A Bis(carbene) Adduct of Iodine(1+)

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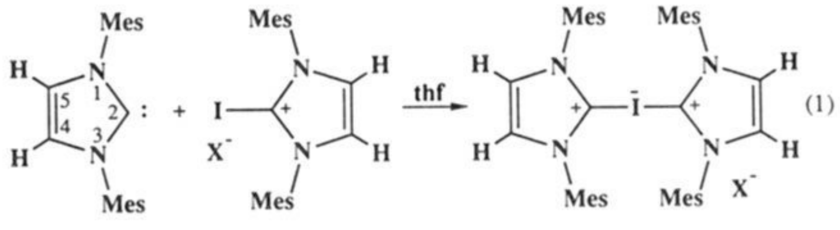
Carbene **1**[1] reacts with 2-iodo-1,3-dimesitylimidazolium salts (**2a** or **2b**) to form the bis(carbene)–iodine(1+) complexes (**3a** or **3b**[2]). The bis(carbene)–iodine adducts **3a** and **3b** are colorless, high melting (255–258 °C and 218–221 °C respectively) solids, consistent with their ionic structures. The FAB-MS of **3b** shows a base peak at *m/z* 735 corresponding to the bis(carbene)–I$^+$ ion.



(1)

1 Mes ≡ 1,3,5-mesityl

2a X = I
2b X = Ph$_4$B

3a X = I
3b X = Ph$_4$B

Iodanides **3a** and **b** are colorless and stable in acetonitrile solution, from which they crystallize on cooling. The ^{1}H and ^{13}C NMR spectra of the cation in **3a** and **3b** are essentially identical, which suggests that the anions do not play an important role in bonding of the 10-I-2 cation. The resonance for the former carbene carbons in **3b** (δ 155.2) is not quite the average (δ 163.5) resonances for the free carbene (δ 220, **1**) and the 2-iodoimidazolium ion (δ 107, **2b**).

A crystal of **3b** was grown from an acetonitrile solution by cooling. The X-ray crystal structure of **3** is depicted in Figure 1. The central C–I–C unit is almost linear (177.5°), with a small difference between the two C–I distances (228.6 and 236.3 pm). The ring internal angles (N–C–N) at the former carbene centers are 106.2° and 105.3°, which reflects a geometry that is somewhat relaxed from the value of 101.4° found for the free carbene **1**. The four C–N bonds exhibit an average distance of 134.5 pm that is smaller than the same distances in **1**($\bar{r}_{C2N1(3)}$ = 136.8 pm).

It is instructive to compare the solid-state structure of **3b** with those of other 10–I–2 iodanides. The reverse-polarized iodine ylide **4** shows a near linear geometry at iodine (178.9°) similar to that in **3b**, but the two C–I distances are different (215.9 (imidazole) and 275.4 (phenyl) pm) as a result of the different substituents on carbon.[4] The geometry at iodine in the symmetric anion **5** also shows an essentially linear C–I–C angle of 175.2°.[5] However, in **5** the two C–I distances are again more nearly equal (233.1 and 240.3 pm). It is interesting that the average C–I distance (232.4 pm) in **3b** is slightly shorter than it is in **5** (236.7 pm), even though the steric repulsion between the two substituents on iodine could be much larger in **3b**. The average C–I distance in **4** (240.7 pm) is the largest of the three structures (**3b**, **4**, and **5**), but it is still remarkably close to the others, particularly when the bulky adamantyl substituents on nitrogens are considered. The similarity in these average C–I distances suggests a rather wide (flat) potential energy surface for the C–I ← C interaction.

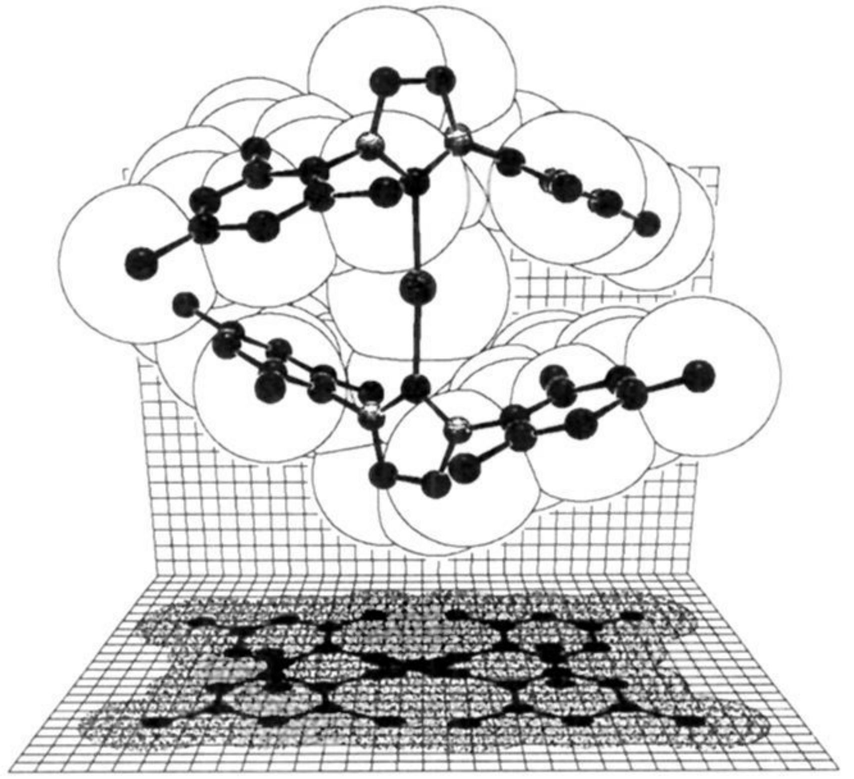
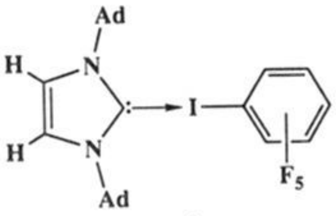
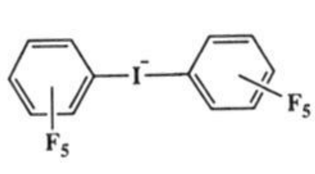


Figure 1. Space-filling KANVAS[3] drawing of the X-ray structure of bis(carbene) iodine complex **3b**.



4
Ad ≡ 1-adamantyl



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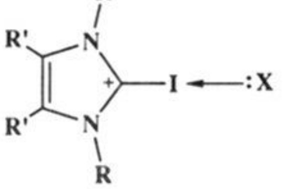
The 2-iodoimidazolium salts **2** and **6** can also serve as useful comparisons. As we have previously reported, these salts are available from the direct reaction of an imidazol-2-ylidene with I$_2$.[4] The salt **6a** shows a weak interaction in the solid state between the iodine in the 2-position of the imidazole ring and the triiodide counterion. The C–I distance in **6a** is 213.1 pm, with an I–I contact distance of 331.0 pm between the terminal iodine of the triiodide anion and the 2-iodoimidazolium cation (θ_{C-I-I} = 173.1°).



6a R = 1-adamantyl
R' = H
X = I$_3^-$

6b R = CH$_2$CH$_3$
R' = CH$_3$
X = I$^-$

The ring internal angle (N–C–N) at the former carbene center in **6a** (109.5°) is relaxed and typical of an imidazolium ion. The

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(1) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(2) Imidazolium tetraphenylborate **2b** (170 mg, 0.2 mmol) in 10 mL of thf was treated with a solution of 70 mg (0.2 mmol) of **1** in 10 mL of thf. After 14 h, the clear solution was evaporated to dryness, and the resulting powder was suspended in toluene, filtered, and washed with toluene and pentane. The residue was recrystallized from acetonitrile to yield 165 mg (69%) of pure **3b**: mp 218–221 °C dec; ^{1}H NMR (CD$_3$CN) δ 1.77 (s, 2,6-C*H*$_3$, 24 H), 2.43 (s, 4-C*H*$_3$, 12 H), 6.84 (t, BPh$_4$ 4-C*H*, 4 H), 6.96 (s, Ar*H*, 8 H), 7.00 (t, BPh$_4$ 2,6-C*H*, 8 H), 7.22 (s, NC*H*, 4 H), 7.27 (m, BPh$_4$ 3,5-C*H*, 8 H); ^{13}C NMR (CD$_3$CN) δ 17.60 (s, 2,6-*C*H$_3$), 21.29 (s, 4-*C*H$_3$), 122.73 (m, $^4J_{^{11}B^{13}C}$ ≈ 0.5 Hz, BPh$_4$ *C*-4), 123.71 (s, N*C*H), 126.56 (m, $^3J_{^{11}B^{13}C}$ ≈ 2.7 Hz, BPh$_4$ *C*-3,5), 129.92 (s, Mes *C*-3,5), 134.81 (s, Mes *C*-4), 135.61 (s, Mes *C*-2,6), 136.72 (m, $^2J_{^{11}B^{13}C}$ ≈ 1.4 Hz, BPh$_4$ *C*-2,6), 140.67 (s, Mes *C*-1), 155.20 (s, *C*-I), 164.78 (q + sext, $^1J_{^{11}B^{13}C}$ ≈ 49.4 Hz, $^1J_{^{10}B^{13}C}$ ≈ 17.2 Hz, BPh$_4$ *C*-1); MS (FAB) m/z 735 ((**1**)$_2$I$^+$, 100%). Anal. Calcd for $C_{66}H_{68}BIN_4$: C, 75.14; H, 6.50; N, 5.31. Found: C, 75.26; H, 6.69; N, 5.53.

(3) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours and 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.

(4) Arduengo, A. J., III; Kline, M.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1991**, *113*, 9704.

(5) Farnham, W. B.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2449.

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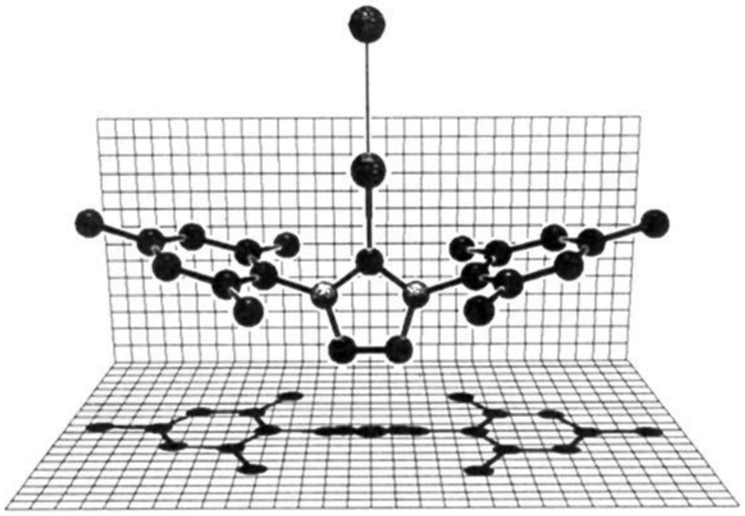


Figure 2. KANVAS[3] drawing of **2a**.

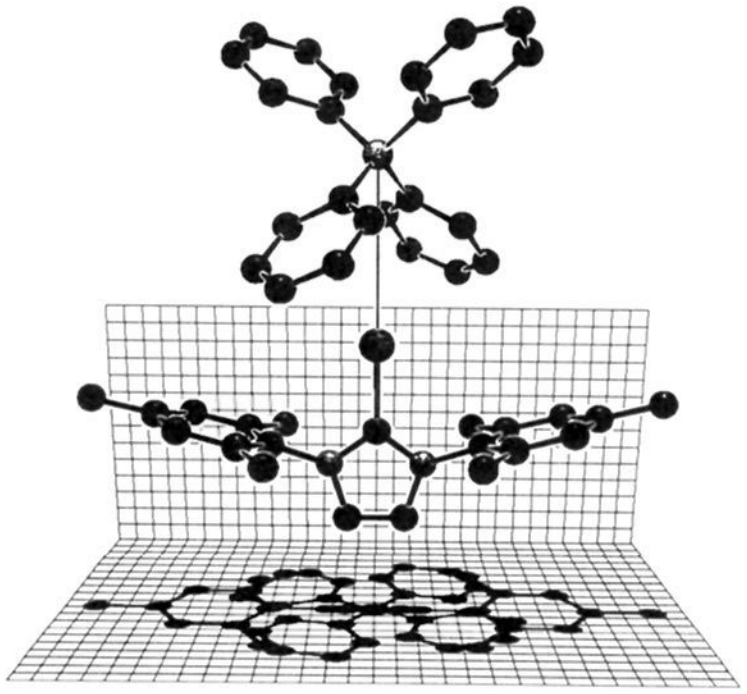


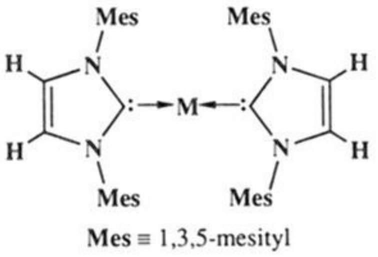
Figure 3. KANVAS[3] drawing of **2b**.

salt **2a** shows a similar arrangement ($\bar{r}_{C-I} = 211.3$ pm, $\bar{r}_{I-I} = 324.9$ pm, $\bar{\theta}_{N-C-N} = 107.0°$, and $\bar{\theta}_{C-I-I} = 179.2°$). This geometric arrangement appears to be general since these results recently have been duplicated for the salt **6b**.[6] The structure of **2a** is illustrated in Figure 2 and is typical of these 2-iodoimidazolium iodides.

If the iodide in **2a** is replaced by tetraphenylborate (**2b**), then there is no chance for the anion to interact covalently with the 2-iodoimidazolium cation. The structure of **2b** is thus a good reference point from which to judge the various C–I interactions described above. The C–I distance in **2b** is 204.2(4) pm, and the ring internal angle at C2 is 107.7(3)°. In the solid-state structure, the C–I bond of the cation in **2b** resides along a crystallographic 2-fold axis. The boron of the anion lies along this same axis 442 pm away from the iodine. This arrangement is illustrated in Figure 3. On the basis of this structure, there are far weaker C–I←I interactions in **2a**, **6a**, and **6b** compared to the C–I–C interaction in **3**.

In solution, the iodide anion of **3a** does not appear to compete with the carbene for complexation with the 2-iodoimidazolium cation. This observation is contrary to the report of Kuhn, which claims that iodine is not exchanged between cations like **2** and **6** and the corresponding free carbenes.[6] Exchanges of this sort would be expected on the basis of an analogy to lithium–halogen exchange reactions widely reported for aryl iodides.[5,7] The near-symmetric structures for **3b** and **5** suggest that such symmetrical structures can indeed be intermediates (with proper substitution) rather than just transition-state structures. If an excess of carbene **1** is added to a thf-d_8 solution of **3b**, separate resonances are observed for the carbene and **3b**, suggesting that exchange with the symmetric structure (**3b**) is slow on the NMR time scale. We have observed similar complexes and exchanges between other imidazol-2-ylidenes and the lighter halogens. These systems are under further study and will be reported elsewhere. We have found that the tellurone that is isoelectronic with the cation in **3** can exchange the tellurium with imidazol-2-ylidenes in a similar fashion.

Finally, we should mention that we have also recently synthesized homoleptic bis(carbene) adducts of transition metals (**7**)[8] which are structurally related to iodine complex **3**. These



Mes ≡ 1,3,5-mesityl

7a M = Cu$^+$ **7c** M = Ni(0)
7b M = Ag$^+$ **7d** M = Pt(0)

transition-metal adducts show similar near-linear geometries at the central atom but have very much shorter distances to the carbene centers ($\bar{r}_{C-Ni} = 182.9$, $\bar{r}_{C-Pt} = 195.1$, and $\bar{r}_{C-Ag} = 207.3$ pm). There is also a recent review that covers other related polycoordinated iodine compounds.[9]

Acknowledgment. The authors are indebted to F. Davidson for his work on the NMR spectroscopy of **2** and **3**. The excellent technical assistance of W. Marshall made the crystal structures possible.

Supplementary Material Available: Description of the preparation, NMR spectra, and elemental analyses of **2a**, **2b**, and **3a**; complete description of the X-ray crystallographic determination on **2a**, **2b**, and **3b**, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(7) (a) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414. (b) Beak, P.; Allen, D. J.; Lee, W. K. *J. Am. Chem. Soc.* **1990**, *112*, 1629. (c) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444.

(8) (a) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405. (b) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.*, in press.

(9) Varvoglis, A. *The Chemistry of Polycoordinated Iodine*; VCH: New York, 1992.