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Effects of Complexation with 18-Crown-6 on the Hypernucleofugality of Phenyl-λ^3-iodanyl Groups. Synthesis of Vinyl-λ^3-iodane·18-Crown-6 Complex

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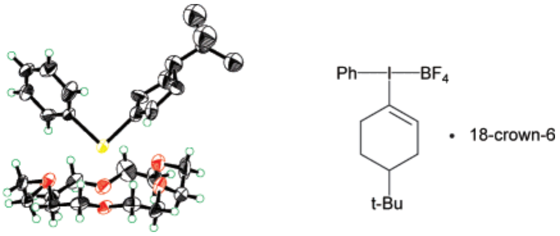
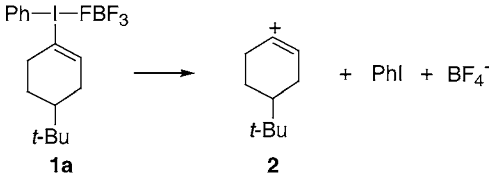
ABSTRACT



4-*tert*-Butyl-1-cyclohexenyl(phenyl)(tetrafluoroborato)-λ^3-iodane forms a discrete supramolecular complex by the reaction with 18-crown-6. Solvolysis of the cyclohexenyl-λ^3-iodane in the presence of 18-crown-6 indicates that the complexation with 18-crown-6 tends to decrease the leaving group ability of hypervalent phenyl-λ^3-iodanyl groups.

Solvolysis of 4-*tert*-butyl-1-cyclohexenyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**1a**) proceeds at a reasonable rate in aqueous alcoholic solution even at room temperature and generates a reactive 1-cyclohexenyl cation **2** with reductive elimination of iodobenzene (Scheme 1).[1] The phenyl-λ^3-iodanyl group was found to be an excellent nucleofuge with a leaving group ability of 10^6 times greater than the superleaving group triflate (TfO). The origin of this high nucleofugality of the phenyl-λ^3-iodanyl group is attributed to the involvement of an energetically favorable reduction of the hypervalent iodine(III) to the normal valency with octet structure during the leaving process.[2] This process is also associated with an increase in entropy.[1] The high nucleofugality of phenyl-λ^3-iodanyl groups makes possible the unusual vinylic S_N2 displacement of β-alkylvinyl(phenyl)-λ^3-iodanes by the reaction with a wide range of nucleophiles.[3]

Scheme 1



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Recently, we found that 18-crown-6 (18C6) forms discrete complexes with aryl(tetrafluoroborato)-λ^3-iodanes, in which the iodine(III) contacts with the three adjacent oxygen atoms of 18C6 through two hypervalent secondary bonding and a weak interaction.[4] The complexation with 18C6 increases the stability of λ^3-iodanes. For instance, the hydroxy(phenyl)-λ^3-iodane PhI(OH)BF_4 is thermally labile and decomposes at room temperature within a few minutes; however, no decomposition of the crown ether complex PhI(OH)BF_4·18C6 was detected when it was left standing under ambient conditions over 10 days.[5] We report herein that 1-cyclohexenyl(aryl)(tetrafluoroborato)-λ^3-iodane **1** forms a supramolecular complex with 18C6. The complexation with 18C6 slows down the rates of solvolysis of the 1-cyclohexenyl-λ^3-iodane **1** in chloroform and methanol and decreases the leaving group ability of phenyl-λ^3-iodanyl groups.

Slow evaporation of a dichloromethane−hexane−ethyl acetate (1:2:4) solution of a 1:2 mixture of 4-*tert*-butyl-1-cyclohexenyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**1a**) and 18C6 in a refrigerator at 4 °C afforded an 82% yield of single crystals of a 1:1 complex **3**[6] suitable for X-ray analysis.

The solid-state structure of **3** (Figure 1) illustrates that the cyclohexenyl(phenyl)-λ^3-iodanyl group protrudes above one face of 18C6.[7] The iodine(III) contacts with three adjacent oxygen atoms (O1, O2, and O6) of 18C6, and the complex adopts a distorted pentagonal planar geometry about the iodine, with root-mean-square (rms) deviation (0.3560(2) Å for I1, C1, C7, O1, O2, and O6) from their least-squares plane and the sum of the iodine-centered bond angles ($\Sigma°$I = 357.6°). The I1···O2 and I1···O6 distances (3.023(4) and 3.175(5) Å) are shorter than the van der Waal's distance (3.50 Å),[8] and both C7−I1···O2 and C1−I1···O6 triads are nearly linear. Therefore, these close contacts are indicative of hypervalent secondary interactions, in which each oxygen atom donates an electron pair into an I−C σ^* orbital.[4,5]

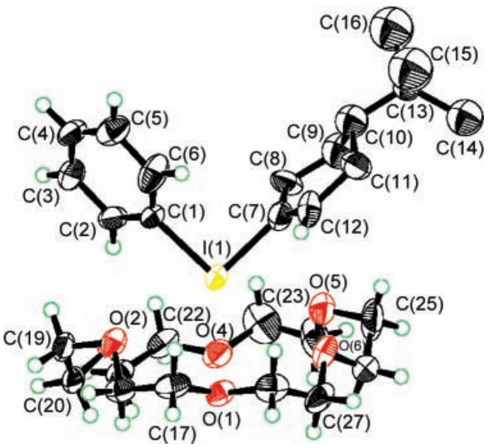

Figure 1. Crystal structure of 1:1 complex **3** (with $^1/_2$ hexane). Hexane and BF_4 were omitted for clarity. Selected interatomic distances (Å) and angles (°): I1−C1 2.091(7); I1−C7 2.092(7); I1···O1 3.215(4); I1···O2 3.023(4); I1···O6 3.175(5); C1−I1−C7 92.5(2); C1−I1···O6 167.4(2); C7−I1···O2 161.0(2).

In solution, the complex formation between **1a** and 18C6 is clearly evident in ^{1}H NMR experiments: A methylene singlet of 18C6 in CD_2Cl_2 (0.01 M) exhibits an upfield shift of 0.03 ppm by the addition of 1 equiv of **1a**. The ^{13}C resonance of 18C6 at δ 70.7 ppm in $CDCl_3$ is also shifted to higher field (δ 70.3 ppm) by the addition of **1a**. The 1:1 stoichiometry for the complexation in CD_2Cl_2 solution was determined from the Job plots by the ^{1}H NMR experiments.[9] The complexation-induced shifts of a methylene singlet of 18C6 were small but distinct and reproducible. A plot of complex concentration versus [**1a**]/([**1a**] + [18C6]) shows a maximum at near 0.5 (Figure 2).

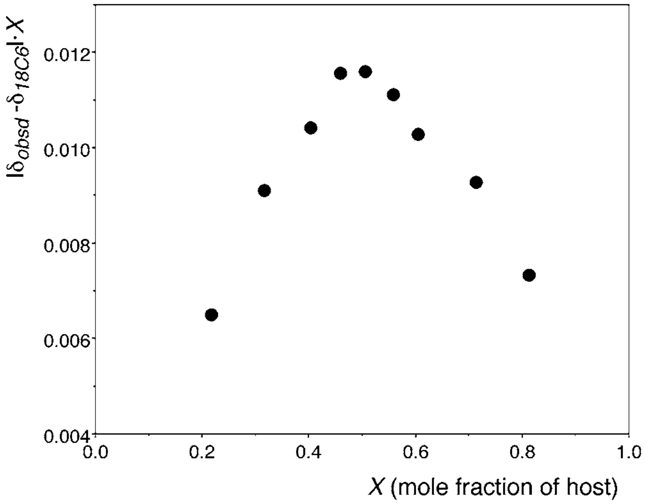

Figure 2. Job plot for complexation between the λ^3-iodane **1a** and 18C6 in CD_2Cl_2 at 23 °C. Concentration: [**1a**] + [18C6] = 0.01 M.

The binding constants were measured by ^{1}H NMR titrations of CD_2Cl_2 solutions of 18C6 with **1a** at 24 °C. The

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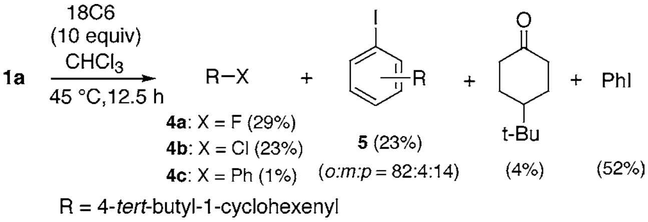
[6] Selected physical data for complex **3**: colorless plates; mp 75−77 °C.; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J = 7.7 Hz, 2H), 7.72 (t, J = 7.3 Hz, 1H), 7.56 (dd, J = 7.7, 7.3 Hz, 2H), 7.06−6.98 (m, 1H), 3.68 (s, 24H), 2.76−2.59 (m, 2H), 2.57−2.42 (m, 1H), 2.37−2.25 (m, 1H), 1.99−1.89 (m, 1H), 1.54−1.35 (m, 2H), 0.86 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.6, 135.9, 132.7, 132.3, 115.8, 112.1, 70.3, 42.0, 35.3, 32.3, 31.8, 27.2, 27.0; IR (KBr) 3560, 2880, 1627, 1475, 1353, 1150−1100 cm^{-1}. Anal. Calcd for $C_{28}H_{46}BF_4IO_6$: C, 48.57; H, 6.70. Found: C, 48.49; H, 6.79.

[7] Crystallographic data for complex **3** involving $^1/_2$ hexane: $C_{31}H_{53}BF_4IO_6$, M = 735.46, T = 93 K, triclinic, space group P-1 (no. 2), a = 9.757(9) Å, b = 10.998(8) Å, c = 16.41(2) Å, α = 98.73(8)°, β = 91.47(7)°, γ = 101.80(7)°, V = 1700(2) Å^3, Z = 2, D_c = 1.436 g cm^{-3}, μ (Mo Kα) = 10.03 cm^{-1}. 19 486 reflections were collected; 9743 were unique. R_1 = 0.083 [$I > 2\sigma(I)$], wR_2 = 0.220 [$I > 3\sigma(I)$]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-250402. Data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: +44 (0) 1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk]

resulting binding curve gave an excellent fit with a 1:1 binding model and was analyzed by the nonlinear least-squares method to give a binding constant (K_a) value of 2.84 × 10^2 M^{-1} in CD_2Cl_2 (correlation coefficient 0.97).

Recently, Okuyama and co-workers reported that the thermal decomposition of 1-cyclohexenyl-λ^3-iodane **1a** in chloroform generates 1-cyclohexenyl cation **2** in a manner similar to the solvolysis in an aqueous alcoholic solution.[10] Thermolysis of **1a** in the presence of a large excess of 18C6 (10 equiv) in chloroform at 45 °C resulted in a comparable product profile shown in Scheme 2. Nucleophilic attack of tetrafluoroborate ion,[10] chloroform,[11] and iodobenzene to the initially generated 1-cyclohexenyl cation **2** produces vinyl fluoride **4a** (29%), vinyl chloride **4b** (23%), and a mixture of vinylated iodobenzenes **5** (23%), respectively. Predominant formation of the ortho isomer of **5** indicates the intervention of an intimate ion−molecule pair of **2** and iodobenzene during the thermal decomposition.[1]

Scheme 2



Rates for thermal decomposition of 1-cyclohexenyl-λ^3-iodane **1a** (1 × 10^{-4} M) in the absence and presence of 18C6 at varying concentrations were measured spectrophotometrically in chloroform and methanol. The pseudo-first-order rate constants k_{obsd} obtained were plotted against the ratios of [18C6]/[**1a**] (Figure 3). In methanol at 50 °C (Figure 3b), an increasing concentration of 18C6 results in a gradual decrease in the rates of decomposition of **1a**, although the extent of the decrease is very small. Interestingly, however, both acceleration and retardation were observed in the decomposition of **1a** in chloroform at 45 °C, depending upon the concentrations of added 18C6. At low concentrations of 18C6, a slight increase in the rates of decomposition of **1a** was detected as shown in the inset of Figure 3a; however, increased concentrations of 18C6 decreased the rates. A similar concentration dependence of the rates was also observed in the thermal decomposition of *p*-methylphenyl-(**1b**) and *p*-chlorophenyl(4-*tert*-butyl-1-cyclohexenyl)(tetrafluoroborato)-λ^3-iodane (**1c**) (Table 1): slightly increased rates of decomposition at low concentration (1 × 10^{-4} M) and decreased rates at higher concentration (1 × 10^{-2} M) were again observed.

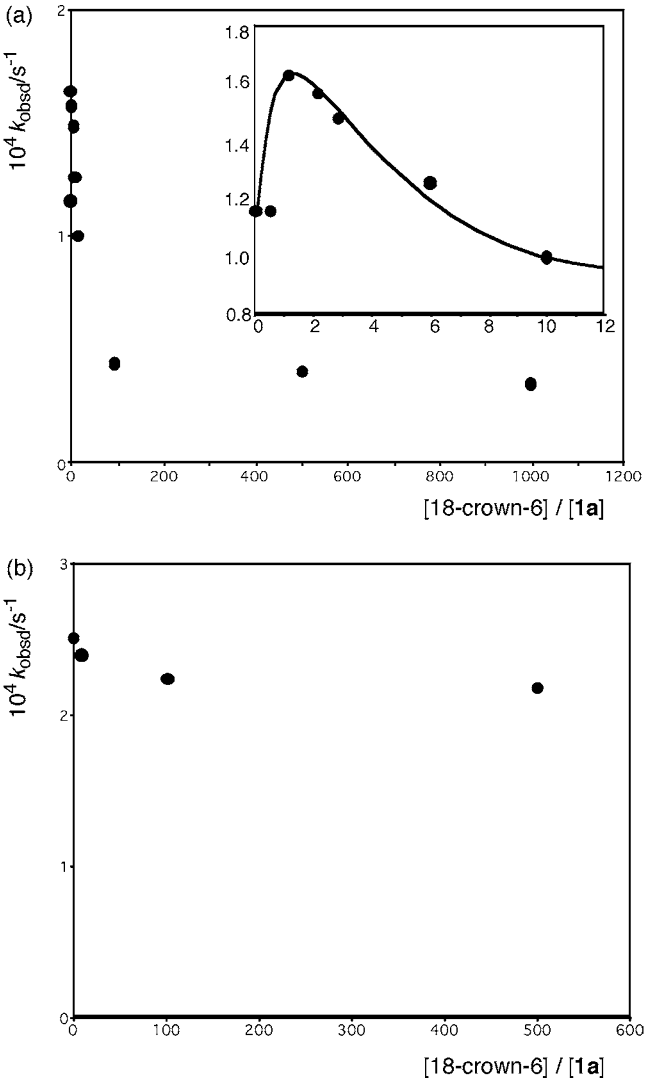


Figure 3. Observed rate constants for thermal decomposition of **1a** (1 × 10^{-4} M) in the presence of 18C6. (a) In $CHCl_3$ at 45 °C. The inset shows details at low concentrations of 18C6. (b) In MeOH at 50 °C.

From the equation shown in Scheme 3, the association constant (K_a) and the rate constant ($k_{complex}$) for decomposition of the 1:1 complex **3** in $CHCl_3$ at 45 °C were estimated by using the four sets of data in Figure 3a, where [18C6]/[**1a**]

Table 1. Observed Rate Constants (10^4 k_{obsd}/s^{-1}) for Thermal Decomposition of **1** in $CHCl_3$ in the Presence of 18C6 at 45 °C[a]

[18C6]/M	**1a**	**1b**	**1c**
	1.15	0.45	4.48
1 × 10^{-4}	1.63	0.50	4.77
1 × 10^{-2}	0.43	0.43	2.35

[a] The initial concentration of **1** was 1 × 10^{-4} M.

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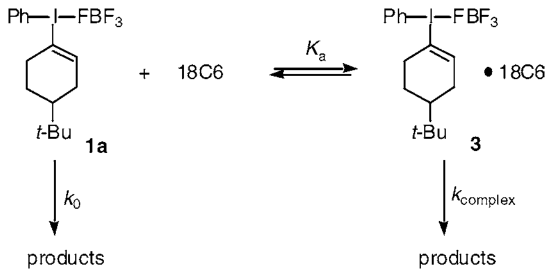
Scheme 3



is greater than 10: K_a = ca. 3.3×10^2 M^{-1} and $k_{complex}$ = ca. 3.1×10^{-5} s^{-1}. Comparison of $k_{complex}$ with k_0 (Table 1) indicates that the complexation with 18C6 decreases the decomposition rate constant of **1a** in $CHCl_3$ solution to about $^1/_4$. Thus, the nucleofugality of the phenyl-λ^3-iodanyl group was considerably decreased by the complexation with 18C6.

The estimated association constant (K_a) in $CHCl_3$ solution is rather small, and therefore, at low concentrations ([18C6]/[**1a**] < 5) of 18C6, the proportion of the complexed λ^3-iodane **3** is quite small and calculated to be less than 15%, which suggests that the effect of complexation with 18C6 on the decomposition rates would be negligible at the low concentrations of 18C6. It seems reasonable to assume that initial increase in the decomposition rates in $CHCl_3$ (Figure 3a) is presumably due to the increased polarity of the medium by the addition of 18C6. In fact, the rate of thermal decomposition of **1a** in alcohol and aqueous solutions is known to depend on the solvent polarity and increase with the increasing solvent ionizing power Y_{OTs}.[1]

In conclusion, 1-cyclohexenyl(aryl)(tetrafluoroborato)-λ^3-iodane forms a supramolecular 1:1 complex with 18C6 in the solid state as well as in solution. The complexation with 18C6 decreases the leaving group ability of phenyl-λ^3-iodanyl groups.

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Supporting Information Available: Typical experimental procedures and spectral data for **4** and **5**; CIF file for X-ray structure of complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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