstrated that **4a** reacts under mild conditions in dry DMF with an excess of NaSR leading exclusively to the dithioether derivatives of type $[Ph_2C{=}N{-}C(H){=}C(SR)_2]$ (R = Ph, *p*-Tolyl, *i*Pr), consistent with formal substitution of the two chloro-substituents on the vinylic C3 atom by SR^-. Their crystal structures have been already published [14,15,19a]. An addition-elimination mechanism, initiated by nucleophilic addition to the C3 atom, elimination of chloride followed by addition of a second thiolate on the C3 atom and termination by dissociation of the remaining chloride has been suggested [14]. A mono-substituted thioether intermediate, $[Ph_2C{=}N{-}C(H){=}C(Cl)(SPh)]$, in which the SR group is *cis*-situated relative to the imine nitrogen, has been structurally characterized [19b]. Note, that for vinylic substitutions also other mechanisms such as $S_{RN}1$-type single-electron transfer may operate [27–29].

With the exception of **5a**, **5b** and **5d**, which were isolated as viscous oils, all other derivatives (Scheme 3) formed yellow solids. An X-ray structure analysis has been carried out on a crystal of **5i** grown from EtOH (Fig. 1). The *s-trans* conformation of the azabutadiene chain found in precursor **4a** and in **5f, 5g** and **5j** is also observed in the solid-state structure of **5i**. Metric parameters and crystallographic data are gathered in Tables 1 and 2. All in all, they resemble much to those of $[Ph_2C{=}N{-}C(H){=}C(SPh)_2]$ **5j** [14] and $[Ph_2C{=}N{-}C(H){=}C(p\text{-}STol)_2]$ **5g** [15] and deserve no further comment.

In contrast to the facile preparation of compounds $[Ph_2C{=}N{-}C(H){=}C(SR)_2]$ **5** bearing a $Ph_2C{=}N$ imine function, the synthesis of derivatives $[(p\text{-}ClC_6H_4)_2C{=}N{-}C(H){=}C(SR)_2]$ **5e** and **5k** was less straightforward. $[(p\text{-}ClC_6H_4)_2C{=}N{-}C(H){=}C(SMe)_2]$ **5e** could be isolated only in a quite modest yield of 20% as a yellow solid. Furthermore, chromatography of the crude residue of **5e** provided a second



Scheme 3. Reaction of **4** with aliphatic and aromatic thiolates.

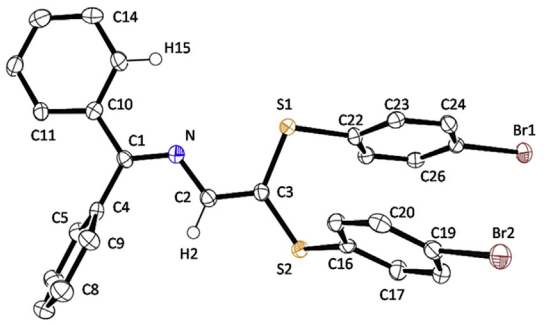


Fig. 1. ORTEP view of **5i** at the 50% probability level.

fraction containing the tris(thioether) [(MeSC$_6$H$_4$)(*p*-ClC$_6$H$_4$)C=N–C(H)=C(SMe)$_2$], albeit in a low yield of 3%. A high-resolution mass spectrum of this bright-yellow solid displayed a peak at *m*/*z* 379.66 (Fig. S1), whose simulation matches well with a composition of $C_{18}H_{18}ClNS_3$, corroborating the formation of a triply SMe-substituted azabutadiene.

During the synthesis of the compound [(*p*-ClC$_6$H$_4$)$_2$C=N–C(H)=C(S^{i}Pr)$_2$] **5k**, spectroscopic analysis did not allow to elucidate its structure unequivocally. Only in the case of [(*p*-ClC$_6$H$_4$)$_2$C=N–C(H)=C(STol-*p*)$_2$] **5h**, a high-yield synthesis could be performed. Since aromatic halides are known to undergo nucleophilic substitutions of the S_NAr type with highly nucleophilic aliphatic thiolates NaSMe

Table 1
Significant metric parameters, distances (Å) and angles (°) for thiolate- and piperidine-substituted azabutadienes **5i**, **7a,b**, **10** as well as for the dinuclear copper complex **11**.

Compound	**5i** 115K	**7a** 293K	**7b** 115K	**10** 115K	**11** 115K
C1–N	1.304(4)	1.274(3)	1.286(2)	1.298(1)	1.302(6)
N–C2	1.379(5)	1.411(3)	1.424(2)	1.385(1)	1.396(6)
C2–C3	1.352(5)	1.330(3)	1.327(3)	1.369(1)	1.353(7)
C1–C(//)[a]	1.469(5)	1.487(4)	1.484(2)	1.483(1)	1.490(7)
C1–C(⊥)[a]	1.499(5)	1.498(4)	1.495(2)	1.497(1)	1.497(7)
C3–X$_{trans}$[b]	1.749(4)	1.769(3)[c]	1.778(2)[c]	1.407(1)	1.778(5)
C3–X$_{cis}$[b]	1.777(4)	1.740(3)	1.747(2)	1.389(1)	1.751(5)
N/C1/C(//)/C5	−8.0	12.2	16.2	−14.5	32.3(7)
N/C1/C(⊥)/C15	75.0	69.8	71.0	−61.1	52.7(7)
N/C1/C(//)[a]	117.4(3)	118.0(3)	118.6(2)	117.85(10)	119.3(4)
N/C1/C(⊥)[a]	123.5(3)	123.5(3)	123.4(2)	124.44(10)	122.9(4)
C1/N/C2/C3	−176.7	−111.6	−116.5	178.4(1)	151.6(5)

[a] C(//) and C(⊥) are the ipso carbon atoms of aryl groups, respectively, nearly coplanar and roughly perpendicular with respect to the plane of the azadiene chain.
[b] X = S or N, *trans* and *cis* refer to the *N* atom of the azabutadiene chain.
[c] C2–S^{t}Bu.

Table 2
Crystallographic and refinement data for compounds **5i, 7a, 7b, 10** and the Cu complex **11**.

Compound	**5i**	**7a**	**7b**	**10**	**11**
Empirical formula	$C_{27}H_{19}Br_2NS_2$	$C_{23}H_{29}NS_2$	$C_{23}H_{27}Cl_2NS_2$	$C_{25}H_{31}N_3$	$C_{54}H_{74}Br_2Cu_2N_2S_8$
Formula weight	581.37	383.62	452.51	373.53	1294.06
Temperature, K	115(2)	293(2)	115(2)	115(2)	115(2)
Wavelength, Å	0.71073 Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å and °)	$a = 6.8333(2)$ $b = 12.6786(5)$ $c = 14.1754(6)$ $\alpha = 102.577(1)$ $\beta = 97.714(2)$ $\gamma = 93.156(2)$	$a = 12.3662(5)$ $b = 10.5268(4)$ $c = 17.1480(8)$ $\alpha = 90$ $\beta = 97.109(2)$ $\gamma = 90$	$a = 9.3277(2)$ $b = 14.8893(4)$ $c = 17.3373(5)$ $\alpha = 90$ $\beta = 98.964(1)$ $\gamma = 90$	$a = 9.5449(4)$ $b = 10.1818(4)$ $c = 10.9957(3)$ $\alpha = 95.864(2)$ $\beta = 96.571(2)$ $\gamma = 103.203(1)$	$a = 10.4760(5)$ $b = 11.9864(5)$ $c = 12.9220(4)$ $\alpha = 101.519(2)$ $\beta = 101.928(2)$ $\gamma = 108.867(2)$
Volume, Å^3	1183.27(8)	2215.11(16)	2378.45(11)	1024.39(7)	1438.68(10)
Z	2	4	4	2	1
Density, calcd	1.632 Mg/m^3	1.150 Mg/m^3	1.264 Mg/m^3	1.211 Mg/m^3	1.493 Mg/m^3
Linear Abs. Coef.	3.618 mm^{-1}	0.247 mm^{-1}	0.458 mm^{-1}	0.071 mm^{-1}	2.455 mm^{-1}
Abs. correction	(T_{min} 0.6707; T_{max} 0.9312)			(T_{min} 0.9824; T_{max} 0.9915)	
F(000)	580	824	952	404	667
Crystal size (mm)	0.12 × 0.07 × 0.02	0.15 × 0.15 × 0.05	0.25 × 0.2x0.1	0.25 × 0.15 × 0.12	0.12 × 0.02 × 0.02
Theta range for data collection	1.49 to 27.47°	2.90 to 27.57°	2.71 to 27.51°	3.22 to 27.55	2.13 to 25.00°
Index ranges	$-8 \le h \le 8$ $-16 \le k \le 16$ $-18 \le l \le 18$	$-15 \le h \le 15$ $-13 \le k \le 12$ $-22 \le l \le 22$	$-12 \le h \le 12$ $-19 \le k \le 17$ $-22 \le l \le 22$	$-12 \le h \le 12$ $-13 \le k \le 13$ $-9 \le l \le 14$	$-13 \le h \le 13$ $-15 \le k \le 15$ $-16 \le l \le 16$
Refl. collected	16609	8505	9446	7680	38706
Independent refl. (R(int))	5403 (0.0749)	5029 (0.1045)	5416 (0.0388)	4585 (0.0165)	6331 (0.1057)
Data/restraints/parameters	5403/0/289	5029/0/235	3043/0/217	4585/0/253	6331/0/370
Refl. gt [$I>2\sigma(I)$]	4373	1639	3806	4068	4936
GoF on F^2	1.099	0.857	1.025	1.068	1.039
Final R factors [$I>2\sigma(I)$]	$R_1 = 0.0452$, $wR_2 = 0.0877$	$R_1 = 0.0530$, $wR_2 = 0.0849$	$R_1 = 0.0412$, $wR_2 = 0.0791$	$R_1 = 0.0427$, $wR_2 = 0.1022$	$R_1 = 0.0426$, $wR_2 = 0.1171$
R factors (all data)	$R_1 = 0.0626$, $wR_2 = 0.0963$	$R_1 = 0.2351$, $wR_2 = 0.1208$	$R_1 = 0.0736$, $wR_2 = 0.0885$	$R_1 = 0.0500$, $wR_2 = 0.1094$	$R_1 = 0.0524$ $wR_2 = 0.1171$
Largest ρ_{max}/ρ_{min} (e.Å^{-3})	0.482/−0.584	0.175/−0.216	0.296/−0.322	0.321/−0.176	1.589/−1.851

and NaS^{i}Pr, we reacted **4c** with a 10-fold excess of NaS^{i}Pr in DMF under gentle heating. Indeed, after workup, we succeeded in isolating the azadienic tetrakisthioether [(^{i}PrSC$_6$H$_4$)$_2$C═N–C(H)═C(S^{i}Pr)$_2$] **6** with 48% yield in the form of a yellow solid (Scheme 3) [30,31].

2.3. Reactivity of *4a* and *4c* towards sodium tert-butylthiolate

We extended the reactivity study of **4a,c** towards thiolates also on the reaction with NaS^{t}Bu in DMF as solvent. Surprisingly, the spectroscopic features of the substitution products **7**, which were isolated after workup as orange-red stable crystalline solids, diverged much from those of **5**. For example, the vinylic H resonance of **7a** and **7b** were detected at δ 5.98 and 6.01 ppm in the ^{1}H NMR spectrum, whereas the vinylic H atom of **5** gives rise to a singlet at a much lower field of about 7.1 ppm. The ^{t}Bu groups appear as a set of close, but distinct singlets for **7a** at δ 1.39 and 1.40 ppm (δ 1.35 and 1.43 for **7b**). In the case of **7a**, comparison of the experimental chemical shift (5.98 ppm) with the values of the chemical shifts at 5.94 (*trans* or *E* with respect to both ^{t}Bu substituents) and 6.61 (*cis* or *Z*) ppm calculated by the incremental method of Pascual, [32] allowed us to assign *E*-stereochemistry around the olefinic double bond. This *E*-stereochemistry was furthermore ascertained by X-ray crystallography.

X-ray quality crystals of **7a,b** were grown from EtOH and the molecular structures are depicted in Fig. 2. The outstanding information got from concerns the position of the S^{t}Bu substituents. One S^{t}Bu is found, as in all our thioether compounds **5**, at the C3 atom and in the *cis*-position relative to the imine nitrogen. However, and for the first time in this series, we observe the second SR substituent on the C2 atom. The torsion C1–N–C2–C3 angles are far from 180° (**7a** 111.6(2)°, **7b** 116.5(2)°, Table 2), approaching a limit of 90° for which both formal double bonds are perpendicular and their conjugation is almost completely broken. This is nicely demonstrated by the N–C2 bonds (**7a** 1.411(3) Å, **7b** 1.424(2) Å), which are longer than those observed in the *s-trans* structures where the C2 atom bears the hydrogen atom (see other compounds in Table 1). Thus the *s-trans* conformation of the azabutadiene chain seen for **5** is strongly perturbed. Such a large distortion from ideal *s-trans* conformation has been already observed in other 2-aza-1,3-butadiene structures substituted at the C2 atom [33–40] The dihedral angles between "nearly parallel" phenyl ring C4–C9 and the three atom C1–N–C2 plane of the azadienic chain are equal to 15.0(3)° (**7a**) and 18.6(2)° (**7b**) with the corresponding N/C1/C4/C5 torsion angles of 12.2° and 16.2°, respectively. These experimental values fall in the range observed for compound **5i**. The N/C1/C4 and N/C1/C10 angles in the imine part of the molecules also have values close to those found in **5**.

Of course the question arises, why **4** exhibits a different substitution pattern in the case of NaS^{t}Bu compared to the other sodium thiolates, including even steric demanding

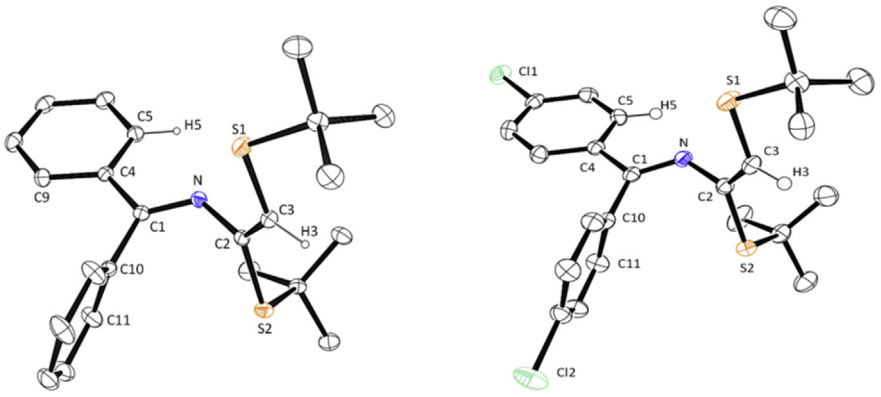


Fig. 2. ORTEP views of **7a** (left, 20% probability level) and **7b** (right, 50% probability level).

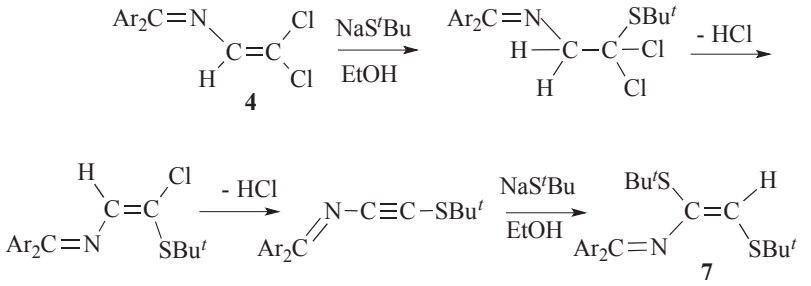
thiolates such NaS^{i}Pr and NaSC$_6$H$_{11}$. At the first glance, one may suspect a strong sterical repulsion between two geminal -S^{t}Bu groups residing on the terminal carbon atom of a hypothetical isomer [Ar$_2$C═N–C(H)═C(S^{t}Bu)$_2$](**7′**). However, a literature survey reveals that polythioethers with two *gem*-S^{t}Bu groups attached on the same carbon atoms exist, [41] for instance the allene [(^{t}BuS)$_2$C═C═C(Ph)(S^{t}Bu)] [42]. Another example is the structurally characterized butatriene-type tetrakisthioether [(^{t}BuS)$_2$C═C═C═C(S^{t}Bu)$_2$] [43]. But in all these examples, the adjacent carbon atom is an allenic one of the ═C═ type. But there is also a report on the diene 7,8,8-tris[(*tert*-butyl)thio]-6-vinylpentafulvene [(^{t}BuS)$_2$C═C(^{t}BuS)–C(H)═C$_5$H$_4$] [44].

Let's have a look on the simplest model compound, *e.g.* dichlorovinylidene. Truce *et al.* have studied the reactivity of Cl$_2$C═CH$_2$ toward NaSTol-*p* and NaS^{t}Bu [45,46]. In the case of the more nucleophilic NaS^{t}Bu reagent, they established an addition-elimination pathway *via* a transient alkyne species rationalizing the formation of *cis*-1,2-bis(*tert*-butylmercapto)ethene as the sole product [45,46]. Some intermediates such as 1,1-dichloro-2-(*tert*-butylmercapto)ethane and *trans*-1-chloro-2-(*tert*-butylmercapto)ethene could be isolated. Later work of Tanimoto *et al.* confirmed that the reaction of dichlorovinylidene with sodium phenylthiolate in DMF affords exclusively *cis*-1,2-bis(phenylmercapto)ethane [47–49]. We propose a similar addition-elimination mechanism explaining the formation of **7** (Scheme 4).

More recently our group demonstrated that upon the reaction of dibromovinylferrocene [Br$_2$C═C(H)-Fc] with NaS^{t}Bu and NaSAr (Ar = Ph, *p*-tol) the structurally characterized rearrangement products *Z*-[(^{t}BuS)(H)C═C(H)-Fc] and *Z*-[(ArS)(H)C═C(SAr)-Fc] were formed [50a]. In a similar manner, treatment of dibromovinyl[2.2]paracyclophane [Br$_2$C═C(H)-PCP] with excess of NaSAr in DMF gives rise to the vicinal dithioethers *Z*-[(ArS)(H)C═C(SAr)-PCP] [50b]. Therefore one may conclude from the above discussion that the formation of the azabutadienes **5** bearing two *geminal* SR functions could be considered as an exceptional case, whereas the rearrangement encountered in the case of NaS^{t}Bu leading to **7** corresponds rather to the "classical" pathway. We suppose that a combination of both steric and electronic factors is decisive for the formation of **7** using the bulky and highly nucleophilic NaS^{t}Bu. The NaS^{n}Bu reagent leading to **5a** should have a comparable basicity and nucleophilicity with NaS^{t}Bu, but is doubtlessly sterically less demanding.

2.4. Reactivity of *4a* towards sodium ethylthiolate

In analogy to the synthesis of compounds **5**, the reaction of **4a** with NaSEt in DMF at room temperature afforded exclusively [Ph$_2$C═N–C(H)═C(SEt)$_2$] **5d,** as confirmed by the presence of the vinylic hydrogen as a singlet at δ 7.10 ppm and two sets of SEt groups in the ^{1}H NMR spectrum. However, when the reaction of **4a** (Scheme 5) was conducted with an excess of NaSEt under reflux in neat ethanethiol for 4 days, imine [Ph$_2$C═N–C(H)(SEt)–CCl$_2$H] **8** was isolated as a yellow solid. The constitution of **8** has been elucidated from mass spectroscopy and NMR data.



Scheme 4. Possible mechanism of the conversion of **4** to **7** in the presence of NaS^{t}Bu.

Both the ^{1}H (Fig. S2) and ^{13}C NMR spectra of **8** reveal the presence of only one thioethyl group. This unexpected product results probably from formal EtSH addition across the C=C bond of **4a**, similar to the first step of the reaction sequence shown in Scheme 4.

It seems that the basicity of NaSEt does not permit the elimination of HCl. However, the reaction of compound **8** in toluene with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or an equivalent of NaOMe in methanol yields quantitatively the dehydrochlorinated compound **9**. We identified a mixture of two diastereomers (*Z*)-**9**/(*E*)-**9** in a 9:1 ratio. The proton NMR spectrum allows distinguishing two vinylic protons at 5.22 and 5.52 ppm. By comparison with the chemical shifts at 5.23 and 5.51 ppm respectively, calculated by the incremental method of Pascual, [32] we can assign the major compound (singlet at 5.52 ppm) to the stereoisomer (*Z*)-**9**. The synthesis of the azabutadiene **7c,** which is structurally related to **7a,b**, was achieved by reacting **9** with an excess of NaSEt in ethanol. The proton NMR spectrum revealed again the presence of a mixture of two stereoisomers (*Z*)-**7**/(*E*)-**7** in an approximate 8:2 ratio. Two vinylic protons are observed at 5.20 and 5.47 ppm. Again, the incremental method of Pascual allowed a stereochemical assignment of the resonances. For the dominating stereoisomer (*Z*)-**7c**, a chemical shift of 5.23 ppm was calculated. For the vinylic hydrogen of the minor isomer (*E*)-**7c**, a chemical shift of 5.47 ppm was calculated, demonstrating the excellent match with the experimental data.

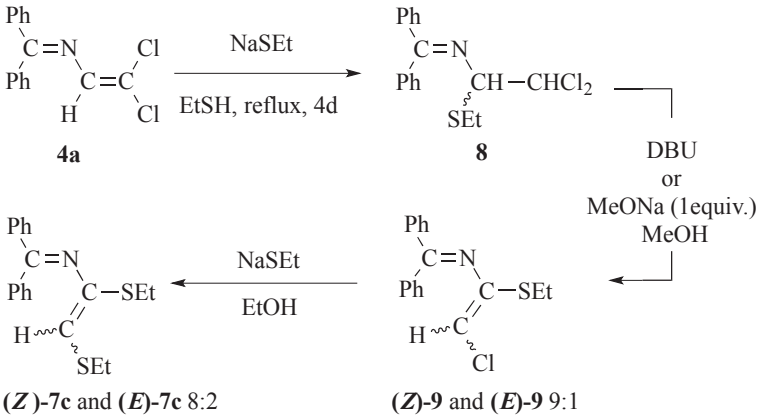
2.5. Reactivity of *4a* towards the sodium salt of piperidine

With the aim to prepare amine-substituted azabutadienes related to **5** and **7**, we have reacted **4a** with secondary amides $X_2N^-Na^+$ (X = Ph, Et) as well as with $NaNH_2$. But despite varying the reaction conditions, we failed to isolate any product. Fortunately, treatment of **4a** with cyclic amides was more successful. We have communicated that the reaction of **4a** with the sodium salt of pyrrole leads, through an addition-elimination process, to (*E*)-4-chloro-1,1-diphenyl-3-(1-pyrrolyl)-2-azabuta-1,3-diene, in which the chloro and the *N*-pyrrole substituents are in a *trans*-configuration [16]. For comparison, we treated **4a** with the *in situ* prepared sodium salt of piperidine using neat piperidine as the reaction medium. After work-up, a yellow solid [Ph_2C=N–C(H)=$C(NC_5H_{10})_2$] (**10**) was isolated in 45% yield (Scheme 6).

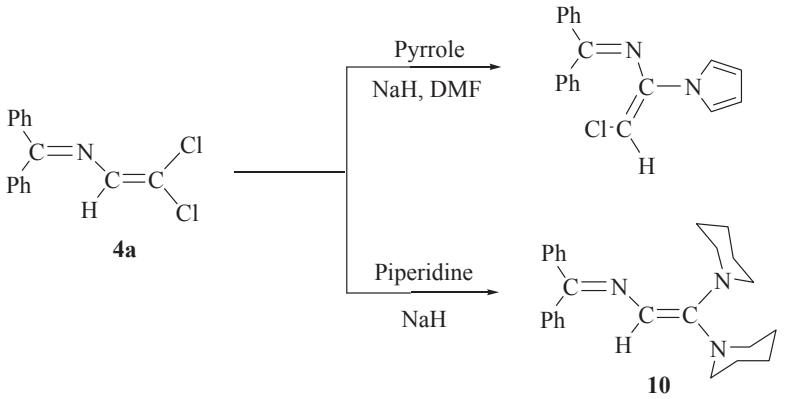
Since the spectroscopic data, notably the chemical shift of the vinylic H-proton resonating at δ 5.40 ppm did not allow an unambiguous assignment of the substitution pattern of the azadienic chain, we have grown single-crystals of **10** from ethanol and determined the molecular structure of this piperidino-functionalized 2-azabutadiene. An ORTEP plot depicted in Fig. 3 confirms that the molecular geometry and substitution pattern correspond to that of [Ph_2C=N–C(H)=$C(OPh)_2$] [14] and [Ar_2C=N–C(H)=$C(SR)_2$] (**5**). Again, one aryl group is almost coplanar with the transoid azabutadiene array (N1/C1/C4/C5 torsion angle −14.5(2)°, Table 1). The torsion angle of the azadiene array (C1/N1/C2/C3) reaches 178.4(1)°. Both piperidine substituents on the C3 atom adopt a chair conformation. The mean C–N distance of the $C=C(NC_5H_{10})_2$ moiety bearing the two bulky piperidyl groups amounts to 1.395(2) Å and compares well with that reported for methyl-3,3-dipiperidinodithioacrylate [MeSC(=S)–C(H)=$C(NC_5H_{10})_2$] (1.35(4) Å) [51] as well as with other structures reported in this article.

2.6. Coordination of *6* on CuBr yielding a 16-membered macrocyclic complex

As stated in the introduction, one of the aims of this work was the preparation of a wide range of potentially bi- or poly-dentate unsaturated ligands for coordination chemistry. In a preliminary study on the coordination properties of tetrathioether **6**, we reacted this ligand with CuBr in a 1:1 metal-to-ligand ratio. A single-crystal diffraction study (Fig. 4) indicates that from four available sulphur coordination sites in the ligand, only one aryl-bound S*i*Pr group and one vinylic S*i*Pr group are involved in the complexation of **6** on CuBr leading to the original dinuclear 16-membered macrocyclic complex [{Cu_2Br_2(*p*-*i*PrSC_6H_4)$_2$C=N–C(H)=C(S*i*Pr)$_2$}$_2$] (**11**). The cycle is built over the crystallographic symmetry centre in the $P\bar{1}$ space group. Consequently, the central phenyl rings (C4 through



Scheme 5. Reactivity of **4a** towards sodium ethylthiolate.



Scheme 6. Reaction of **4a** with cyclic amides.

C9 between the Cu/Cu* atoms) are parallel but slipped with respect to each other. The distance between these two planes is close to 3.4 Å and may so suggest a kind of intramolecular π stacking (Fig. S3) as encountered in cyclophanes.

3. Conclusion and perspectives

We have shown that *p*-aryl-substituted 2-azadienes of type [$Ar_2C{=}N{-}C(H){=}CCl_2$] (**4**) (Ar = Ph, *p*-C_6H_4Cl, *p*-C_6H_4OMe) are accessible by 1,3-dipolar cycloaddition of $Ar_2C{=}N_2$ across $Cl_3C{-}CH{=}N{-}CO_2Et$ and observed that the nucleophilic attack of RS^- and $NaNC_5H_{10}$ leads preferentially to [$Ar_2C{=}N{-}C(H){=}C(SR)_2$] (**5**) and [$Ph_2C{=}N{-}C(H){=}C(Pip)_2$] (**8**) bearing the SR and NR_2 substituents at the C^3 carbon. However, the fact that the nucleophilic attack of Na*t*SBu affords the dithioethers [$Ar_2C{=}N{-}C(S$*t*$Bu){=}C(H)(S$*t*$Bu)$] (**7a,b**) as sole products demonstrates that the outcome of the reaction is difficult to predict and depends in a sensitive manner on several parameters. This was illustrated in the reaction of **4a** with EtSNa in DMF or EtSH as solvents, leading to the formation of mono- and di-substituted compounds **5d** or **8**, respectively. The organic chemistry of the intermediate triazolines heterocycles is currently extended to the preparation of mixed alkyl-aryl systems of the type [Ar(Alkyl)C=N–C(H)=CCl_2].

The straightforward preparation of ligands **5** and **7** permits furthermore a promising development in coordination chemistry, where a subtle fine-tuning of the stereoelectronic parameters exerted by the substituents ^-SR is of great importance. The design of the polydentate tetrakisthioether **6** and its coordination on CuBr giving rise to the unusual macrocyclic compound **11** demonstrates the potential of this ligand for the assembly of polymetallic systems and metal-organic frameworks [52]. In this context, we are currently extending the reactivity studies of **4** towards other nucleophiles and are exploring the coordination chemistry vis-à-vis numerous transition metals like Re, Mn, Cu, Ag, Ru and Fe and are investigating the electrochemical and photophysical properties of resulting mono- and di-nuclear systems. The potential of these polydentate ligands to act as *C,N,S* and *C,N,N* pincer ligands after cyclometallation reactions with Pd(II), Pt(II) and Ir(I), the electronic and molecular structures of the resulting organometallic compounds possessing a reactive covalent

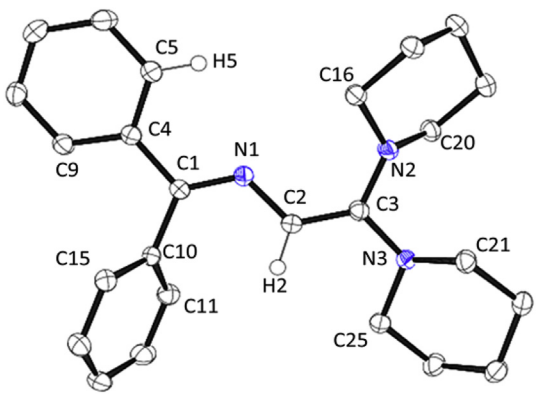


Fig. 3. ORTEP view of **10** at the 50% probability level. Hydrogen atoms (except H2 and H5) are omitted for clarity.

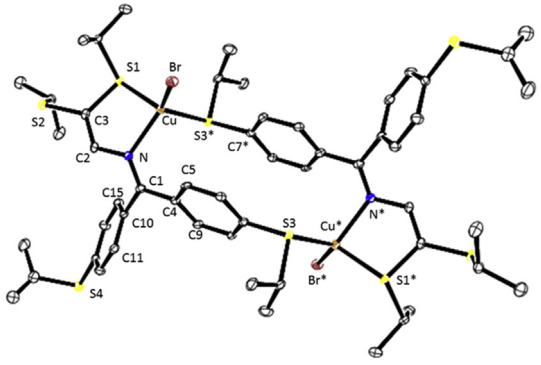


Fig. 4. ORTEP view of the dinuclear macrocyclic complex **11** at the 30% probability level. Selected bond lengths [Å] and angles [°]: Cu–Br 2.3635(8), Cu–N 2.120(4), Cu–S1 2.3537(13), Cu–S3 2.3382(14), N–Cu–S1 83.88(11), N–Cu1–S3 100.28(11), N–Cu–Br 123.81(11), S1–Cu–S3 103.18(5), S1–Cu–Br 118.38(4), S3–Cu–Br 120.19(4), see also Table 1 for the parameters inside the ligand.

metal-aryl bond towards insertion reactions will be the topic of a forthcoming paper.

4. Experimental

4.1. General methods

The NMR spectra were recorded on a Bruker Avance 300 apparatus (300.13 and 75.1 MHz for ^1H and ^{13}C) in $CDCl_3$, unless otherwise stated. FT-IR analysis was performed on a Shimadzu IR Affinity-1 apparatus (KBr, ν in cm^{-1}). Melting points were obtained on a Büchi (SMP10) capillary melting point apparatus. UV–vis spectra were measured with a VARIAN-Cary 100 spectrophotometer in CH_2Cl_2 at room temperature, λ_{max} in nm (ε in M^{-1} cm^{-1}). The hydrazones $Ar_2C{=}N{-}NH_2$ were prepared according to the literature and converted to Ar_2CN_2 using yellow HgO [53–55]. The thiols were purchased commercially from Aldrich and Alfa Aesar.

4.2. General procedure for the synthesis of the Δ^3-1,2,4-triazolines

An equimolar mixture (10 mmol) of the diaryldiazomethanes and *N*-ethoxycarbonyl-*N*-(2,2,2-trichloroethylidene)amine in 10 mL of toluene or dichloromethane, was stirred at room temperature for 2–3 days. The solvent was then evaporated, and the residue was filtered and washed with ethanol.

4.2.1. 5-Trichloromethyl-3-p-chlorophenyl-4-ethoxycarboxylate-3-phenyl-Δ^3-1,2,4-triazoline **2b**

Colourless powder; Yield: 68%; mp 78 °C; ^1H NMR: δ = 0.68 (s br, 3H, $CO_2CH_2CH_3$), 3.75 (s br, 2H, $CO_2CH_2CH_3$), 6.75–7.72 (m, 10H, 9 Ar–*H* + 1*CH*); ^{13}C NMR: δ = 14.2 (q, J = 127.5 Hz, $CO_2CH_2CH_3$), 62.9 (t, J = 148.5 Hz, $CO_2CH_2CH_3$), 96.0 (s, CCl_3), 109.6 (d, J = 163.0 Hz, *C-5*), 122.5 (s, *C-3*), 125.0–140.0 (6 s, 9 CH_{ar}), 135.7–137.0 (2s, 2 C_{ar}), 155.0 (s, *C*=O); IR: 1710 (C=O); $C_{18}H_{15}Cl_4N_3O_2$ (447.14): Anal. Calcd C 48.35, H 3.38, N 9.40, Cl 13.72; found: C 48.23, H 3.41, N 9.34, Cl 13.67.

4.2.2. 5-Trichloromethyl-3,3-bis(4-chlorophenyl)-4-ethoxycarbonyl-Δ^3-1,2,4-triazoline **2c**

Colourless powder; Yield: 60%; mp 119 °C; ^1H NMR (DMSO-d_6): δ = 0.80 (s br, 3H, $CO_2CH_2CH_3$), 3.85 (s br, 2H, $CO_2CH_2CH_3$), 7.00–7.90 (m, 8H, Ar–*H*), 8.02 (s, 1H, *CH*); ^{13}C NMR (DMSO-d_6): δ = 13.2 (q, J = 127.0 Hz, $CO_2CH_2CH_3$), 62.7 (t, J = 148.0 Hz, $CO_2CH_2CH_3$), 96.4 (s, CCl_3), 109.0 (d, J = 164.0 Hz, *C-5*), 113.8 (s, *C-3*), 125.0–132.0 (4 s, 4 CH_{ar}), 131.6–136.1 (4 s, 4 C_{ar}), 153.5 (s, *C*=O); IR: 1706 (C=O); $C_{18}H_{14}Cl_5N_3O_2$ (481.60): Anal. Calcd C 44.89, H 2.93, N 8.73, Cl 36.81; found: C 45.02, H 2.98, N 8.48, Cl 36.96.

4.2.3. 5-Trichloromethyl-4-ethoxycarbonyl-3,3-bis(4-methoxyphenyl)-Δ^3-1,2,4-triazoline **2d**

Pale yellow powder; Yield: 75%; mp 99 °C; ^1H NMR: δ = 0.75 (s br, 3 H, $CO_2CH_2CH_3$), 3.75 (s br, 2 H, $CO_2CH_2CH_3$), 3.77 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.50–7.80 (4 d, 8H, Ar–*H*), 7.35 (s, 1 H, *CH*); ^{13}C NMR: δ = 13.5 (q, J = 126.3 Hz, $CO_2CH_2CH_3$), 55.0 (q, J = 144.0 Hz, 2C, OCH_3), 62.5 (t, J = 148.0 Hz, $CO_2CH_2CH_3$), 96.3 (s, *C-3*), 113.2 (d, J = 151.0 Hz, *C-5*), 126.0–132.0 (5 s, 4 CH_{ar} + C_{ar}), 133.7 (s, C_{ar}), 155.4 (s, C_{ar}–O), 156.0 (s, C_{ar}–O), 159.5 (s, *C*=O); IR: 1702 (C=O); $C_{20}H_{20}Cl_3N_3O_4$ (472.76): Anal. Calcd C 50.76, H 4.23, N 8.88, Cl 22.52; found: C 50.92, H 4.36, N 5.56, Cl 22.73.

4.3. General procedure for the synthesis of azadienes **4**

An equimolar mixture (10 mmol) of the diazo compound and of *N*-ethoxycarbonyl-*N*-(2,2,2-trichloroethylidene) amine in 10 mL of toluene is stirred at 65 °C for 3 days. Then, the toluene is evaporated and the oily residue is chromatographed on silica or on neutral alumina, using a CH_2Cl_2-petroleum ether mixture (50:50) as the eluant. Recrystallization from ethanol provided **4** in the form of pale yellow crystals.

4.3.1. 4,4-Dichloro-1-(4-chlorophenyl)-1-phenyl-2-azabuta-1,3-diene **4b**

Yellow crystals; Yield: 52%; mp 65 °C; IR: 1545 (C=N), 1600 (C=C); UV–vis: 256 sh (11100), 307 (18250); $C_{15}H_{10}Cl_3N$ (310.61): Anal. Calcd C 58.00, H 3.25, Cl 34.24, N 4.51; found: C 57.87, H 3.29, Cl 34.11, N 4.53.

Major isomer: ^1H NMR: δ = 7.03 (s, 1H, *CH*), 7.10–7.80 (m, 10H, Ar–*H* + *CH*) ppm; $^{13}C\{^1H\}$ NMR: δ = 124.0 (C, *C-4*), 127.5–137.1 (9C, C_{ar}), 137.3 (C, *C-3*), 167.0 (C, *C*=N) ppm.

Minor isomer: ^1H NMR: δ = 7.02 (s, 1H, *CHb*), 7.10–7.80 (m, 10H, Ar–*H* + *CHa*); $^{13}C\{^1H\}$ NMR: δ = 124.0 (C, *C-4*), 127.5–137.1 (9C, CH_{ar}), 138.2 (C, *C-3*), 166.9 (C, *C*=N).

4.3.2. 4,4-Dichloro-1,1-bis(4-chlorophenyl)-2-azabuta-1,3-diene **4c**

Yellow needles; Yield: 48%; mp 119 °C; ^1H NMR (acetone-d_6): δ = 7.07 (s, 1H, *CH*), 7.27–7.80 (4d, 8H, Ar–*H*); ^{13}C NMR (acetone-d_6): δ = 124.7 (s, *C-4*), 128.0–131.0 (4 s, 4CH_{ar}), 133.2–137.5 (4s, 4C_{ar}), 134.7 (d, J = 172.0 Hz, *C-3*), 165.5 (s, *C*=N); IR: 1580 (C=N), 1660 (C=C); UV–vis: 270 (13900), 316 (22600); $C_{15}H_9Cl_4N$ (345.05): Anal. Calcd C 52.21, H 2.63, Cl 41.10, N 4.06; found: C 52.05, H 2.63, Cl 41.23, N 3.98.

4.3.3. 4,4-Dichloro-1,1-bis(4-methoxyphenyl)-2-azabuta-1,3-diene **4d**

Yellow powder; Yield: 58%; mp 117 °C; ^1H NMR: δ = 3.83 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.80–7.80 (4d, 8H, Ar–*H*), 7.07 (s, 1 H, *CH*) ppm; ^{13}C NMR: δ = 55.2 (q, J = 144.0 Hz, OCH_3), 55.3 (q, J = 144.0 Hz, OCH_3), 113.0–136.0 (5 s, 4 CH_{ar} + *C-3*), 121.3 (s, *C-4*), 127.7–131.8 (2s, 2 C_{ar}), 160.2–162.0 (2s, 2 OC_{ar}), 167.9 (s, *C*=N). IR: 1603 (C=N), 1634 (C=C); UV–vis: 293 (17400); $C_{17}H_{15}Cl_2NO_2$ (336.23): Anal. Calcd C 60.73, H 4.50, Cl 21.11, N 4.17; found: C 60.59, H 4.55, Cl 21.47, N 4.20.

4.4. General procedure for the synthesis of 2-azabuta-1,3-dienes **5**, **6**, and **7**.

1,1-Diaryl-4,4-dichloro-2-azabuta-1,3-diene (1.1 mmol) was stirred with an excess of thiolate (10 mmol) in dry DMF (10 mL). The reaction mixture was stored at room temperature for 8 h, then poured into water (100 mL) and

extracted with diethyl ether (150 mL). The organic solution was washed three times with water, dried over anhydrous sodium sulfate and evaporated. The crude residue was recrystallized from ethanol or hexane.

4.4.1. 4,4-Bis(butylthio)-1,1-diphenyl-2-azabuta-1,3-diene ***5a***

Yellow oil; yield: 76%; ^{1}H NMR: $\delta = 0.75$ (t, $J = 7.3$ Hz, 3H, $-CH_3$), 0.82 (t, $J = 7.3$ Hz, 3H, $-CH_3$), 1.16–1.26 (sex, $J = 7.5$ Hz, 2H, $-CH_2-CH_3$), 1.30–1.46 (m, 4H, $-CH_2-$), 1.51–1.61 (quin, $J = 7.3$ Hz, 2H, $-CH_2-C_2H_5$), 2.55 (t, $J = 7.3$ Hz, 2H, $-SCH_2$), 2.93 (t, $J = 7.3$ Hz, 2H, $-SCH_2$), 7.00 (s, 1H, C*H*), 7.06–7.64 (m, 10H, Ar–*H*); ^{13}C{^{1}H} NMR: $\delta = 13.7$ (*C*H$_3$), 13.9 (*C*H$_3$), 21.8–22.0 (2C, *C*H$_2$CH$_3$), 31.3–32.2 (2C, *C*H$_2$C$_2$H$_5$), 32.9–33.1 (2C, SCH$_2$), 128.2–139.4 (9C$_{ar}$); 139.5 (C, *C*H), 164.4 (C, *C*=N); IR: 1599 (C=N), 1663 (C=C); UV–vis: 255 (15100), 376 (13700); $C_{23}H_{29}NS_2$ (383.61): Anal. Calcd C 72.01, H 7.62, N 3.65, S 16.72; found: C 71.98, H 7.83, N 3.67, S 16.70.

4.4.2. 4,4-Bis(cyclohexylthio)-1,1-diphenyl-2-azabuta-1,3-diene ***5b***

Yellow oil; yield: 80%; ^{1}H NMR: $\delta = 1.25–2.34$ (m, 20H, C*H*$_2$ of cyclohexyl), 2.90–3.04 (m, 2H, S–C*H*), 7.13–7.84 (m, 11H, Ar–*H* + C=C*H*); ^{13}C{^{1}H} NMR: $\delta = 25.3–26.0$ (6C, *C*H$_2$ of cyclohexyl), 32.7 (2C, S–CH–*C*H$_2$), 33.4 (2C, S–CH–*C*H$_2$), 45.1 (C, S–*C*H); 45.9 (C, S–*C*H); 127.3–130.2 (12C$_{ar}$ + *C*=CH); 141.3 (*C*H), 164.8 (C, *C*=N); UV–vis: 256 (12900), 378 (11200). ; $C_{27}H_{33}NS_2$ (435.69): Anal. Calcd C 74.43, H 7.63, N 3.21, S 14.72; found: C 73.56, H 7.49, N 3.03, S 14.56.

4.4.3. 4,4-Bis(methylthio)-1,1-diphenyl-2-azabuta-1,3-diene ***5c***

Yellow powder; Yield: 68%; mp 76 °C; ^{1}H NMR: $\delta = 2.25$ (s, 3H, SC*H*$_3$), 2.55 (s, 3H, SC*H*$_3$), 7.04 (s, 1H; C*H*), 7.22–7.79 (m, 10H; Ar–*H*); ^{13}C{^{1}H} NMR: $\delta = 16.3$ (C, S*C*H$_3$), 17.7 (C, S*C*H$_3$), 128.1–137.3 (8C$_{ar}$ + *C*=CH), 139.5 (C, *C*H), 163.7 (C, *C*=N); IR: 1554 (C=N), 1589 (C=C); UV–vis: 248 (9200), 366 (9700); $C_{17}H_{17}NS_2$ (299.08): Anal. Calcd C 68.18, H 5.72, N 4.68, S 21.42; found: C 68.43, H 5.70, N 4.44, S 21.31.

4.4.4. 4,4-Bis(ethylthio)-1,1-diphenyl-2-azabuta-1,3-diene ***5d***

Yellow oil; yield: 80%; ^{1}H NMR: $\delta = 1.18$ (t, $J = 7.3$ Hz, 3H, $-CH_3$), 1.34 (t, $J = 7.3$ Hz, 3H, $-CH_3$), 2.70 (q, $J = 7.3$ Hz, 2H, C*H*$_2$), 3.06 (q, $J = 7.3$ Hz, 2H, C*H*$_2$), 7.11 (s, 1H, C*H*), 7.20–7.90 (m, 10H, Ar–*H*); ^{13}C{^{1}H} NMR: $\delta = 14.2$ (*C*H$_3$), 14.9 (*C*H$_3$), 27.2 (C, *C*H$_2$), 28.1 (C, *C*H$_2$), 127.5–130.5 (6C$_{ar}$), 133.0 (*C*=CH), 136.0–139.2 (2C$_{ar}$), 139.4 (C, *C*H), 164.5 (C, *C*=N); IR: 1626 (C=N), 1660 (C=C); $C_{19}H_{21}NS_2$ (327.52): Anal. Calcd C 69.68, H 6.46, N 4.28, S 19.58; found: C 69.40, H 6.37, N 4.35, S 19.88.

4.4.5. 1,1-Bis(4-chlorophenyl)-4,4-bis(methylthio)-2-azabuta-1,3-diene ***5e***

Yellow powder; Yield: 25%; ^{1}H NMR: $\delta = 2.25$ (s, 3H, SC*H*$_3$), 2.51 (s, 3H, SC*H*$_3$), 6.91 (s, 1H; C*H*), 7.13–7.63 (m, 8H; Ar–*H*); ^{13}C{^{1}H} NMR: $\delta = 15.9$ (C, S*C*H$_3$), 17.5 (C, S*C*H$_3$), 128–137.5 (12C$_{ar}$ + *C*=CH), 139.3 (C, *C*H), 160.4 (C, *C*=N); UV–vis: 261 (8100); 381 (8600); $C_{17}H_{15}Cl_2NS_2$ (368.34): Anal. Calcd C 55.43, H 4.10, Cl 19.25, N 3.80, S 17.41; found; C 55.58, H 3.90, Cl 19.41, N 3.71.

4.4.6. 4,4-Bis(isopropylthio)-1,1-diphenyl-2-azabuta-1,3-diene ***5f***

Yellow powder; Yield: 55%; ^{1}H NMR: $\delta = 1.17$ (d, 6H, $J = 6.8$ Hz, CH(C*H*$_3$)$_2$), 1.32 (d, 6H, $J = 6.8$ Hz, CH(C*H*$_3$)$_2$), 3.25 (sept, 1H, $J = 6.8$ Hz, SC*H*), 3.83 (sept, 1H, $J = 6.8$ Hz, SC*H*), 7.10 (s, 1H, C*H*), 7.10-7.75 (m, 10 H, Ar–*H*); ^{13}C{^{1}H} NMR: $\delta = 22.6$ (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$), 37.0 (*C*H(CH$_3$)$_2$), 37.7 (*C*H(CH$_3$)$_2$), 127.5–131.0 (5C$_{ar}$), 132.2–139.3 (2 C$_{ar}$ + *C*S$_2$), 141.6 (*C*H), 165.2 (*C*=N); IR: 1523 (C=N), 1555 (C=C); UV–vis: 251 (17000), 375 (10700); $C_{21}H_{25}NS_2$ (355.57): Anal. Calcd C 70.94, H 7.09, N 3.94, S 18.04; found: C 70.73, H 7.12, N 4.10, S 18.00.

4.4.7. 4,4-Bis(4-thiotolyl)-1,1-diphenyl-2-azabuta-1,3-diene ***5g***

Yellow needles (recrystallized from ethanol); yield: 75%; mp 109 °C; ^{1}H NMR: $\delta = 2.30$ (s, 3H, Ar–C*H*$_3$), 2.33 (s, 3H, Ar–C*H*$_3$), 6.99–7.02 (m, 8H, Ar–*H*), 7.10 (s, 1H, C*H*), 7.23–7.28 (m, 10H, Ar–*H*); ^{13}C{^{1}H} NMR: $\delta = 21.3$ (2C, Ar–*C*H$_3$), 129.3–137.4 (24C$_{ar}$ + *C*=CH), 140.4 (C, *C*H), 165.9 (C, *C*=N); IR: 1544 (C=N); UV–vis: 256 (37900), 378 (30300); $C_{29}H_{25}NS_2$ (451.65): Anal. Calcd C 77.12, H 5.58, N 3.10, S 14.20; found: C 76.98, H 5.39, N 3.17, S 14.12.

4.4.8. 1,1-Bis(4-chlorophenyl)-4,4-bis(4-thiotolyl)-2-azabuta-1,3-diene ***5h***

Yellow powder (recrystallized from ethanol); yield: 55%; mp 149 °C; ^{1}H NMR: $\delta = 2.35$ (s, 3H, Ar–C*H*$_3$), 2.36 (s, 3H, Ar–C*H*$_3$), 6.81 (s, 1H; C*H*), 6.99–7.64 (m, 16H; Ar–*H*); ^{13}C{^{1}H} NMR: $\delta = 21.3$ (C, Ar–*C*H$_3$), 21.4 (C, Ar–*C*H$_3$), 128.6–137.5 (24C$_{ar}$ + *C*=CH); 138.3 (C, *C*H), 162.0 (C, *C*=N); UV–vis: 251 (27700), 387 (13200); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 520 ([M+H]$^+$, 100); $C_{29}H_{23}Cl_2NS_2$ (520.54): Anal. Calcd C 66.91, H 4.45, Cl 13.62, N 2.69 S 12.32; found C 67.08, H 4.43, Cl 13.77, N 2.64.

4.4.9. 4,4-Bis(4-bromobenzenethio)-1,1-diphenyl-2-azabuta-1,3-diene ***5i***

Yellow needles (recrystallized from ethanol); yield: 65%; mp 144 °C; ^{1}H NMR: $\delta = 6.95–7.84$ (m, 18H, Ar–*H*) ppm; IR: 1461 (C=N), 1547 (C=C); UV–vis: 261 (28800), 374 (19500); $C_{27}H_{19}Br_2NS_2$ (581.38): Anal. Calcd C 55.78, H 3.29, Br 27.49, N 2.41, S 11.03 fond C 55.94, H 3.22, Br 27.53, N 2.37 S 11.18.

4.4.10. 4,4-Bis(isopropylthio)-1,1-bis(4-isopropylthiophenyl)-2-azabuta-1,3-diene ***6***

Yellow needles (recrystallized from ethanol); yield: 53%; mp 57 °C; ^{1}H NMR: $\delta = 1.21–1.22$ (d, 6H, CH(C*H*$_3$)$_2$), 1.26–1.28 (d, 6H, CH(C*H*$_3$)$_2$), 1.31–1.39 (m, 12H, 2Ar–S–CH(C*H*$_3$)$_2$), 3.11–3.20 (m, 1H, Ar–S–C*H*(CH$_3$)$_2$), 3.22–3.34 (m, 1H, Ar–S–C*H*(CH$_3$)$_2$), 3.43–3.61 (m, 1H, Ar–S–C*H*(CH$_3$)$_2$), 3.74–3.87 (m, 1H, Ar–S–C*H*(CH$_3$)$_2$), 6.93 (1H, C*H*), 7.11–7.72 (m, 8H, Ar–*H*); ^{13}C{^{1}H} NMR: $\delta = 22.6–23.5$ (8C, CH(*C*H$_3$)$_2$); 36.6–38.0 (4C, *C*H(CH$_3$)$_2$); 126.4–132.6 (12C, *C*$_{ar}$), 162.3 (C, *C*=N); UV–vis: 256 (37900), 378 (30300); $C_{27}H_{37}NS_4$ (503.85): Anal. Calcd C 64.36, H 7.04, N 2.78, S 25.46, found: C 64.48, H 6.89, N 2.87, S 25.28.

4.4.11. 1,1-Diphenyl-3,4-bis(tertbutylthio)-2-azabuta-1,3-diene **7a**

Orange crystals (recrystallized from hexane); yield: 60%; mp 114 °C; ^{1}H NMR: δ = 1.39 (s, 9H, −C(C*H*$_3$)$_3$), 1.40 (s, 9H, −C(C*H*$_3$)$_3$), 5.97 (s, 1H, C*H*), 7.28–7.82 (m, 10H, Ar−*H*); ^{13}C{^{1}H} NMR: δ = 31.1–31.7 (6C, C(*C*H$_3$)$_3$), 44.2–46.9 (2C, *C*(CH$_3$)$_3$), 127–130 (m, 13C, C_{ar} + *C*H), 135.8 (C, N−*C*=C), 137.6 (C, *C*=N); IR: 1576 (C=N), 1611 (C=C); UV–vis: 256 (37900), 378 (30300); $C_{23}H_{29}NS_2$ (383.61): Anal. Calcd C 72.01, H 7.62, N 3.65, S 16.72; found: C 71.83, H 7.69, N 3.60, S 16.81.

4.4.12. 1,1-Bis(4-chlorophenyl)-3,4-bis(tertbutylthio)-2-azabuta-1,3-diene **7b**

Orange crystals (recrystallized from hexane); yield: 54%; mp 137 °C; ^{1}H NMR: δ = 1.35 (s, 9H, −C(C*H*$_3$)$_3$), 1.43 (s, 9H, −C(C*H*$_3$)$_3$), 5.98 (s, 1H; C*H*), 7.19–7.63 (m, 8H; Ar−*H*); UV–vis: 261 (30000), 403 (1600); $C_{23}H_{27}Cl_2NS_2$ (452.50): Anal. Calcd C 61.05, H 6.01, Cl 15.67, N 3.10, S 14.17; found: C 60.86, H 5.97, Cl 15.74, S 14.04.

4.4.13. 4,4-Dichloro-1,1-diphenyl-3-ethylthio-2-azabut-1-ene **8**

A mixture of 1.1 mmol of **4a** and an excess of sodium ethylthiolate (6 mmol) in 3 mL of ethanethiol was refluxed for 4 days, then poured into water (150 mL) and extracted with diethyl ether (150 mL). The organic solution was washed two times with 50 mL of water, dried over anhydrous sodium sulfate and evaporated. The crude residue was recrystallized from ethanol. Yellow powder; yield: 64%; mp = 60 °C; ^{1}H NMR: δ = 1.45 (t, 3H, J = 7.5 Hz, C*H*$_3$), 2.67 (2qd, 2H, J = 4.0 Hz, J = 7.5 Hz, C*H*$_2$), 4.74 (d, 1H, J = 6.70 Hz, C*H*-S) ; 5.98 (d, 1H, J = 6.70 Hz, C*H*Cl$_2$), 7.30–7.70 (m, 10H, Ar−*H*); ^{13}C NMR: δ = 14.8 (q, J = 138.0 Hz, *C*H$_3$), 23.8 (t, J = 141.0 Hz, *C*H$_2$), 72.2 (d, J = 156.0 Hz, *C*H-S), 73.8 (d, J = 181.0 Hz, *C*HCl$_2$), 127.0–138.8 (8 s, 8 C_{ar}), 170.6 (s, *C*=N); IR: 1662 (C=N); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 338 ([M$^+$+H], 15), 340 ([M$^+$+2+H], 11), 302 ([M$^+$−Cl], 83), 304 ([M$^+$+2-Cl], 35), 276 ([M$^+$-HSEt], 100), 278 ([M$^+$+2-HSEt], 69); $C_{17}H_{17}Cl_2NS$ (338.31): Anal. Calcd C 60.36, H 5.06, N 4.14, S 9.48; found: C 60.23, H 5.00, N 4.19, S 9.61.

4.4.14. Z,E-4-Chloro-1,1-diphenyl-3-ethylthio-2-azabuta-1,3-diene **9**

A solution of 1.2 mmol of **4a** and 4 mL of DBU in 8 mL of toluene was stirred 17 h at room temperature, then poured into 150 mL of a 0.5 M HCl solution. The organic solution was washed two times with 50 mL of water, dried over anhydrous sodium sulfate and evaporated. Yellow oil; IR: 1664 (C=C); 1626 (C=N).

Major isomer: ^{1}H NMR: δ = 1.27 (t, 3H, J = 7.30 Hz, C*H*$_3$); 2.72 (q, 2H, J = 7.30 Hz, C*H*$_2$); 5.52 (s, 1H, C*H*); 7.10–7.80 (m, 10H, Ar−*H*). ^{13}C NMR: δ = 14.8 (q, J = 127.6 Hz, *C*H$_3$); 27.1 (t, J = 140.5 Hz, *C*H$_2$); 101.1 (d, J = 20.3 Hz, *C*H); 125.0–132.3 (8 s, 8 C_{ar}); 139.0 (s, *C*S); 170.6 (s, *C*=N).

Minor isomer: ^{1}H NMR: δ = 1.35 (t, 3H, J = 7.40 Hz, C*H*$_3$); 2.85 (q, 2H, J = 7.40 Hz, C*H*$_2$); 5.22 (s, 1H, C*H*); 7.10–7.80 (m, 10H, Ar−*H*). FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 301 ([M$^{+\cdot}$], 37.0); 303 ([M$^+$+2], 16.4).

4.4.15. Z,E-1,1-Diphenyl-3,4-bis(ethylthio)-2-azabuta-1,3-diene **7c**

A mixture of 1.2 mmol of **8b** and an excess of sodium ethylthiolate (10 mmol) in 6.5 mL of ethanol was heated at 65 °C for 24 h, then poured into water (100 mL) and extracted with diethyl ether (150 mL). The organic solution was washed two times with 50 mL of water, dried over anhydrous sodium sulfate and evaporated. The oily residue was chromatographed on alumina, using a CH_2Cl_2-petroleum ether (50:50) mixture as the eluant. Orange oil; yield: 41%; IR: 1660 (C=C); 1620 (C=N).

Major isomer: ^{1}H NMR: δ = 1.00 (t, 3H, J = 7.30 Hz, C*H*$_3$); 1.20 (t, 3H, J = 7.35 Hz, C*H*$_3$); 2.58 (q, 2H, J = 7.30 Hz, C*H*$_2$); 2.60 (q, 2H, J = 7.30 Hz, C*H*$_2$); 5.47 (s, 1H, C*H*); 7.20–7.80 (m, 10H, Ar−*H*); ^{13}C RMN: δ = 15.9 (q, J = 126.1 Hz, *C*H$_3$) ; 16.7 (q, J = 127.7 Hz, *C*H$_3$); 28.3 (t, J = 140.1 Hz, *C*H$_2$); 29.1 (t, J = 139.5 Hz, *C*H$_2$); 112.0 (d, J = 177.5 Hz, *C*H); 128.0–134.0 (4 s, 4 C_{ar}); 158.9 (s, *C*=N).

Minor isomer: ^{1}H NMR: δ = 1.17 (t, 3H, J = 7.35 Hz, C*H*$_3$); 1.25 (t, 3H, J = 7.35 Hz, C*H*$_3$); 2.40 (q, 2H, J = 7.35 Hz, C*H*$_2$); 2.76 (q, 2H, J = 7.35 Hz, C*H*$_2$); 5.21 (s, 1H, C*H*); 7.20–7.80 (m, 10H, Ar−*H*). FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 327 ([M$^{+\cdot}$], 73.1); 298 ([M$^+$−Et], 79.5); 266 ([M$^+$−SEt], 9.4).

4.4.16. 1,1-Diphenyl-4,4-bis(1-piperidyl)-2-azabuta-1,3-diene **10**

A mixture of 6.0 mmol of NaH, 8 mL of piperidine was stirred for 15 min at 0 °C and 20 min at room temperature. Then, 1.1 mmol of **4a** was added. After 36 h at 65 °C, the mixture was poured in water and extracted with diethyl ether. The organic was washed three times with water, dried over anhydrous sodium sulphate and evaporated. The crude residue was recrystallized from ethanol. Yellow powder; yield: 45%; mp = 126 °C; ^{1}H NMR: δ = 1.45 (s br, 6H, C*H*$_2$), 1.65 (s br, 6H, C*H*$_2$), 2.80 (s br, 4H, N−C*H*$_2$), 3.45 (s br, 4H, N−C*H*$_2$), 5.40 (s, 1H, C=C*H*), 7.10–7.70 (m, 10H, Ar−*H*); ^{13}C{^{1}H} NMR: δ = 24.8–26.76 (4C, *C*H$_2$), 50.1–50.9 (2C, N−*C*H$_2$), 102.4 (C, *C*H), 126.5–141.2 (8 C_{ar}), 148.9 (C, *C*=CH), 157.8 (C, *C*=N); IR: 1574 (C=N); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 373 ([M]$^+$, 100), 374 ([M+H]$^+$, 90), 289 ([M−NC$_5$H$_{10}$]$^+$, 39); $C_{25}H_{31}N_3$ (373.25): Anal. Calcd C 80.39, H 8.37, N 11.25; found: C 80.90, H 8.53, N 11.45.

4.4.17. [{Cu_2Br_2(p-i*PrSC*$_6$*H*$_4$)$_2$*C*=*N*−*C*(*H*)=*C*(*SiPr*)$_2$}$_2$] **11**

To a suspension of CuBr (143 mg, 1 mmol) in dichloromethane (10 mL) was added (554 mg, 1.1 mmol) of ligand **6**. The mixture was refluxed for 24 h, and then the solution was allowed to reach room temperature. The filtrate was concentrated to 5 mL. After the addition of diethyl ether, the filtrate was stored at −20 °C affording red crystals. Yield: 60%; UV–vis: 257 (36900), 378 (26200); $C_{54}H_{74}Br_2Cu_2N_2S_8$ (1294.6): Anal. Calcd C 50.10, H 5.75, N 2.16, S 19.81; found: C 49.89, H 5.44, N 2.11, S 19.70.

4.5. Crystal structure determinations

Single crystals of **5i**, **7a, 7b, 10** and **11** were mounted on a Nonius Kappa Apex-II CCD diffractometer equipped with a nitrogen jet stream low-temperature system (Oxford

Cryosystems). The X-ray source was graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) from a sealed tube. The lattice parameters were obtained by least-squares fit to the optimized setting angles of the entire set of collected reflections. Intensity data were recorded as ϕ and ω scans with κ offsets. No significant intensity decay or temperature drift was observed during data collections. Data were reduced by using DENZO software [56]; the missing absorption corrections were partially compensated by the data scaling procedure in the data reduction. Absorption correction was further applied by using MULTI-SCAN [57]. The structures were solved by direct methods with SHELXS97 [58a] or SIR [58b] programs. Refinements were carried out by full-matrix least-squares on F^2 using the SHELXL97 program on the complete set of reflections [58a]. All non−hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions and included in final refinement in a riding model with the isotropic temperature parameters set to $U_{iso}(H) = 1.2U_{eq}(CH)$, $U_{iso}(H) = 1.3U_{eq}(C_{aromatic})$ and $U_{iso}(H) = 1.5U_{eq}(CH_3)$.

Crystallographic data (cif files) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 835275 (**5i**), 835276 (**7a**), 835277 (**7b**), 889646 (**10**) and 941426 (**11**). Copy of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK, fax: 144-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.crci.2015.09.017.

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