

photoprocess for α -diazo carbonyl compounds.^{10,24} If the radiationless decay channels in **1*** are coupled to this kind of C=C=N=N bond bending, the rigid matrix could suppress this motion and enhance the probability of N₂ extrusion and subsequent rearrangement.

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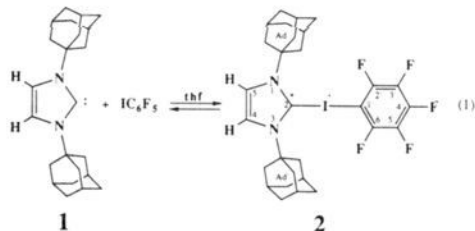
Synthesis of a Reverse Ylide from a Nucleophilic Carbene

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Carbene **1** reacts with iodopentafluorobenzene to give the 1:1 adduct **2**. In solution, **2** is in equilibrium with free carbene and iodopentafluorobenzene as evidenced by the observation of averaged NMR chemical shifts in the presence of either excess carbene or iodopentafluorobenzene. If solutions of **2** are allowed



to stand at room temperature for several hours, resonances for pentafluorobenzene and 1,3-di-1-adamantyl-2-iodoimidazolium ion are evident in the proton NMR spectrum. These observations suggest that either C-I bond may cleave in solution. We have made a similar observation of adduct formation between carbene **1** and iodotrifluoromethane, and decomposition products of 1,3-di-1-adamantyl-2-iodoimidazolium ion and fluoroform were observed on standing.²

Ylide **2** is stable in solid form and crystallizes from thf with 3 molecules of thf. Crystals of **2** gradually lose the thf of crystallization on warming and melt at 110 °C. At room temperature the ¹H NMR spectrum of **2** in thf-*d*₆ gives δ 1.76 (m, Ad_{4,6,10}, 12 H), 2.18 (m, Ad_{2,3,5,7,8,9}, 18 H), 7.03 (br s, NCH, 2 H). The NMR spectra of **2** in thf-*d*₈ at -50 °C are ¹H NMR δ 1.78 (m, Ad_{4,6,10}), 2.21 (m, Ad_{3,5,7}), 2.38 (m, Ad_{2,8,9}), 7.24 (s, NCH); ¹³C NMR [¹H] δ 30.90 (s, Ad_{3,5,7}), 36.70 (s, Ad_{4,6,10}), 44.36 (s, Ad_{2,8,9}), 57.79 (s, Ad₁), 87.35 (m, ICCF), 115.15 (br s, NCH), 137.23 (dm, ¹J_{CF} = 260.4 Hz, ICCCF), 140.65 (dm, ¹J_{CF} = 256.4 Hz,

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(2) The NMR spectra of the ICF₃ adduct with **1** in thf-*d*₆ at -80 °C were as follows: ¹H NMR δ 1.76 (s, Ad_{4,6,10}, 12 H), 2.20 (br s, Ad_{2,3,5,7,8,9}, 18 H), 7.35 (s, NCH, 2 H); ¹³C NMR [¹H] δ 30.68 (s, Ad_{3,5,7}), 36.67 (s, Ad_{4,6,10}), 44.27 (s, Ad_{2,8,9}), 57.36 (s, Ad₁), 93.60 (q, ¹J_{CF} = 370.3 Hz, ICF), 195.15 (br s, NCN); ¹⁹F NMR δ -24.77 (s).

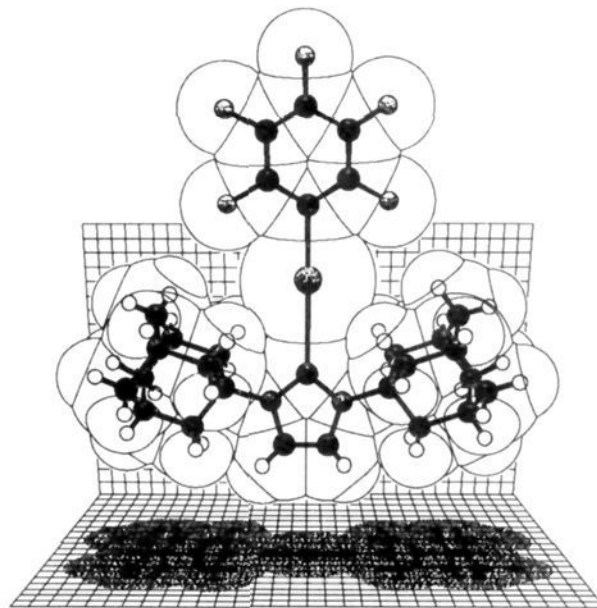


Figure 1. Space-filling KANVAS⁴ drawing of the X-ray structure of ylide **2**.

ICCCCF), 147.46 (dm, ¹J_{CF} = 235.6 Hz ICCF), 193.64 (br s, NCN); ¹⁵N NMR δ -161.07 (reference NH₄¹⁵NO₃); and ¹⁹F NMR δ -123.75 (br m, 2 F, ICCF), -159.44 (t, ICCCF), -163.63 (m, 2 F, ICCCF). A sample of vacuum-dried **2** gave a satisfactory elemental analysis (C₂₉H₂₃N₂IF₅; Calcd: C, 55.25; H, 5.12; N, 4.44; F 15.07. Found: C, 55.55; H 5.22; N 4.21; F, 14.45).

A crystal of **2** was grown from a 1:2 mixture of **1** and iodopentafluorobenzene in thf at -25 °C. The X-ray crystal structure of **2** is depicted in Figure 1.³ Selected bond lengths and angles are given in Table I.

The X-ray structure of **2** shows some change in the imidazole ring as a result of incorporation of IC₆F₅. The N-C-N angle has increased 2° from the characteristically small angle observed in **1**. The ring internal angles at nitrogen have decreased by an average of 1.4°. The C₂-N₁₍₃₎ bonds are slightly shortened (ΔR = 0.7 pm) and the N₁-C₅ and N₃-C₄ bonds are slightly lengthened (ΔR = 0.5 pm) relative to the corresponding bonds in **1**. The C₄=C₅ bond length is longer in **2** by 0.9 pm. These changes suggest an augmented imidazole π -delocalization in **2** as compared to **1**. This change in π -delocalization is also supported by the downfield shift in the imidazole ring proton in **2** versus **1** (δ 7.02 → 7.24).¹

The large C-I-C angle in **2** is consistent with 10-I-2 (hypervalent) bonding at the iodine center. There is considerable asymmetry in the two C-I bond distances but, as mentioned above, either C-I bond can be cleaved or retained in subsequent chemistry. The length of the C-I to the imidazole fragment is not the result of steric interactions. The C-I bond distance in the 1,3-di-1-adamantyl-2-iodoimidazolium ion (formed from carbene **1** and I₂) is 213.1 (11) pm.⁵ A flat potential surface for such

(3) Crystal data for **2** at 203 K with Mo K α radiation: *a* = 1135.3 (2) pm, *b* = 1333.3 (2) pm, *c* = 1422.0 (2) pm, α = 71.98 (1)°, β = 75.89 (1)°, γ = 82.51 (1)°, triclinic, P $\bar{1}$, *Z* = 2, 5354 unique reflections with *I* > 3 σ (*I*). The final *R* factors were *R* = 0.035 and *R*_w = 0.037. The largest residual electron density in the final difference Fourier map was 0.62 e/Å³ near one of the thf units. Further details of the crystal structure are available in the supplementary material.

(4) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.

Table I. Selected Bond Lengths (pm) and Angles (deg) in **1**

	bond length		angle
C ₂ -I	275.4 (3)	C ₂ -I-C ₁	178.9 (2)
C ₁ -I	215.9 (3)	imid-phen	1.2
C ₂ -N ₁	136.0 (4)	N ₁ -C ₂ -N ₃	104.1 (3)
C ₂ -N ₃	136.6 (4)	C ₅ -N ₁ -C ₂	111.0 (3)
C ₄ -C ₅	132.9 (5)	C ₄ -N ₃ -C ₂	110.6 (3)
N ₁ -C ₅	138.6 (4)	N ₁ -C ₅ -C ₄	107.3 (3)
N ₃ -C ₄	139.2 (4)	N ₃ -C ₄ -C ₅	107.0 (3)
N ₁ -C ₁ -Ad	149.0 (4)	C ₂ -N ₁ -C ₁ -Ad	124.3 (2)
N ₃ -C ₁ -Ad'	148.7 (4)	C ₂ -N ₃ -C ₁ -Ad'	124.9 (2)
C ₁ -C ₂	137.4 (5)	C ₂ -C ₁ -C _{6'}	116.4 (3)
C ₁ -C _{6'}	138.8 (5)	C ₁ -C ₆ -C _{5'}	122.0 (3)
C ₂ -F	134.3 (4)	C ₁ -C ₂ -F	119.9 (3)
C ₅ -F	133.7 (4)	C ₁ -C ₆ -F	120.0 (3)
H _{eq-Ad-6} -F _{2'}	312.1	C-H-F	171.5
H _{eq-Ad-6} -F _{6'}	393.4	C-H-F	173.8

distortions in hypervalent (linear 3-center, 4-electron) bonds has been noted.⁶⁻⁹ Given the vastly different substituents on the carbon centers, the asymmetry in **2** is not surprising. An interesting feature of the solid-state structure of **2** is the near planarity of the imidazole and phenyl rings (interplane angle = 1.2°). This arrangement places the ortho fluorines of the phenyl ring proximal to the pseudo-equatorial protons at C₆ of the adamantyl units. Dipole interactions may play a role in determining this orientation.

Whereas electrophilic carbenes typically form ylides with halogen centers which result in halonium methylides (RX⁺-CR'₂) with a characteristically small C-X-C angle,¹⁰⁻¹² the structure of **2** demonstrates formation (from a nucleophilic carbene) of a "reverse ylide" in which the formal charge assignments at halogen and carbon are reversed (RX⁻+CR'₂).¹³ The resulting linear geometry is best described as carbenium λ³-halanide (10-X-2). The linear 10-I-2 arrangement in **2** is also related to the transition state (or intermediate) for metal halogen exchange reactions.¹⁴⁻¹⁷

Acknowledgment. The excellent technical assistance of W. Marshall made the crystal structure of **2** possible.

Supplementary Material Available: A complete description of the X-ray crystallographic determination on **2** and 1,3-di-1-adamantyl-2-iodoimidazolium triiodide, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, bond angles, and structure factors (14 pages). Ordering information is given on any current masthead page.

(5) Crystal data for 1,3-di-1-adamantyl-2-iodoimidazolium triiodide at 203 K with Mo Kα radiation: *a* = 1164.4 (7) pm, *b* = 1117.9 (7) pm, *c* = 1996.0 (10) pm, β = 99.20 (1)°, monoclinic, *P*₂₁/*c*, *Z* = 4, 2429 unique reflections with *I* > 3σ(*I*). The final *R* factors were *R* = 0.037 and *R*_w = 0.037. The largest residual electron density in the final difference Fourier map was 0.74 e/Å³. Further details of the crystal structure are available in the supplementary material.

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Photoinduced Charge Transfer between Fullerenes (C₆₀ and C₇₀) and Semiconductor ZnO Colloids

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We report here the first photoinduced charge transfer between a semiconductor (ZnO) cluster and a carbon cluster. The reduced clusters of C₆₀ and C₇₀ exhibit absorption characteristics that are quite different from the photogenerated triplet excited states. Transient absorption studies which describe the formation of C₆₀⁻ and C₇₀⁻ in optically excited ZnO suspensions are presented here.

It has been shown that C₆₀ and C₇₀ clusters can be reduced electrochemically up to five successive electron reductions.¹⁻⁴ The first reduction occurs at a potential of -0.44 V vs SCE. Efforts have been made recently to characterize the absorption spectra of reduced products by steady-state spectroelectrochemical³ and γ-radiolysis⁵ experiments. Ultraviolet photoelectron spectra of mass-selected negative carbon clusters are also reported by Yang et al.⁶ Characterization of the triplet excited state has recently been made by transient absorption measurements.^{7,8} Arbogast et al.⁷ have reported that both the C₆₀ and C₇₀ are photochemically stable and do not interact with singlet oxygen. The photoelectrochemical behavior of C₆₀ films has also been reported recently.⁹ The photochemical reduction of these clusters has not therefore been achieved.¹⁷

ZnO colloidal suspensions were prepared by the method of Spanhel and Anderson¹⁰ in which a zinc complex was hydrolyzed with stoichiometric addition of LiOH in ethanol. The pH of the colloidal ZnO suspension was around 8, which is close to the point of zero charge. The size of these particles as measured from the onset of absorption¹¹ was 20-25 Å in diameter. Samples of C₆₀ and C₇₀ were the generous gift of Dr. Ying Wang of Du Pont Co. The separation of C₆₀ and C₇₀ was carried out chromatographically on an alumina column with hexane-toluene (95:5) as an eluant. The absorption spectra of these samples matched well with the spectra reported in the literature.¹² Laser flash photolysis experiments were performed with 308-nm laser pulses (pulse width 10 ns, ~10 mJ/pulse) from a Lambda Physik excimer laser system. All the experiments were performed at 296 K.

The transient absorption spectra recorded following the 308-nm laser pulse excitation of ZnO colloids and C₆₀ (or C₇₀) clusters in 50/50 (v/v %) benzene-ethanol are shown in Figure 1, A and B. Although the ground-state absorption at 308 nm is dominated

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