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Reactivity of 4,4-Dichloro-1,1-diphenyl-2-azabutadiene Towards Alkoxides and Thiolates: Synthesis of Functionalised π-Conjugated 2-Azabutadienes and Unexpected 1,4-Thiazine Formation

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Treatment of 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene [Cl_2C=C(H)-N=CPh_2] (**1**) with excess sodium isopropylthiolate or sodium thiophenolate in DMF yielded the 2-azabutadiene derivatives $(RS)_2C$=C(H)–N=CPh_2 (**2**) (**2a** R = *i*Pr; **2b** R = Ph). Nucleophilic attack of the sodium salt of ethyl thioglycolate on **1** afforded as the sole product the six-membered heterocyclic compound ethyl 2-ethoxycarbonylmethylthio-5,5-diphenyl-5,6-dihydro-4*H*-1,4-thiazine-6-carboxylate (**5**). The reaction is initiated by substitution of the two vinyl-bound chloro substituents to give $\{EtO(O=)CCH_2S\}_2C$=C(H)–N=CPh_2 (**2c**) as intermediate. A mechanism that accounts for the subsequent cyclisation reaction is proposed. The 2-azabutadiene derivative $(PhO)_2C$=C(H)–N=CPh_2 (**7**) was obtained by the reaction of **1** with sodium phenolate. The regioselectivity of the incoming nucleophile is roughly correlated with its hardness/softness in accord with Pearson's HSAB principle. The molecular structures of **2a**,**b**, **5** and **7** were determined by single-crystal X-ray diffraction.

Introduction

The design of novel π-conjugated organic ligand systems is of current interest in organometallic and coordination chemistry since the interplay of a π-conjugated ligand and a metal centre may confer interesting properties for electrochemical studies[1–4] and optoelectronic applications such as luminescence and nonlinear optics.[5,6] In recent years, the complexation of 1,4-diazabutadienes (α-diimine ligands) to various transition metals has allowed the development of efficient catalysts for olefin polymerisation[7,8] and metal-mediated organic synthesis[9,10] as well as coordination compounds with intriguing photophysical properties.[11] Much work has also been devoted to the metal-mediated activation of 1-azabutadienes, which may adopt several coordination modes at metal centres.[12–17] In contrast, the organometallic coordination chemistry of 2-azabutadiene was almost unexplored before our initial studies.[18]

In a precedent paper, we described the two-step synthesis of 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**1**) by 1,3-dipolar cycloaddition of Cl_3C–CH=N–CO_2Et onto diphenyldiazomethane and subsequent thermolysis of the cyclic triazoline intermediate 1-ethoxycarbonyl-2,2-diphenyl-5-trichloromethyl-Δ^3-1,3,4-triazoline.[19] The presence of two reactive vinyl–chlorine bonds has been exploited for oxidative addition reactions of **1** across low-valent centres in order to synthesise σ-alkenyl complexes *trans*-[MCl{(C(Cl)=C(H)–N=CPh_2)}$(PPh_3)_2$] (M = Pd, Pt) ligated by a π-conjugated organic array.[20] In the context of our research on dithioether coordination chemistry,[21–23] we were interested in the functionalisation of **1** with thioether groups in order to assemble a polydentate ligand system that potentially possesses both sulfur and nitrogen donor sites. With this objective, we treated **1** with various thiolates and present here the molecular structures of the resulting thioether-functionalised substitution products. Furthermore, we have examined the reaction of **1** with sodium phenolate and revealed that its reactivity is similar to that of SPh^-. Part of this work, that concerning the *i*PrS-substituted azadiene **2a**, has recently appeared in a preliminary communication.[24]

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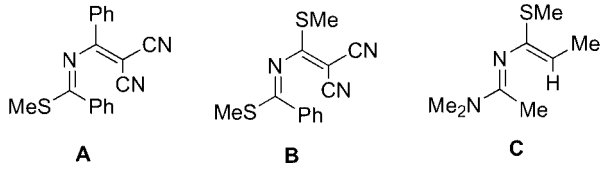
Results and Discussion

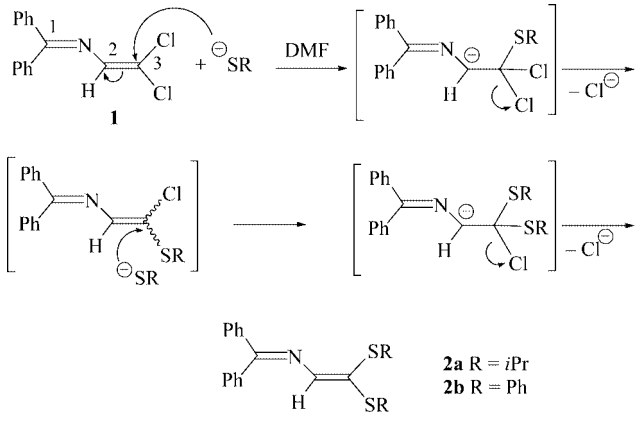
Reactivity of 1 Towards Sodium Isopropylthiolate and Thiophenolate

Two 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 methoxy-

methylene compounds or ketene dithioacetals and subsequently methylated,[25,26] whilst 3-aza-2-(dimethylamino)-4-(methylthio)hexa-2,4-diene (**C**) was obtained by the treatment of *N*-(thiopropionyl)acetamidine with CH_3I and subsequent deprotonation of the resulting *N*-ylidene amidinium salt.[27]



Previous studies by our group have shown that 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**1**) is reactive towards nucleophiles like cyanide,[28] the sodium salt of pyrrole[29] and sodium alkoxides.[30] In contrast to these examples, for which nucleophilic attack occurred at the electrophilic C2 atom, the reaction of **1** with an excess of thiolate in dry DMF led under mild conditions exclusively to the dithioether derivatives $(RS)_2C{=}C(H){-}N{=}CPh_2$ (**2a** R = *i*Pr; **2b** R = SPh), consistent with the formal substitution of the two chloro substituents on the vinylic C3 atom by SR^-. After work up, **2a**,**b** were isolated as stable yellow crystalline solids in yields of 55 and 70%, respectively. As outlined in Scheme 1, we suggest an addition–elimination mechanism initiated by nucleophilic addition to the C3 atom, elimination of chloride followed by the addition of a second thiolate to the C3 atom and termination by the dissociation of the remaining chloride.



Scheme 1. Suggested mechanism for the formation of the dithioether derivatives **2a**,**b**.

The ^1H NMR spectra of both derivatives **2a** and **2b** exhibit a resonance due to the vinylic hydrogen on the C2 atom in the aromatic region at δ = 7.10 and 7.20 ppm, respectively. The UV/Vis absorption spectrum of **1** in the range of 220–450 nm exhibits only one absorption band at 298 nm (ε = 14000 $M^{-1}cm^{-1}$), whereas two absorption maxima are observed for compound **2a** at 251 (ε = 17000, with a shoulder at 232 nm) and 375 nm (ε = 10700 $M^{-1}cm^{-1}$). Three absorption maxima are recorded for compound **2b** at 228 (ε = 21100), 250 (ε = 19500) and 355 nm (ε = 12300 $M^{-1}cm^{-1}$). As can be seen from Figure 1 (parts a and b), substitution of the chloro substituents in **1** by alkylthio or arylthio groups results in absorption bands of lower energy and lower molar extinction coefficients. These experimental values correctly match the values obtained by calculation (vide infra: DFT Calculations).

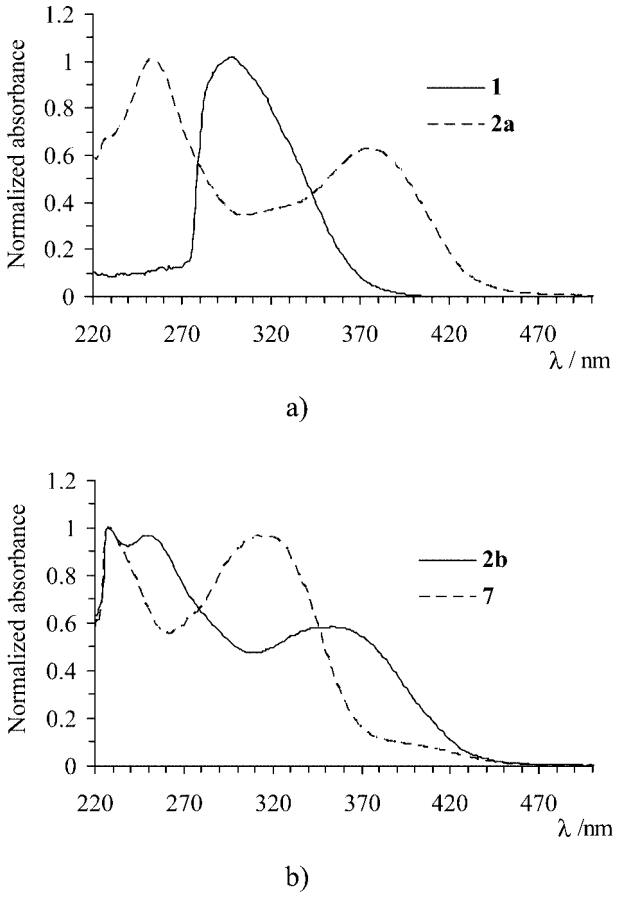


Figure 1. a) Absorption spectra of **1** and **2a** recorded in CH_2Cl_2 at 298 K. b) Absorption spectra of **2b** and **7** recorded in CH_2Cl_2 at 298 K.

Reaction of 1 with the Sodium Salt of Ethyl Thioglycolate

After adding a large excess of the sodium salt of ethyl thioglycolate[31] to **1** at room temperature in anhydrous DMF for 5 h (see Scheme 2), work up and chromatography afforded a white powder in 60% isolated yield. Surprisingly, the spectroscopic data of this product did not match with the anticipated 2-azabutadiene $\{EtO(O{=})CCH_2S\}_2$-$C{=}C(H){-}N{=}CPh_2$ (**2c**). In particular, the ^1H NMR spectrum revealed the presence of two distinct ethyl ester functions, but only one $–S–CH_2–CO_2Et$ group is apparent. Moreover, the two protons of the $–S–CH_2$ group were found to be diastereotopic. The presence of a vinylic proton is evidenced by a doublet at δ = 7.10 ppm, which is coupled [^3J(H-H) = 5.1 Hz] with a N–H proton resonating at δ = 4.78 ppm. The unexpected formation of a cyclic thiazine derivative ethyl 2-ethoxycarbonylmethylthio-5,5-diphenyl-5,6-dihydro-4*H*-1,4-thiazine-6-carboxylate (**5**) was finally confirmed by an X-ray diffraction study carried out on ethanol-grown single crystals of **5**.

Molecular Structure of 5

The molecular structure of **5** in Figure 2 shows that the six-membered thiazine cycle has been fused by carbon–carbon coupling between the imine carbon C(1) and the methylene carbon C(4) of the –S–CH_2–CO_2Et function. An initial nucleophilic attack of two ethyl thioglycolate ions at C(3) can be deduced from the substitution of this olefinic carbon atom by a –S–CH_2–CO_2Et function [C(3)–S(2) 1.737(3) Å] and the S(1) atom [C(3)–S(1) 1.755(3) Å] making part of the cycle. Consistent with the sp^2 hybridisation of C(3), the S(2)–C(3)–S(1) angle is 116.40(18)°. The ethoxy group of the terminal thioglycol fragment situated on the S(2) atom is disordered in the crystal, contrary to the S(1) atom in the thiazine cycle which is found in ordered positions.

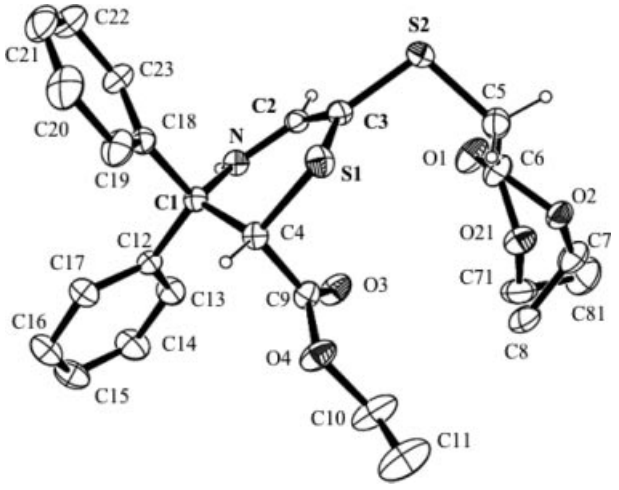
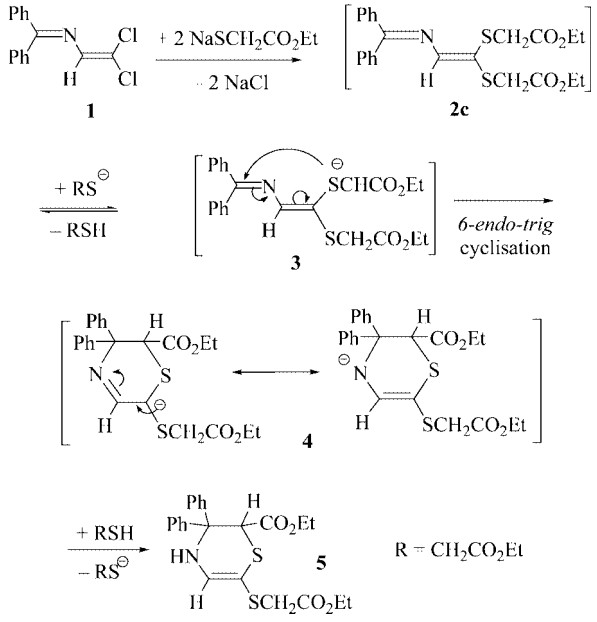


Figure 2. Molecular structure of **5** (ORTEP diagram at the 20% probability level). The bold labelled atoms define the substituted azadienic chain prior to cyclisation. Selected bond lengths [Å] and angles [°]: C(3)–S(1) 1.755(3), C(4)–S(1) 1.817(3), C(3)–S(2) 1.737(3), C(5)–S(2) 1.791(3), N–C(1) 1.448(3), N–C(2) 1.344(4), C(1)–C(4) 1.548(4), C(2)–C(3) 1.332(4); S(1)–C(3)–S(2) 116.40(18), C(3)–S(2)–C(5) 101.56(16), C(3)–S(1)–C(4) 98.45(14), S(1)–C(4)–C(9) 107.2(2), C(1)–C(4)–S(1) 111.51(19), C(2)–C(3)–S(2) 121.2(2), N–C(2)–C(3) 127.3(3), C(1)–N–C(2) 122.8(2), N–C(1)–C(4) 108.8(2), N–C(1)–C(18) 110.2(2), N–C(1)–C(12) 108.5(2), C(12)–C(1)–C(18) 111.3(2).

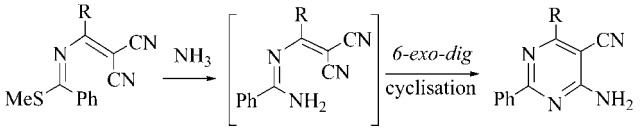
These structural features have allowed us to propose a mechanism that accounts for the formation of **5** (Scheme 2). (i) After double nucleophilic substitution at the vinylic CCl_2 carbon atom by $^-SCH_2CO_2Et$ by an addition–elimination process (see Scheme 1), the transient azadienic species **2c** is formed. (ii) Owing to the basicity of the reaction medium, deprotonation of the α-carbon atom of one of the –S–CH_2–CO_2Et functions occurs to give the carbanion **3**. (iii) Then a 6-*endo*-trig intramolecular cyclisation reaction (favoured according to Baldwin's rules)[32,33] occurs. (iv) Subsequent protonation of the cyclic anionic intermediate **4** by excess thiol finally affords the 1,4-thiazine derivative **5**.

To the best of our knowledge, only a few examples of the nucleophilic substitution reactions of 2-azabutadienes, followed by cyclisation, have been reported. For example, Lorente and co-workers observed such reactions by using

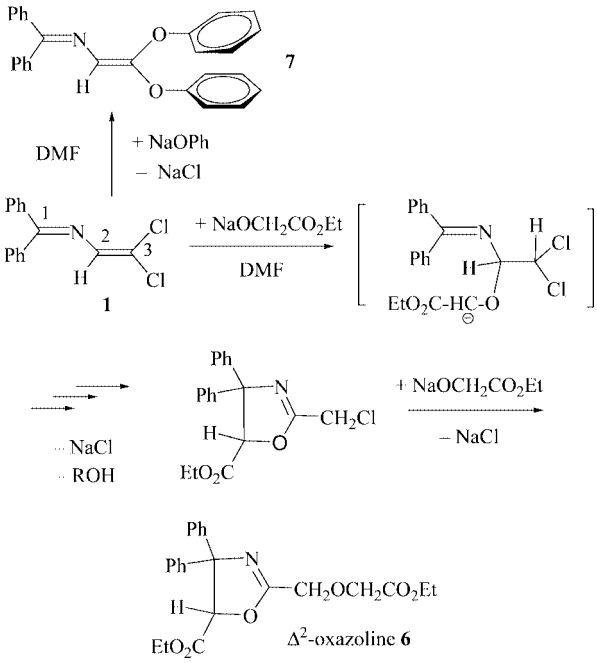


Scheme 2. Suggested mechanism for the formation of the thiazine **5**.

ammonia and amines as nucleophiles (Scheme 3). In these cases, the first step was a nucleophilic substitution reaction which was followed by 6-*exo*-dig cyclisation to afford cyanopyrimidine derivatives.[34,35]



Scheme 3. Example of the results of work by Lorente and coworkers.



Scheme 4. Reaction of **1** with ethyl sodioglycolate and sodium phenolate leading to **6** and **7**.

It is instructive to remember that nucleophilic attack by the harder sodium salt of ethyl glycolate (according to the HSAB principle, see below) on **1** in DMF also leads to a heterocyclic compound **6**, as summarised in Scheme 4. However, in this case, the initial attack by $NaOCH_2CO_2Et$ occurs at the vinylic C2 carbon atom of **1** and is followed by deprotonation of the α-carbon atom of the $–O–CH_2–CO_2Et$ function and cyclisation on the C1 atom to afford a five-membered Δ^2-oxazoline. This transient compound was further transformed by nucleophilic substitution with a second equivalent of ethyl glycolate to the final oxazoline derivative **6**.[30]

Reactivity of 1 towards Sodium Phenolate

The striking differences in the regioselectivity of the nucleophilic attack of OR^- and SR^- intrigued us and led us to ask whether sodium phenoxide would react in analogy with OR^- (R = Me, Et, *i*Pr) at the C2 centre or in analogy with SPh^- at the C3 centre: Treatment of **1** with a saturated solution of NaOPh in DMF at 65 °C for one day yielded, after work up, colourless $(PhO)_2C=C(H)–N=CPh_2$ (**7**) in76% yield.

The UV/Vis spectrum of **7** depicted in Figure 1 (b) exhibits two intense absorptions at 227 (ε = 20900) and 311 nm (ε = 20200 $M^{-1}cm^{-1}$) and a weak shoulder at 407 nm (ε = 1600 $M^{-1}cm^{-1}$). The IR spectrum [ν(C=C) = 1655, ν(C=N) = 1590 cm^{-1}] and the observation of a vinylic resonance in the ^1H NMR spectrum at δ = 6.42 ppm suggests substitution at the C3 atom. That **2b** and **7** have similar structures was finally corroborated by X-ray diffraction studies.

Molecular Structures of 2b and 7

Suitable crystals of **2b** and **7** were grown from hot EtOH. The molecular structures are shown in Figure 3 and Figure 4 together with selected bond lengths and angles. The transoid conformation of the azabutadiene chain found in precursor **1** and the S*i*Pr derivative **2a** is also observed in the solid-state structures of **2b** and **7**. Both compounds belong to the family of $(Ph)_2C=N–C=CX_2$ (X = Cl, OPh, SPh, S*i*Pr) azadienes. One might expect that one of the two phenyl groups bound to C(1) would contribute to the π-conjugation of the phenylazadiene chain. However, the dihedral angles between the phenyl rings C(10)–C(15) of **7** and C(22)–C(27) of **2b** and the C(1)–N–C(2)–C(3) chain are equal to 15.2(2) and 21.1(2)°, respectively. These values do not clearly support the occurrence of extended π conjugation in this class of compounds. Note also that the values of these dihedral angles are 28.7(1)° in **1** (X = Cl)[19] and 38.8(3)° in **2a** (X = S*i*Pr).[24] The length of the C(2)–C(3) double bond in **7** [1.319(3) Å] is the same as in **1** [1.319(3) Å], while that of **2b** is slightly longer [1.348(4) Å]. An intermediate value [1.337(5) Å] was found for disubstituted S*i*Pr derivative **2a**. The N–C(2) bonds lengths are essentially the same in all four compounds: **1**: 1.392(3), **7**: 1.385(3), **2a**: 1.398(5), **2b**: 1.393(4) Å. Thus, substitution of Cl (**1**) by OPh (**7**) has no effect on the metric parameters of the azadienic array, while a slight elongation of the C=C bond is observed with thiolates SPh and S*i*Pr. A similar trend is observed for the X–C(3)–X angles; the bond angles are quite similar in **1** [114.6(1)°] and **7** [115.6(2)°], but larger in dithioether compounds **2a** [119.9(3)°] and **2b** [123.1(2)°].

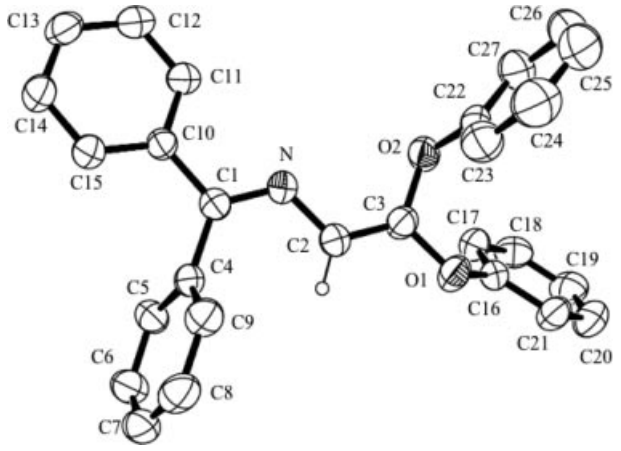


Figure 3. Molecular structure of **7** (ORTEP diagram at the 30% probability level). Selected bond lengths [Å] and angles [°]: N–C(1) 1.293(3), N–C(2) 1.385(3), C(3)–C(2) 1.319(3), C(3)–O(1) 1.336(3), C(3)–O(2) 1.370(3); O(1)–C(3)–O(2) 115.6(2), N–C(2)–C(3) 121.0(2), C(1)–N–C(2) 121.1(2), C(3)–O(1)–C(16) 118.9(2), C(3)–O(2)–C(22) 117.4(2), C(4)–C(1)–C(10) 120.0(2), N–C(1)–C(4) 123.4(2), N–C(1)–C(10) 116.7(2).

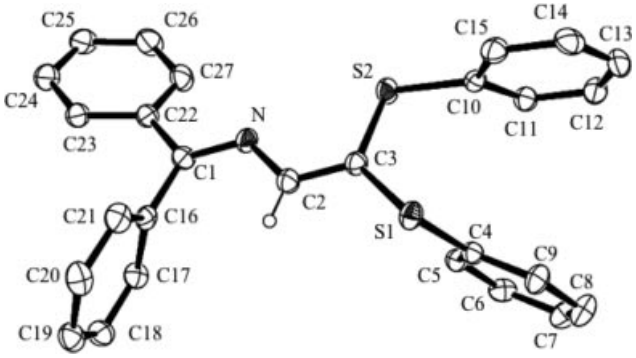


Figure 4. Molecular structure of **2b** (ORTEP diagram at the 30% probability level). Selected bond lengths [Å] and angles [°]: C(10)–S(2) 1.778(3), C(4)–S(1) 1.769(3), C(3)–S(1) 1.764(3), C(3)–S(2) 1.767(3), C(3)–C(2) 1.348(4), N–C(2) 1.393(4), N–C(1) 1.303(4); S(1)–C(3)–S(2) 123.1(2), C(3)–S(1)–C(4) 103.81(13), C(3)–S(2)–C(10) 103.54(13), C(2)–C(3)–S(1) 117.7(2), C(2)–C(3)–S(2) 119.2(2), N–C(2)–C(3) 119.0(3), C(1)–N–C(2) 120.0(3), N–C(1)–C(16) 124.9(3), N–C(1)–C(22) 116.93(3), C(16)–C(1)–C(22) 118.3(2).

DFT Calculations

To date, we have solved 10 crystal structures of compounds resulting from nucleophilic attack on **1**. The sulfur-based anions SPh, S*i*Pr and $SCH_2C(O)COEt$ (SGly) and OPh seem to initially attack the C3 atom of the azadiene C1=N–C2=C3 chain in **1**, while the alkoxides OMe, OEt, $OCH_2C(O)COEt$ (OGly),[19] cyanide[28] and the pyrrole anion[29] first attack the C2 atom of this chain. Such a diverging reactivity pattern of **1** towards different nucleophilic

reagents led us to investigate its electronic structure. DFT calculations were carried out with the Gaussian 03 package[36] using the B3LYP/6-311G functional/basis-set couple. First the molecular geometry of **1** was optimised, followed by wave function and frequency calculations. The metric parameters calculated for **1** are similar to those obtained from the X-ray diffraction studies.[19] The maximum difference in bond lengths does not exceed 0.01 Å for C–C and C–N bonds and 0.08 Å for C–Cl bonds. The energy of the HOMO is equal to –6.406 eV and that of the LUMO is of –2.139 eV (ΔE_{H-L} = 4.087 eV). The Mulliken charges on the C1, N, C2 and C3 atoms of the azadiene chain are equal to +0.08, –0.35, +0.21 and –0.44, respectively.

The value of ΔE_{H-L}, the $E_{LUMO} - E_{HOMO}$ energy gap, is 4.09 eV for **1**. Similar calculations carried out on **2b** show that in this case it is equal to 3.64 eV. Both these ΔE_{H-L} values excellently corroborate the UV spectra (Figure 1) if simple HOMO–LUMO excitation is taken into account for the low-energy transitions recorded for **1** and **2b**. The calculated ($\Delta E_{H-L} = hc/\lambda$) λ wavelengths are equal to 304 nm (vs. exp. 298 nm) for **1** and to 341 nm (vs. exp. 355 nm) for **2b**. A very close match between theoretical and experimental values (304 vs. exp. 311 nm) was also obtained for derivative **7**, but for the *i*Pr compound **2a** a difference of 38 nm was found (λ_{calc} = 337 nm vs. λ_{obs} = 375 nm). A more detailed discussion of the electronic structures of **1** and of **2a**, **2b** and **7** will be reported in a forthcoming paper.

The shapes of the HOMO and LUMO of **1** are depicted in Figure 5. Considering the HOMO of **1**, the calculations show that some 55% of the C2=C3 bond and 45% of the C1=N bond make π contributions to the azadienic chain atoms (p π atomic orbitals). The LUMO in **1** is constructed quite differently, with % contributions of C1(34), N(24), C2(13) and C3(29). One would expect that nucleophilic (basic) attacks should occur on the LUMO. The C2 centre of **1** bears the highest Mulliken positive charge in the azadiene array and is well represented (13% contribution of p π atomic orbital) in this molecular orbital. Consequently, the C2 atom may behave as an electrophilic/hard site and it is not surprising that the hard alkoxides OMe and OEt, OGly, CN and the pyrrole anion preferentially attack this site (HSAB principle).[37] The Mulliken atomic charges of the carbon atoms in **1** decrease from positive to negative in the order C2 > C1 > C3. It is therefore not surprising that the second substitution on **1** with hard OEt [see the molecular structure of $Ph_2C(OEt)NC(OEt)CH_2Cl$ in ref.[19]] occurs at the C1 atom of the azadiene.

The reactivity of **1** towards the "thio" nucleophiles SPh, $SCH_2C(O)COEt$ (SGly) and S*i*Pr[24] and OPh reported in this paper is quite different compared with that reported for the hard bases. Why in the X-ray structures are they found on the C3 atom of azadiene **1**? The following rationale is an attempt to answer this question. The head sulfur atom of the "thio" reagents is larger and thus more easily polarisable than the oxygen atom in the hard oxo-bases; this is the condition necessary for the "thio" molecules to be considered soft and the oxo ones hard. Remember Klopman's explanation of the HSAB principle:[38] hard acids and bases are ionically bound while soft acids and bases are largely covalently bound. Once applied to our reactions this explanation means that the hard bases will prefer ionic interactions with the positively charged sites of **1** (C2 and C1). The softer ones (thio molecules) will prefer covalent interactions with the soft C3 site of **1** despite its negative Mulliken charge. The p π atomic orbital of the C3 atom makes an appreciable contribution (29%) to the LUMO of **1** and thus corroborates our hypothesis. From structural analogies, the phenoxide ion may be considered as a soft anion like the SPh one.

Conclusions and Perspectives

We have shown that functionalised 2-azadienes of the type $(RE)_2C=C(H)–N=CPh_2$ (E = O, S) are accessible by the treatment of $Cl_2C=C(H)–N=CPh_2$ (**1**) with thiolates and phenolate. The softer nucleophiles RS^- and PhO^- in DMF as solvent preferentially attack the electrophilic C3 atom, whereas the harder alkoxides and the sodium salts of pyrrole and cyanide attack the electrophilic C2 atom of **1**, demonstrating that the outcome of the reaction is difficult to predict and is sensitive to several parameters. It seems that the HSAB principle may explain in part the observed reactivity pathways. However, a more detailed theoretical analysis of the electronic structures of the incoming nucleophiles (hardness/softness/electronegativity) and of the iso-

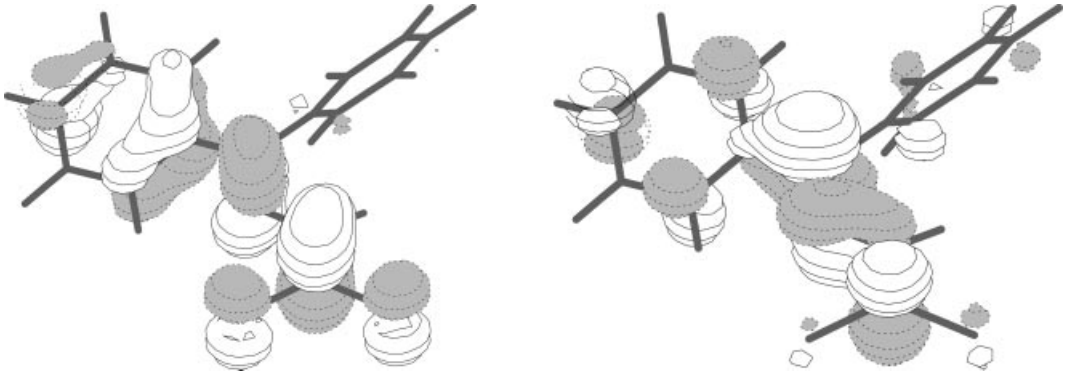


Figure 5. Shapes of the HOMO (left) and LUMO (right) of **1**.

mers of substituted products is needed for a clearer understanding of the reactivity of these azabutadiene molecules. Furthermore, the easy preparation of **2a**,**b** and **7** is a promising development in coordination chemistry. As communicated for the molybdenum complex *cis*-[$(OC)_4Mo\{(iPrS)_2$-$C{=}C(H)$–$N{=}CPh_2\}$],[24] these ligand systems are prone to ligate to metal centres via the soft thioether function or the harder imine nitrogen atom. We are currently investigating the coordination chemistry of these ligands with other transition metals like rhenium, copper and mercury as well as the photophysical properties of these systems. The potential of these polydentate ligands to act as *C*,*N*,*S* 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 metal–aryl bond and their potential towards insertion reactions will be the topic of a forthcoming paper.

Experimental Section

All reactions were performed in Schlenk-tube flasks under purified nitrogen. Solvents were dried and distilled under nitrogen before use, toluene and heptane with sodium, dichloromethane from P_4O_{10}. The ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer (300.13 and 75.1 MHz, respectively, for ^1H and ^{13}C NMR). All NMR spectra were recorded in $CDCl_3$ unless otherwise stated. FTIR spectra were measured with a Nexus-470 Nicolet spectrometer as KBr pellets. UV/Vis spectra were recorded with a Uvikon-XL spectrometer in dichloromethane at ambient temperature.

General Procedure: 4,4-Dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**1**) (1.1 mmol) was stirred with an excess of thiolates or phenolate (6 mmol) as nucleophile in dry DMF (4 mL). The temperature and reaction time are given in each case. The reaction mixture was then poured into water (100 mL). Ether extraction, followed by washing, drying and evaporation provided the crude products. Purification was carried out by crystallisation in hot ethanol or by chromatography on neutral alumina using diethyl ether or a mixture of CH_2Cl_2/petroleum ether as eluent.

1,1-Diphenyl-4,4-bis(isopropylthio)-2-azabuta-1,3-diene (2a): Reaction time: 30 min at room temperature; a yellow powder from ethanol, m.p. 59 °C; yield: 0.215 g (55%). $C_{21}H_{25}NS_2$ (355.57): calcd. C 70.87, H 7.03, N 3.93, S 17.99; found C 71.02, H 7.08, N 3.88, S 18.02. IR (KBr): $\tilde{\nu}$ = 1660 (C=C), 1626 (C=N) cm^{-1}. ^1H NMR: δ = 1.17 [d, ^3J = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.32 [d, ^3J = 6.8 Hz, 6 H, $CH(CH_3)_2$], 3.25 (sept, ^3J = 6.8 Hz, 1 H, H_c or H_b), 3.83 (sept, J = 6.8 Hz, 1 H, H_c or H_b), 7.10 (s, 1 H, H_a), 7.10–7.75 (m, 10 H, Ar-H) ppm. ^{13}C NMR: δ = 22.6 [q, J = 127 Hz, $CH(CH_3)_2$], 23.2 [q, J = 127 Hz, $CH(CH_3)_2$], 37.0 [d, J = 145.3 Hz, $CH(CH_3)_2$], 37.7 [d, J = 142.8 Hz, $CH(CH_3)_2$], 127.5–131.0 (5 signals for 10 CH of Ph), 132.2, 136.2, 139.3 (3 signals for 2 C of Ph and C-4), 141.6 (d, J = 168 Hz, C-3), 165.2 (s, C=N) ppm.

1,1-Diphenyl-4,4-bis(phenylthio)-2-azabuta-1,3-diene (2b): Reaction time: 3 h at room temperature; yellow needles from ethanol, m.p. 102 °C; yield: 0.326 g (70%). $C_{27}H_{21}NS_2$ (423.61): calcd. C 76.48, H 4.95, N 3.30, S 15.10; found C 76.39, H 4.91, N 3.32, S 15.12. IR (KBr): $\tilde{\nu}$ = 1575 (C=C), 1553 (C=N) cm^{-1}. ^1H NMR: δ = 7.05–7.45 (m, 21 H, Ar-H + H_a) ppm. ^1H NMR (C_6D_6): δ = 6.80–7.20 (m, 16 H, Ar-H), 7.35–7.50 (m, 2 H, Ar-H), 7.64 (s, 1 H, H_a), 7.90–8.50 (s, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 126.0–133.0 (6 signals for 20 CH of Ph + C-3), 129.2, 130.6, 131.4, 132.6, 134.3 (5 signals for 4 C of Ph and C-4), 166.5 (s, C=N) ppm.

Ethyl 2-[(Ethoxycarbonyl)methylthio]-5,5-diphenyl-5,6-dihydro-4*H*-1,4-thiazine-6-carboxylate (5): Reaction time: 5 h at room temperature. After work up, the product was separated by chromatography using a mixture (75:25) of $CHCl_2$/petroleum ether. Crystallisation from hot ethanol gave a colourless powder, m.p. 87 °C; yield: 0.29 g (60%). $C_{23}H_{25}NO_4S_2$ (443.59): calcd. C 62.28, H 5.68, N 3.16, S 14.46; found C 62.29, H 5.67, N 3.10, S 14.31. IR (KBr): $\tilde{\nu}$ = 1602 (C=C), 1730 (C=O), 3362 (N–H) cm^{-1}. ^1H NMR: δ = 1.18 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.23 (t, ^3J = 7.1 Hz, 3 H, CH_3), 3.09 (d, AB system, ^2J = 14.8 Hz, 1 H, SCH_2CO_2Et), 3.09 (d, AB system, ^2J = 14.8 Hz, 1 H, SCH_2CO_2Et), 4.12 (q, ^3J = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 4.17 (q, ^3J = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 4.34 (s, 1 H, 6-H), 4.78 (d, ^3J = 5.15 Hz, 1 H, NH), 7.10 (d, ^3J = 5.1 Hz, 1 H, 3-H), 7.15–7.40 (m, 10 H, Ar-H) ppm. ^{13}C NMR: δ = 13.8 (q, J = 127.3 Hz, $CO_2CH_2CH_3$), 14.0 (q, J = 127.3 Hz, $CO_2CH_2CH_3$), 38.2 (t, J = 141.4 Hz, SCH_2CO_2Et), 45.5 (d, J = 142.2 Hz, C-6), 60.8 (t, J = 148.1 Hz, $CO_2CH_2CH_3$), 61.0 (t, J = 148.1 Hz, $CO_2CH_2CH_3$), 62.9 (s, C-5), 88.8 (s, C-2), 125.29–128.7 (6 signals for 10 aromatic CH), 136.6 (d, J = 176.4 Hz, C-3), 143.9, 145.05 (2 signals for 2 aromatic C), 167.7 (s, C=O), 169.8 (s, C=O) ppm.

4,4-Diphenoxy-1,1-diphenyl-2-azabuta-1,3-diene (7): Reaction time: 24 h at 65 °C; colourless needles from ethanol, m.p. 121 °C; yield: 0.327 g (76%). $C_{27}H_{21}NO_2$ (391.48): calcd. C 82.76, H 5.36, N 3.57; found C 82.81, H 5.39, N 3.54. IR (KBr): $\tilde{\nu}$ = 1655 (C=C), 1590 (C=N) cm^{-1}. ^1H NMR: δ = 6.42 (s, 1 H), 6.95–7.60 (m, 20 H, Ar-H) ppm. ^{13}C NMR: δ = 111.0 (d, J = 168.5 Hz, C-3), 116.0–130.0 (10 signals for 20 CH of Ph), 135.8 (s, C of Ph), 139.3 (s, C of Ph), 152.6 (s, C-4), 154.8 (s, C of Ph), 155.4 (s, C of Ph); 163.3 (s, C=N) ppm.

X-ray Crystal Structure Determinations: X-ray quality crystals of **2b**, **5** and **7** were grown from ethanol solutions. Their shape, colour and dimensions are given in Table 1. All diffraction data (unit cell and intensities) were recorded with an Enraf-Nonius CAD4 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The measured intensities were reduced using PROCESS in the MolEN suite of programs.[39] The structures were solved using both the Patterson synthesis and by direct methods using the SHELXS97 routines.[40] The models were further refined using the SHELXL97 software.[40] All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the calculated positions and refined isotropically using a riding model. The PhO-substituted compound **7** is a special case because it crystallises in a noncentrosymmetric space group $P2_12_12_1$. The current Flack parameter for the geometry given in Figure 3 is equal to +2.33(1.64). Inversion of the atomic coordinates led to a Flack parameter of –1.41(1.65) without changing the metric parameters. Thus, the absolute structure of **7** cannot be determined reliably. All attempts to solve this structure in centrosymmetric space groups failed.

CCDC-275790, -275791 and -275789 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 1. Crystallographic data for compounds **2b**, **5** and **7**.

Compound	**2b**	**5**	**7**
Empirical formula	$C_{27}H_{21}NS_2$	$C_{23}H_{25}NO_4S_2$	$C_{27}H_{21}NO_2$
Formula weight	423.57	443.56	391.45
Temperature [K]	293(2)	293(2)	293(2)
Shape, colour	prism, yellow	prism, colourless	prism, colourless
Dimensions	0.25 × 0.20 × 0.15	0.40 × 0.25 × 0.25	0.5 × 0.3 × 0.2
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
Unit cell dimensions			
a [Å]	12.8964(13)	9.971(3)	9.146(1)
b [Å]	6.5504(7)	10.312(3)	10.176(1)
c [Å]	26.679(3)	13.331(4)	23.129(4)
A [°]	90	71.64(2)	90
B [°]	102.854(2)	67.32(2)	90
γ [°]	90	67.09(2)	90
Volume [Å^3]	2197.3(4)	4982.1(17)	2152.6(5)
Z	4	2	4
Density (calcd.) [Mg m^{-3}]	1.280	1.289	1.208
Absorption coefficient [mm^{-1}]	0.256	0.261	0.076
F(000)	888	468	824
Crystal size [mm]	0.25 × 0.20 × 0.15	0.40 × 0.25 × 0.25	0.5 × 0.3 × 0.2
θ range for data collection [°]	1.57–25.03	3.01–26.29	2.19–26.30
Index ranges	$-15 \le h \le 14$, $0 \le k \le 7$, $0 \le l \le 31$	$-11 \le h \le 12$, $-12 \le k \le 12$, $0 \le l \le 16$	$-11 \le h \le 10$, $-12 \le k \le 6$, $-28 \le l \le 2$
Reflections collected	3879	4828	4928
Independent reflections	3879	4623	3043
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	3879/0/271	4623/0/298	3043/0/217
GoF for F_2	1.069	1.029	1.073
Final R factors [$I > 2\sigma(I)$]			
R_1	0.0498	0.0529	0.0320
wR_2	0.1328	0.1449	0.0743
R factors (all data)			
R_1	0.0757	0.1060	0.0940
wR_2	0.1567	0.1717	0.0935
Largest $\rho_{max.}/\rho_{min.}$ [e·Å^{-3}]	0.329/–0.401	0.385/–0.242	0.085/–0.124

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