J. Org. Chem. **2001,** *66,* 5713−5716

Generation of Azines by the Reaction of a Nucleophilic Carbene with Diazoalkanes: A Synthetic and Crystallographic Study

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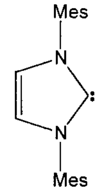
Received October 24, 2000 (Revised Manuscript Received June 1, 2001)

Reactions of the nucleophilic carbene 1,3-dimesityl-imidazol-2-ylidene (**1**) with diazofluorene, diphenyldiazomethane, and azidotrimethylsilane were examined. Specifically, carbene **1** reacts with diazofluorene and diphenyldiazomethane to give addition products (azines: **3** and **4**, respectively). Compounds **3** and **4** were further characterized in the solid-state by single-crystal X-ray crystallographic studies. [**3** (a = 9.7936(6) Å, b = 10.0529(7) Å, c = 16.251(1) Å, α = 75.765(1)°, β = 79.711(1)°, γ = 64.321(1)°, Z = 2, space group $P\bar{1}$); **4** (a = 11.681(3) Å, b = 11.861(4) Å, c = 21.186(3) Å, α = 90°, β = 97.05(2)°, γ = 90°, Z = 4, space group $P2_1/n$)]. The structural parameters of **3** and **4** are discussed with reference to previously characterized symmetrical and unsymmetrical azines. Structural data suggest that charge separation is possible in **3**.

Introduction

Azines ($R_2C{=}N{-}N{=}CR_2$) are extremely useful compounds and recently they have received attention due to their utility in a number of interesting reactions and applications. For example, azines undergo unusual [1, 3] dipolar cycloaddition reactions (the crisscross addition reaction) with dienophiles providing an easy route to five membered rings.[1] Azines also participate in [3 + 2] cycloaddition reactions as an *ene* fragment.[2] Furthermore, they have received attention as possible nonlinear optical materials.[3] Polyazines, which are conjugated polymers, can be doped with iodine to give conducting materials.[4]

Coincident with the discovery of the synthetic utility of azines was the discovery of the first isolable carbenes. In 1991, Arduengo comprehensively characterized a stable, crystalline nucleophilic (singlet) carbene.[5] Since then numerous derivatives have been reported including **1**.[6] More recently, Tomioka has isolated persistent electrophilic (triplet) carbenes such as **2**.[7]



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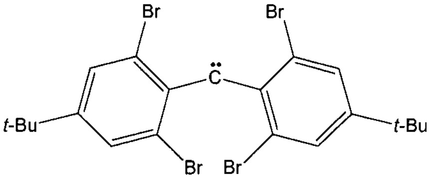

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Mes = 2, 4, 6-trimethylphenyl

The chemistry of nucleophilic carbenes (such as **1**) has been explored and the majority of the reactivity that has been studied has focused on the coordination behavior of these species as strong σ-donor ligands (i.e. they act as Lewis Bases). Numerous examples of main group element and transition metal complexes have been prepared and this topic has been the subject of recent reviews.[8,9]

As part of our studies examining the chemistry of nucleophilic carbenes, we have prepared azines from the reaction of **1** with diazoalkanes.[10] Two adducts (**3** and **4**) were comprehensively characterized, including solid-state characterization by single-crystal X-ray crystallography. The structures of the product azines are relevant to discussions concerning charge transfer within unsymmetrical azines. Finally, the reactivity of **1** was further explored by studying its reaction with TMS−N_3 (TMS = trimethylsilyl).

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10.1021/jo001515b CCC: $20.00

Experimental Section

General. All manipulations were carried out under an atmosphere of dry nitrogen in a glovebox or with a vacuum manifold using standard Schlenk techniques. Anhydrous solvents were used as received from Aldrich Chemical Co. The compounds 1,3-dimesityl-imidazol-2-ylidene,[6] diazofluorene,[11] and diphenyldiazomethane[12] were prepared following literature procedures. NMR spectra were recorded on a Bruker AC 250 spectrometer in 5 mm quartz tubes. NMR (^{1}H and ^{13}C {^{1}H}) chemical shifts are reported in parts per million (ppm) downfield from TMS and are calibrated to the residual signal of the solvent. Infrared spectra were obtained using a Perkin-Elmer Model 683 spectrometer and the transmittance values are reported in cm^{-1}. Melting points were measured using a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab (Norcross, Ga) and electron impact mass spectral data were obtained at Simon Fraser University (Burnaby, B. C.) using an HP 5985 GC mass spectrometer.

Reaction of 1 with Diazofluorene. A solution of **1** (1.60 g, 5.26 mmol) in 20 mL of tetrahydrofuran (THF) was added via cannula (dropwise) to a stirred solution of diazofluorene (1.00 g, 5.26 mmol) in 50 mL of THF at room temperature (RT). The dark red solution was stirred for 3.5 h. Solvent was removed in vacuo and the dried red solid was recrystallized in air from dichloromethane and hexane to produce red/orange crystals of the product (**3**). Yield: 1.28 g (49%). Mp 216−220 °C. NMR ($CDCl_3$): ^{1}H δ 2.38 (s, 12H), 2.45 (s, 6H), 6.54 (d, 2H), 6.57 (s, 2H), 6.90−7.30 (m, 2H), 7.10 (s, 4H), 7.52−7.64 (m, 2H), 7.92−8.00 (m, 2H); ^{13}C{^{1}H} δ 149.8, 146.4, 139.1, 138.1, 135.6, 131.2, 128.8, 127.5, 126.9, 126.3, 120.4, 119.0, 115.7, 21.1, 18.2. IR (thin film): 2930 (m), 2900 (m), 1670 (m, C=N), 1575 (m, C=N), 1485 (s), 1440 (s), 1420 (s), 1360 (m), 1330 (m), 1315 (m), 1285 (m), 1240 (m), 1215 (m), 1195 (m), 1170 (m), 1120 (m), 1095 (m), 1055 (m). LRMS *m/z* 496 (M^+: 100%). Anal. Calcd for $C_{34}H_{32}N_4$: C, 82.22; H, 6.49; N, 11.28. Found: C, 82.30; H, 6.50; N, 11.15.

Reaction of 1 with $(C_6H_5)_2CN_2$. 1,3-Dimesityl-imidazol-2-ylidene (0.80 g, 2.63 mmol) in 20 mL of THF was added via cannula dropwise to a stirred solution of diphenyldiazomethane (0.57 g, 2.63 mmol) in 25 mL of THF at room temperature. The dark red solution was allowed to stir overnight before volatile components were removed in vacuo. The resulting residue was recrystallized from a dichloromethane/hexane (60/40) mixture to afford dark orange crystals of **4**. Yield: 0.63 g (48%). Mp 149−151 °C. NMR ($CDCl_3$): ^{1}H δ 7.26−7.02 (m, 8H), 6.98 (s, 4 H), 6.72−6.68 (m, 2H), 2.41 (s, 6H), 2.1(s, 12H); ^{13}C{^{1}H} δ 151.0, 148.2, 140.3, 137.4, 136.4, 130.4, 128.7, 127.2, 127.1, 126.7, 126.5, 126.4, 115.0, 21.1, 18.2. IR (thin film): 3110 (w), 3005 (m), 2900 (m), 1695 (m, C=N), 1680 (m, C=N), 1580 (s), 1555 (s), 1510 (s), 1480 (s), 1430 (s), 1370 (m), 1335 (m), 1315 (m), 1290 (m), 1245 (m), 1200 (w), 1160 (m), 1125 (m), 1060 (s), 1025 (m), 1000 (m), 920 (m), 850 (m). LRMS *m/z* M^+ 498 (M^+: 60%). Anal. Calcd for $C_{34}H_{32}N_4$: C, 81.89; H, 6.87; N, 11.24. Found: C, 81.46; H, 6.91; N, 11.17.

Reaction of 1 with Azidotrimethylsilane. Compound **1** (0.80 g, 2.63 mmol) in 20 mL of THF was added dropwise via cannula to a stirred solution of azidotrimethylsilane (0.40 mL, 2.63 mmol) in 25 mL of THF at room temperature. A white precipitate formed immediately and the resulting suspension was stirred overnight. The solvent was removed in vacuo and the dried brown solid was then crystallized from dichloromethane/benzene mixture (in air) to afford orange crystals that were characterized as compound **6**. Yield: 0.20 g (24%). Mp > 250 °C. NMR ($CDCl_3$): ^{1}H δ 2.17 (s, 12H), 2.35 (s, 6H), 7.05 (s, 2H), 7.25 (s, 2H), 7.58 (s, 2H), 10.22 (s, 1H); ^{13}C{^{1}H} δ 18.5, 21.0, 99.5, 123.5, 129.5, 134.0, 142.0, 177.5. IR (thin film): 3630 (w, br), 3300 (w), 3030 (w), 2900 (w), 1665 (m, C=N), 1595 (w), 1525 (s), 1470 (m), 1450 (m), 1225 (s), 1055 (w), 780 (w), 670 (m). LRMS *m/z*: 320 $(M + 1)^+$, 319 (M^+). Anal. Calcd for $C_{21}H_{25}N_3$: C, 78.96; H, 7.89; N, 13.15. Found: C, 78.80; H, 7.85; N, 13.10.

X-ray Structure Determination of 3 and 4. 3: A single crystal of **3** was mounted and centered on a Seimans SMART/CCD diffractometer. Data were collected at −50 °C using Mo Kα radiation. Lorentz and polarization corrections were applied and data were also corrected for absorption with the SADABS program. Direct methods and Fourier techniques were used to solve the crystal structure. Refinement was conducted using full-matrix least-squares calculations and SHELX-TL PC V 5.03. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in calculated positions and were refined using a riding model. Full details of the structure and refinement appear in the Supporting Information.

4: A single crystal of **4** was mounted on a Rigaku AFC5R diffractometer equipped with a rotating anode generator and utilizing graphite monochromated Cu Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least squares refinement using the setting angles of 25 carefully centered reflections in the range $74.53° < 2 Å < 79.34°$. Data were collected at room temperature (23 °C) and were corrected for Lorentz and polarization effects. The structure was solved by direct methods[13] and expanded using Fourier techniques.[14] Full matrix least squares refinement was carried out using SHELXL97.[15] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their geometrically calculated positions and allowed to ride on the heavy atoms to which they were bonded, with U_{iso} equal to $1.2U_{eq}$ of the heavy atom ($1.5U_{eq}$ for methyl hydrogens). Full details of the structure and refinement appear in the Supporting Information that is available on the Internet at http://pubs.acs.org.

Results and Discussion

Reaction of 1,3-Dimesitylimidazol-2-ylidene with Diazoalkanes or TMS−N$_3$. Carbene **1** reacts readily with diazofluorene in THF solution to produce a dark red, highly soluble, crystalline material. Recrystallization of this species from a CH_2Cl_2/hexanes mixture affords red crystals that can be isolated in modest yield. Infrared spectroscopic analysis of this solid showed the presence of two absorptions tentatively assigned to C=N vibrations. ^{1}H NMR spectroscopic studies indicated that both the fluorenylidene and carbene fragments are retained in the new compound. Furthermore, mass spectral analysis indicated the presence of an M^+ peak ($M^+_{calc} = 496$) that is consistent with **3.** X-ray analysis of the crystalline material confirmed the identity of **3** as an azine compound. Similar spectroscopic studies on the reaction product formed from the combination of **1** with diphenyldiazomethane were performed, and the data are consistent with the formation of a similar azine compound **4**.[16] It is interesting to note that elimination of N_2 from diazofluorene does not occur under the reaction conditions, a situation that is common in reactions of related Lewis bases such as phosphines with diazoalkanes.

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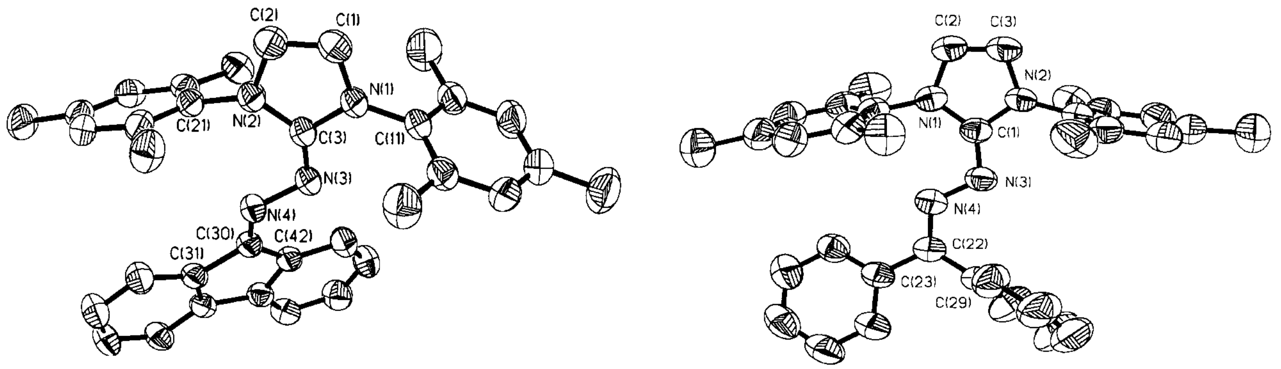
[16] The reaction of carbenes with diazoalkanes has been briefly described in earlier reports, however the products were not comprehensively characterized. See: Bildstein, B.; Malaun, M.; Kopacka, H.; Ongania, K.-H.; Wurst, K. *J. Organomet. Chem.* **1999**, *572*, 177. See also: Wanzlick, H.-W.; Konig, B. *Chem. Ber.* **1964**, *97*, 3513.

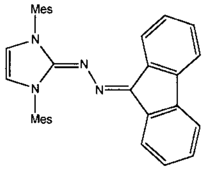


3

4

Figure 1. ORTEP View of **3** and **4**.

Elimination of N_2 would lead to the formation of an alkene such as **5**.



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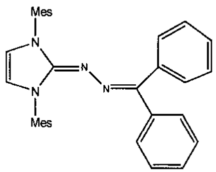

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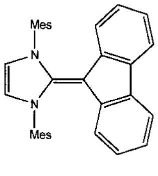

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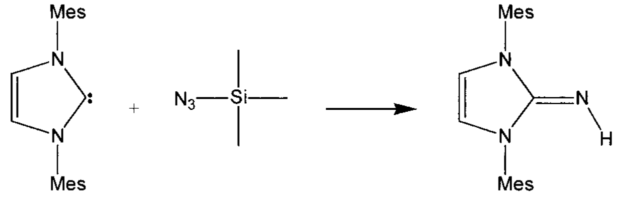
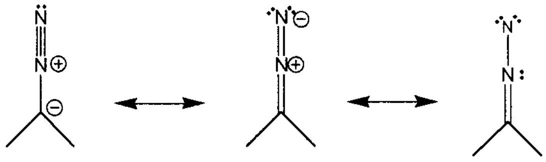
Reaction of azidotrimethylsilane with **1** in THF resulted in the formation of a white precipitate that was not characterized. Removal of solvent from the suspension followed by recrystallization in air from a CH_2Cl_2/benzene mixture gave an orange crystalline material in low yield. Noticeably absent in the ^{1}H NMR spectrum of this material was a peak at ca. 0.0−1.0 ppm that would be consistent with the presence of $(CH_3)_3Si$ fragment. Furthermore, infrared analysis of the solid suggests the presence of both N−H and C=N groups. The presence of an N−H fragment is also suggested by the ^{1}H NMR spectrum (singlet proton resonance $\delta = 10.2$ ppm). The spectroscopic data are, therefore, consistent with imine **6**, and mass spectral data support this assignment. The mechanism for the formation of **6** is unknown, but it is reasonable to suggest that it results from the hydrolysis and loss of N_2 from **1:N$_3$-TMS** (reminiscent of **3** and **4**) or simply hydrolysis of **1:N-TMS** (formed via addition followed by N_2 elimination).



1 6

Analysis of the Solid State Structures of 3 and 4. The crystal structures of **3** and **4** were determined by single-crystal X-ray crystallography. ORTEP diagrams with important bond lengths and angles are shown in Figure 1.

The structures of these compounds are relevant to discussions concerning the bonding modes between nucleophilic carbenes and Lewis acid fragments. To facilitate this discussion, it is important to look at the various resonance structures for a diazoalkane (**7a**−**7c**). From the point of coordination chemistry, we can view **3** and **4** as adducts of carbene **1** and the terminal nitrene center of resonance structure **7c**.



7a 7b 7c

The crystallographic characterization of compounds **3** and **4** provides an opportunity to compare directly the C−N interactions for both singlet and triplet carbenes (such as **1** and **2**, respectively) with a symmetrical acceptor fragment.[17] An examination of the metrical data for **3** reveals that the C_3−N_3 and the C_{30}−N_4 distances are 1.325(3) Å and 1.304(3) Å, respectively. Likewise for **4**, the C_1−N_3 and the C_{22}−N_4 bond lengths are 1.312(3) Å and 1.294(3) Å. For both **3** and **4**, the C−N bonds are the same length (within experimental error) and these lengths are consistent with bona fide C=N double bonds.[18] There is a significant widening of the N−C−N angle within the imidazol ring upon azine formation. For example, in **3** the angle $\angle N_1{-}C_3{-}N_2$ is 105.8 (2)° which is close to the corresponding angle in **4** ($\angle N_1{-}C_3{-}N_2$ is (105.4(2)°). This is wider than the N−C−N angle in the free carbene **1** (101.4(2)°)[6] but narrower than the N−C−N angle in the corresponding imidazolium ion **1·HCl** which is 108.7(4)°.[19]

A final topic worthy of comment is the relevance of compound **3** to the discussion concerning push/pull electronic effects in azines. This stereoelectronic effect is important for their application as nonlinear optical materials. An elegant synthetic and crystallographic

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[17] Fragment analyses of products **3** or **4** are likewise interesting. For example, compound **4** can be formally derived from simultaneous addition of a singlet carbene **1** and a triplet carbene CPh_2 (parent of carbene **2**) to an N_2 molecule.

[18] It is interesting to note that for carbene/phosphinidene adducts the CP bond that is formally derived from the interaction of a triplet carbene (fluorenylidene) with a triplet phosphinidene is 4.6% shorter than the interaction of singlet carbene **1** with a triplet phosphinidene. See: Decken, A.; Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H. *Inorg. Chem.* **1997**, *36*, 3741.

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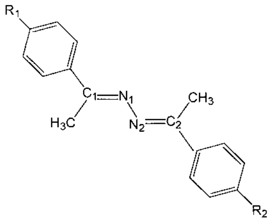
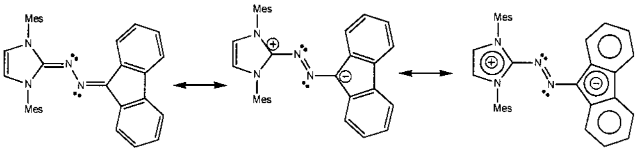
Table 1



compound	C1−N1	N1−N2	N2−C2	reference
R_1=R_2=H	1.278(3)	1.403(3)	1.278(3)	22
R_1=R_2=Br	1.264(7)	1.383(7)	1.269(7)	22
R_1=OMe, R_2=Br	1.282(11)	1.375(11)	1.314(11)	20
R_1=OMe, R_2=NO_2	1.273(4)	1.396(4)	1.293(4)	20
3	1.325(3)	1.369(2)	1.304(3)	this work
4	1.312(3)	1.389(3)	1.294(3)	this work

study has shown that there is little evidence for significant changes of the azine unit due to asymmetric electron distribution in the azine.[20,21] Perhaps the greatest potential for molecular electronic asymmetry in an azine is found in compound **3**. In its extreme (**3c**), charge separation would occur and this should result in significant CN bond lengthening and coincident NN bond shortening with respect to symmetrical azines.



3a **3b** **3c**

Data relevant to this discussion are presented in Table 1. For example, the C=N and N−N bond lengths for acetophenone azine, where there is no charge separation, are 1.278(3) Å and 1.403(3) Å, respectively.[22] These values should be compared with the corresponding bond lengths in compound **3** (C=N 1.325(3) Å and 1.304(3) Å; N−N bond 1.369(2) Å), which are consistent with the suggestion that some separation of charge has occurred. It is possible that the charge separation in **3c** is facilitated by the aromatic nature of both the imidazol and fluorenylidene rings. This observation suggests that unlike previously studied substituted acetophenone azines, charge separation can, under extreme circumstances, be realized. Recognizing this, azines derived from nucleophilic carbenes and substituted fluorenylidene diazo compounds may be ideal targets for nonlinear optical materials.

Conclusions

Nucleophilic carbenes react with diazoalkanes to give addition products. Specifically, carbene **1** reacts with diazoalkanes to give azines, whereas reaction of **1** with trimethylsilyl azide (followed, presumably, by hydrolysis) produces an imine. Finally, the metrical parameters for compound **3** shows some evidence of charge separation, perhaps, by adoption of highly delocalized structures such as **3c**. Hence, compounds of this type may be targets for nonlinear optical materials.

Acknowledgment. The authors gratefully acknowledge the financial support of Saint Mary's University and the Natural Sciences and Engineering Research Council of Canada. The authors also acknowledge the Atlantic Region Magnetic Resonance Centre at Dalhousie University for NMR data and especially Dr. Don Hooper and Dr. Mike Lumsden for their help in obtaining ^{1}H and^{13}C NMR spectra. Thanks are also expressed to Dr. Mel Schriver (Atlantic Baptist University) for the generous loan of glassware and to Deepa Abeysekera and Dr. R. A. Gossage for helpful discussions.

Supporting Information Available: Tables of X-ray structural data for compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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