

Incorporation of an Allene Unit into α -Pinene via β -Elimination

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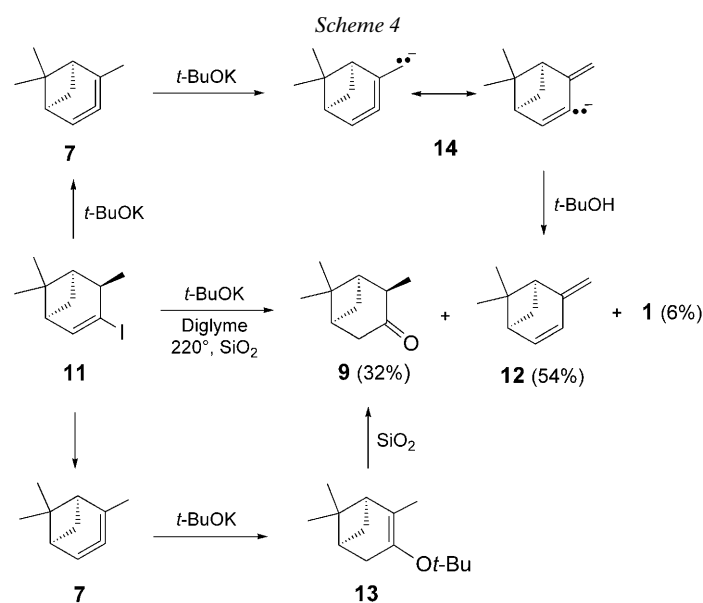
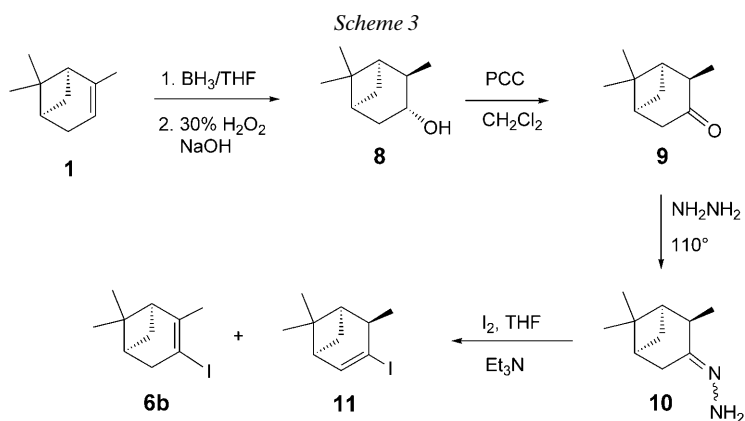
The two double-bond isomers 3-iodo-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (**6b**) and 3-iodo-4,6,6-trimethylbicyclo[3.1.1]hept-2-ene (**11**) were synthesized by reacting 2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (**9**) with hydrazine, followed by treatment with I₂ in the presence of Et₃N. Treatment of **11** with *t*-BuOK as base in diglyme at 220° resulted in the formation of **9** and 6,6-dimethyl-4-methylidenebicyclo[3.1.1]hept-2-ene (**12**). For the formation of **9**, the cyclic allene **7** is proposed as an intermediate. Treatment of the second isomer, **6b**, with *t*-BuOK at 170° gave rise to the diene **12** and the dimerization product **17**. The underlying mechanism of this transformation is discussed. On the basis of density-functional-theory (DFT) calculations on the allene **7** and the alkyne **15**, the formation of the latter as the intermediate was excluded.

Introduction. – The synthesis of cyclic allenes with eight or less skeletal C-atoms, known as highly strained organic compounds, has for the past decades attracted increasing interest [1]. Besides synthetic considerations, theoretical chemists have been keen on investigating these compounds to obtain insight into their structural and unusual physico-chemical properties [2]. Strained cyclic allenes are nonplanar and chiral rather than planar zwitterionic or carbene-like species, even in the case of the highly strained cyclohexa-1,2-diene and cyclohepta-1,2-diene [3].

Among the numerous synthetic approaches [1] to cyclic allenes, the *Doering–Moore–Skattebol* method and the β -elimination method have been most widely studied in the literature. The first one, discovered by *Moore* [4] and co-workers, and by *Skattebol* [5], involves the conversion of 1,1-dihalocyclopropanes [6] to the corresponding cyclic allenes upon treatment with alkyllithium reagents [7][8]. The latter – first attempted by *Favorskii* [9] to prepare cyclopenta-1,2-diene by treatment of vinyl bromide with *t*-BuOK – is the reaction of the corresponding vinyl halides with bases (for recent examples, see [10]).

More recently, we have reported both experimental and theoretical studies related to the *Doering–Moore–Skattebol* reaction to generate a cyclic allene incorporated into α -pinene (**1**) [8]. As shown in *Scheme 1*, four products were isolated, the major being the carbene-insertion product **4**; the others were derived from allene dimerization.

Although the *Doering–Moore–Skattebol* method was successful in obtaining the desired allene, it gave the ring-enlarged product **5** where the allene bonds are located in a seven-membered ring. Hence, incorporation of an allene unit into the α -pinene (**1**) skeleton without ring enlargement would generate the *six-membered* cyclic allene **7** (*Scheme 2*), which would cause considerable deviation from linear geometry. In this



ate **7** gives rise to the enol ether **13**. The hydrolysis of the latter (on silica gel) produces the ketone **9**. Furthermore, deprotonation of **7** by the strong base might also generate the allylic anion **14**, which can take up H^+ to form the conjugated diene **12**.

Recently, *Christl et al.* [14] reacted the allene precursor 3-bromo-1,2-dihydronaphthalene (and derivatives thereof) with *t*-BuOK and obtained a mixture of naphthalene and enol ether as the major products. The formation of the major product was also rationalized by the formation of the desired allene intermediate. Furthermore, we did not have any evidence for an alternative β -elimination, which would lead to the formation of a cyclic alkyne **15**. *Bottini et al.* [15] reported that the change of halide from bromide or iodide to chloride, the use of DMSO in place of Et_2O as solvent, and elevated temperatures all favor allene formation on the cost of alkyne formation. There-

fore, we also run the elimination reaction of **11** in DMSO to see whether the product distribution would be affected or not. However, careful analysis of the reaction mixture did not reveal any remarkable change in product distribution. Actually, the formation of **9** can also be explained by formation of **15**, followed by addition of *t*-BuOH. However, an asymmetric alkyne can be attacked at two different C-atoms. The observation that the ketone **16** was not detected at all thus excludes the formation of **15**.

To further support allene formation, we carried out DFT calculations¹⁾ on the cyclic allene and the alkyne. The cyclic allene **7** is *ca.* 10.6 kcal/mol more stable than the cyclic alkyne **15** (Figure).

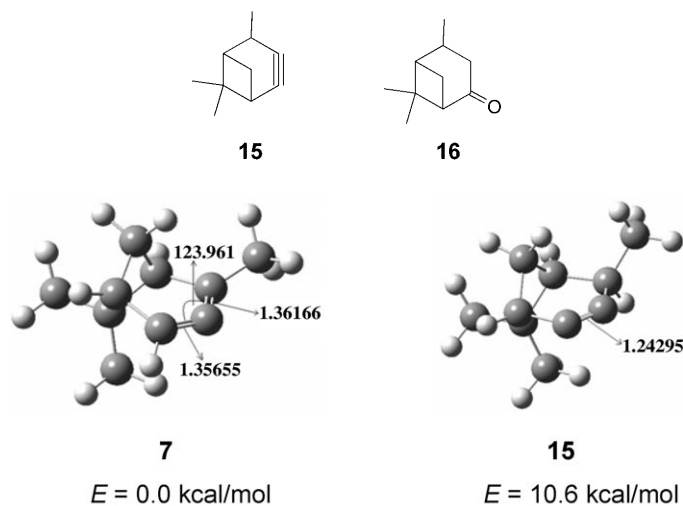
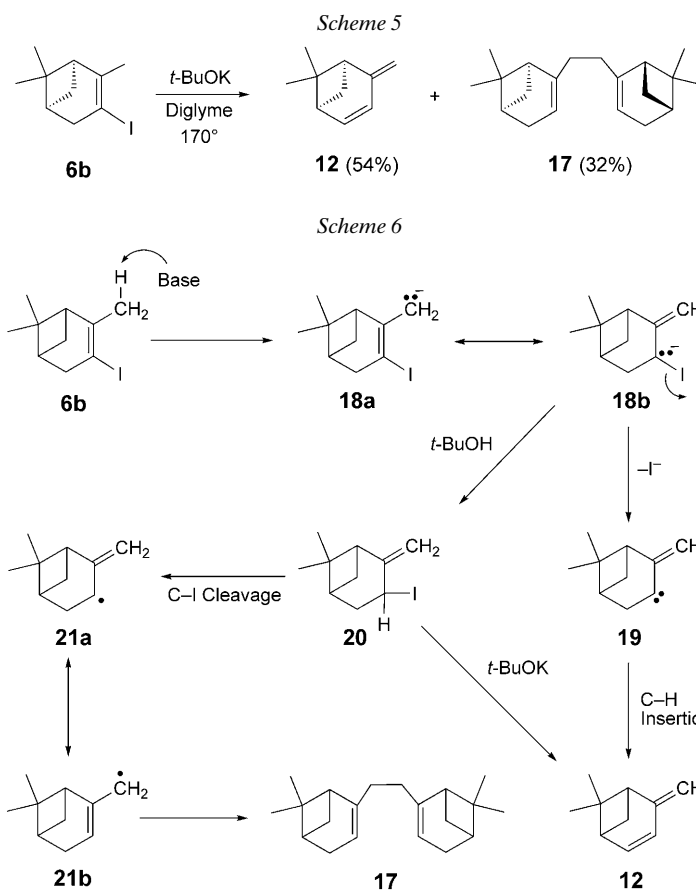


Figure. Optimized structures of the allene **7** and the alkyne **15**. Calculated relative energies (B3LYP/LanL2DZ level) and selected bond distances (in Å) are shown.

Finally, the isomer **6b** was submitted to base-induced HI elimination (Scheme 5). Dehydroiodination occurred at lower temperature (sealed tube, diglyme, 170°), and two compounds, the diene **12** and the dimerization product **17** [16], were formed in 54 and 32% yield, respectively. Meticulous examination of the reaction mixture did not reveal the formation of any other products. Ketone **9**, possibly formed by elimination of **11**, was not detected. Based on this observation, we assume that the allenic intermediate **7** was not formed during the elimination reaction of **6b**. The underlying reaction mechanism is not entirely clear at this stage. However, we tentatively propose the pathway outlined in Scheme 6.

In a first step, the base deprotonates the Me group (instead of the adjacent CH₂ group) under formation of the carbanion **18**. The latter then may displace the I-atom to form the corresponding carbene **19**, which, in turn, undergoes C–H insertion result-

¹⁾ For details, see the *Exper. Part*.

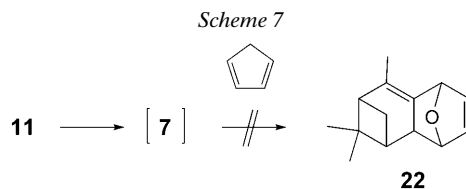


ing in the formation of the conjugated diene **12** as the major product. Furthermore, the allylic anion **18** can take up H^+ to produce the kinetically controlled product **20**.

DFT Calculations (at the RB3LYP/LanL2DZ level of theory) showed that the energy difference between **6b** and **20** is *ca.* 3.4 kcal/mol, the isomer **6b** being thermodynamically more stable. At a reaction temperature of 170°, the C–I bond can easily undergo homolytic cleavage yielding the allylic radical **21**, whose dimerization gives rise to **17**.

To trap the cyclic allene **7** directly with a diene, base-supported elimination of **11** was conducted in the presence of furan in a sealed tube at elevated temperature (*Scheme 7*). However, careful GC/MS studies of the resulting reaction mixture did not reveal any evidence for the formation of the trapping product **22**. The reaction mixture mainly consisted of the dimerization product **17**, beside a complex product mixture.

Conclusion. – We have described a route to the highly strained cyclic allene **7**, which can be generated from 3-iodo-4,6,6-trimethylbicyclo[3.1.1]hept-2-ene (**11**) by β -elimi-



nation of HI with *t*-BuOK as base. Alkyne formation was excluded on the basis of the formed products, and according to theoretical calculations. Interestingly, base-supported elimination of the isomer **6b** follows a different route giving rise to the insertion and dimerization products **12** and **17**, respectively.

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Experimental Part

General. TLC: 0.2-mm silica gel 60 F_{254} aluminum plates (*Merck*). Column chromatography (CC): silica gel (60 mesh; *Merck*). IR Spectra: soln. in 0.1-mm cells or KBr pellets; in cm^{-1} . ^1H - and ^{13}C -NMR: at 400 (^1H) and 100 MHz (^{13}C); apparent multiplicities are given in all cases; δ in ppm, J in Hz. MS: in m/z (rel. %).

(*1R,2R,3R,5S*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-ol (**8**) [11]. To a soln. of **1** (68.0 g, 0.50 mol) and NaBH_4 (19 g, 0.50 mol) in THF (160 ml) was added dropwise precooled $\text{BF}_3 \cdot \text{OEt}_2$ (71.0 g, 0.50 mol) at 0° under N_2 atmosphere. The mixture was kept 3 h at this temp. Then, 3M aq. NaOH soln. (167 ml) and 30% H_2O_2 soln. (250 ml) were added at -10° . After stirring for 2 h, the reaction was complete, and the solvent was evaporated. After addition of H_2O , the mixture was extracted with CH_2Cl_2 , the org. phase was washed with sat. aq. NaHCO_3 soln. and H_2O , and dried (Na_2SO_4). Evaporation of the solvent gave crystalline **8** (71 g, 92%). M.p. $53-55^\circ$. ^1H -NMR (400 MHz, CDCl_3): 4.21 (*dt*, $J=9.2, 4.9, 1\text{ H}$); 2.70–2.63 (*m*, 1 H); 2.55–2.51 (*m*, 1 H); 2.12–2.07 (*m*, 2 H); 1.96 (*dt*, $J=6.3, 1.7, 1\text{ H}$); 1.87 (*ddd*, $J=13.9, 4.5, 2.6, 1\text{ H}$); 1.62 (*br. s*, 1 H); 1.39 (*s*, 3 H); 1.30 (*d*, $J=7.4, 3\text{ H}$); 1.21 (*d*, $J=9.8, 1\text{ H}$); 1.11 (*s*, 3 H). ^{13}C -NMR (100 MHz, CDCl_3): 71.9; 48.2; 48.1; 42.2; 39.5; 38.6; 34.8; 28.1; 24.1; 21.2.

(*1R,2R,5S*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-one (**9**) [12]. A soln. of pyridinium chlorochromate (PCC; 119.8 g, 1.40 mol) in CH_2Cl_2 (800 ml) was added to a soln. of **8** (71.0 g, 0.46 mol) in CH_2Cl_2 (250 ml) at 0° . When the addition was complete, the mixture was stirred at r.t. for 3 h. The solvent was evaporated, and the residue was worked up by extraction with $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$. The org. phase was washed with sat. aq. NaHCO_3 soln. and H_2O , and dried (Na_2SO_4). After solvent removal, the residue was passed over silica gel (70 g), eluting with CH_2Cl_2 , and then further purified by distillation at $55^\circ/5$ Torr to give **9** (63.0 g, 90%). ^1H -NMR (400 MHz, CDCl_3): 2.69–2.64 (*m*, 2 H); 2.55–2.45 (*m*, 3 H); 2.19–2.14 (*m*, 1 H); 2.1 (*dt*, $J=6.4, 1.5, 1\text{ H}$); 1.36 (*s*, 3 H); 1.24 (*d*, $J=7.5, 3\text{ H}$); 0.93 (*s*, 3 H). ^{13}C -NMR (100 MHz, CDCl_3): 214.0, 51.6, 45.4, 45.0, 39.5, 39.3, 34.8, 27.5, 22.3, 17.1.

(*1R,2R,3E,5S*)- and (*1R,2R,3Z,5S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one Hydrazone (**10**). Compound **9** (63.0 g, 0.412 mol) was reacted with neat hydrazine hydrate (21.6 g, 0.45 mol) at 110° for 18 h. The residue was extracted with H_2O and CHCl_3 . The org. phase was washed with sat. aq. NaHCO_3 soln. and H_2O , and dried (K_2CO_3). After removal of the solvent, **10** (64.0 g, 93%) was obtained as a (*Z*)/(*E*) 1 : 3 mixture. IR (KBr): 3465 w , 3400 m , 3209 w , 2974 s , 2939 s , 2865 s , 1635 m , 1469 m , 1365 m . ^1H -NMR (400 MHz, CDCl_3): 4.92 (*br. s*, 2 H); 2.81–2.26 (*m*); 2.48–2.26 (*m*); 2.03 (*m*); 1.82–1.79 (*dt*, $J=5.7, 2.0$); 1.26 (*s*); 1.19 (*d*, $J=6.3$); 1.12 (*d*, $J=7.0$), 0.88 (*s*), 0.83 (*s*). ^{13}C -NMR (100 MHz, CDCl_3): (*E*)-isomer: 153.9; 46.2; 38.8; 38.3; 30.9; 28.6; 27.1; 20.1; 18.6. ^{13}C -NMR (100 MHz, CDCl_3): (*Z*)-isomer: 154.4; 46.4; 43.4; 38.7; 38.3; 33.7; 27.1; 22.2; 20.0. EI-MS (70 eV): 167 (100, $[M+H]^+$), 151 (62), 134 (14), 83 (19). Anal. calc. for $\text{C}_{10}\text{H}_{18}\text{N}_2$: C 72.24, H 10.91; found: C 72.06, H 10.82.

(1*S*,5*S*)-3-Iodo-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (**6b**) and (1*S*,4*R*,5*R*)-3-Iodo-4,6,6-trimethylbicyclo[3.1.1]hept-2-ene (**11**). A soln. of I₂ (97.0 g, 0.38 mol) in anh. THF (160 ml) was added to a mechanically stirred soln. of **10** (64.0 g, 0.383 mol) and Et₃N (40.5 g, 0.4 mol) in THF (300 ml) over a period of 15 min. After the addition, the mixture was stirred for 1 h at r.t. When the reaction was complete, the solvent was evaporated, H₂O (300 ml) was added, and the mixture was extracted with hexane. The org. phase was washed with sat. aq. NaCl soln. and H₂O, dried (Na₂SO₄), and concentrated. The products were distilled under vacuum to afford **6b** and **11** in a ratio of 2 : 3 (total yield: 25 g, 24.7%). The two isomers **6b** and **11** (50 mg) were separated by CC (100 g SiO₂ with 0.4 g AgNO₃; hexane).

Data of 11 (first fraction; anal. pure). IR (KBr): 3037w, 2963s, 1711m, 1382m, 1365m, 957m. ¹H-NMR (400 MHz, CDCl₃): 6.72 (*d*, *J* = 6.8, 1 H); 2.57 (*td*, *J* = 7.0, 2.3, 1 H); 2.27 (*dt*, *A*-part of *AB* system, *J* = 9.1, 5.5, 1 H); 2.1 (*q*-like, *J* = 6.8, 1 H); 1.98 (*dt*, *J* = 6.3, 2.3, 1 H); 1.35 (*d*, *B*-part of *AB*-system, *J* = 9.1, 1 H); 1.29 (*s*, 3 H); 1.11 (*d*, *J* = 7.0, 3 H); 0.95 (*s*, 3 H). ¹³C-NMR (100 MHz, CDCl₃): 146.8; 117.3; 49.4; 46.7; 46; 42.4; 26.3; 25.7; 22; 20.1. EI-MS (70 eV): 263 (100, [*M* + H]⁺), 220 (97), 135 (28), 93 (38), 92 (67). Anal. calc. for C₁₀H₁₅I: C 45.82, H 5.77; found: C 45.68, H 5.62.

Data of 6b (second fraction; 90% pure). IR (KBr): 2861s, 1641w, 1465m, 1381m, 1367m, 898m. ¹H-NMR (400 MHz, CDCl₃): 2.75 (*dt*, *A*-part of *AB* system, *J* = 17.0, 2.1, 1 H); 2.65 (*dt*, *B*-part of *AB* system, *J* = 17.0, 2.3, 1 H); 2.4 (*dt*, *A*-part of *AB* system, *J* = 8.9, 5.5, 1 H); 2.25 (*dd*, *J* = 5.5, 3.8, 1 H); 1.93 (*m*, 1 H); 1.82 (*t*, *J* = 2.1, 3 H); 1.35 (*d*, *B*-part of *AB* system, *J* = 8.9, 1 H); 1.27 (*s*, 3 H); 0.86 (*s*, 3 H). ¹³C-NMR (100 MHz, CDCl₃): 148.4; 90.4; 49.6; 46.4; 45.6; 43.9; 31.6; 27.6; 25.8; 21.4. EI-MS (70 eV): 263 (55, [*M* + H]⁺); 220 (100), 135 (54), 93 (58), 91 (67). Anal. calc. for C₁₀H₁₅I: C 45.82, H 5.77; found: C 45.98, H 5.92.

Reaction of 11 with t-BuOK. A soln. of *t*-BuOK (2.24 g, 0.02 mol) and **11** (2.0 g, 0.007 mol) in diglyme (25 ml) was placed in a glass tube. The tube was sealed and heated to 170° for 8 h. Then, H₂O was added, and the mixture was extracted with Et₂O (3 × 100 ml). The org. phase was washed with sat. aq. NaHCO₃ soln. and H₂O, and dried (Na₂SO₄). After removal of the solvent, the residue was purified by CC (40 g SiO₂; hexane) to afford the diene **12** (0.55 g, 54%), followed by α -pinene (**1**; 0.063 g, 6%). Further elution with CH₂Cl₂ provided the ketone **9** (0.37 g, 32%).

Data of 6,6-Dimethyl-4-methylidenebicyclo[3.1.1]hept-2-ene (12). Colorless oil. ¹H-NMR (400 MHz, CDCl₃): 6.29 (*t*, *J* = 7.5, 1 H); 6.01 (*d*, *J* = 8.5, 1 H); 4.66 (*s*, 1 H); 4.63 (*s*, 1 H); 2.63 (*br. t*, *J* = 5.6, 1 H); 2.55 (*ddd*, *J* = 8.5, 5.4, 3.0, 1 H); 2.28 (*br. q*, *J* = 6.0, 1 H); 1.5 (*d*, *J* = 8.5, 1 H); 1.35 (*s*, 3 H); 0.85 (*s*, 3 H). ¹³C-NMR (100 MHz, CDCl₃): 150.2; 138.3; 126.6; 107.3; 51.9; 43.7; 43; 36.1; 26.3; 22.4.

Reaction of 6b with t-BuOK. A soln. of *t*-BuOK (3.36 g, 0.03 mol) and **6b** (2.5 g, 0.0085 mol) in diglyme (15 ml) was heated in a sealed glass tube at 170° for 8 h. Then, H₂O was added, and the residue was extracted with Et₂O (3 × 50 ml). The org. phase was washed with sat. aq. NaHCO₃ soln. and H₂O, and dried (Na₂SO₄). After removal of the solvent, the residue was purified by CC (25 g SiO₂; pentane). The first fraction gave **12** (0.41 g, 32%), and the second fraction afforded the dimer **17** (1.45 g, 56%).

Data of 2,2'-Ethane-1,2-diylbis(6,6-dimethylbicyclo[3.1.1]hept-2-ene) (17). Colorless oil. ¹H-NMR (400 MHz, CDCl₃): 5.18 (*br. s*, 1 H); 2.35 (*dt*, *A*-part of *AB* system, *J* = 8.5, 5.6, 1 H); 2.25–2.15 (*br. AB* system, *J* = 17.3, 2 H); 2.05 (*m*, 1 H); 1.9 (*t*, *J* = 5.3, 1 H); 1.87 (*s*, 2 H); 1.26 (*s*, 3 H); 1.16 (*d*, *B*-part of *AB* system, *J* = 8.5, 1 H); 0.84 (*s*, 3 H). ¹³C-NMR (100 MHz, CDCl₃): 148.6; 116.1; 46.3; 41.3; 38.4; 35.2; 32; 31.7; 26.8; 21.7. EI-MS (70 eV): 271 (9, [*M* + H]⁺), 228 (20), 202 (6), 171 (10), 135 (50), 93 (100).

Computational Methods. Density-functional-theory (DFT) calculations were carried out with Becke's three-hybrid method [17] and the Lee–Yang–Parr exchange functional (B3LYP) [18], as implemented in the GAUSSIAN 03W software [19]. All calculations were performed with a LANL2DZ basis set, which includes the effective core potential (ECP) proposed by Hay and Wadt plus double basis- ξ for Cl- and I-atoms [20]. Stationary points were characterized as minima or saddle points by analytically evaluating harmonic vibrational frequencies. All energies reported in the discussion were calculated at the B3LYP/LANL2DZ level, and include unscaled zero-point vibrational energies.

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