relative stability to collision of particular ions. For example, the species just noted, 66$^+$ ($C_5H_6^{+}\cdot$) and 65$^+$ ($C_5H_5^+$), have different probabilities of surviving hard collisions, the radical cation showing a twofold greater depletion than the even electron ion as the lab scattering angle was increased from 0 to 0.6°.

The growing importance of collision-induced dissociation (collisional activation) as a method of determining ion structures[8] and in the MIKES (MS/MS) methodology for analysis of complex mixtures[9] underlines the value of the type of data obtained here. It is particularly noteworthy that many species of interest in the above studies do not have stable neutral counterparts (e.g., protonated molecules formed in chemical ionization); so charge exchange cannot be used to obtain breakdown curves. Use of this methodology on instruments with the reverse geometry will allow direct comparisons of all the dissociations of individual mass-selected ions over a range of internal energies.

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X-ray Crystallographic Results on Tantallacyclopentane Complexes Derived from Ethylene and 1,6-Heptadiene: $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ and $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$

Sir:

Although unsaturated metallacyclopentadiene complexes occur commonly as a result of dimerization of acetylenes on transition metal centers, the corresponding *saturated* metallacyclopentane complexes are relatively uncommon. Indeed, there is a distinct paucity of accurate structural data on (saturated) metallacycloalkane complexes in general.

Structural data on some group 8 derivatives—an iridacyclopentane,[1] a platinacyclopentane,[2] and a platinacyclobutane[3] species—have appeared previously.

Schrock and co-workers have reported[4] that $Ta(\eta^5\text{-}C_5H_5)(=CHCMe_3)Cl_2$ reacts with ethylene to give the tantallocyclopentane complex $Ta(\eta^5\text{-}C_5H_5)(C_4H_8)Cl_2$. While this particular species is rather unstable, recent work has led to the obtention of related species of greater stability, including $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ (see eq 1)[5] and $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$ (derived from 1,6-heptadiene[6]—see eq 2).

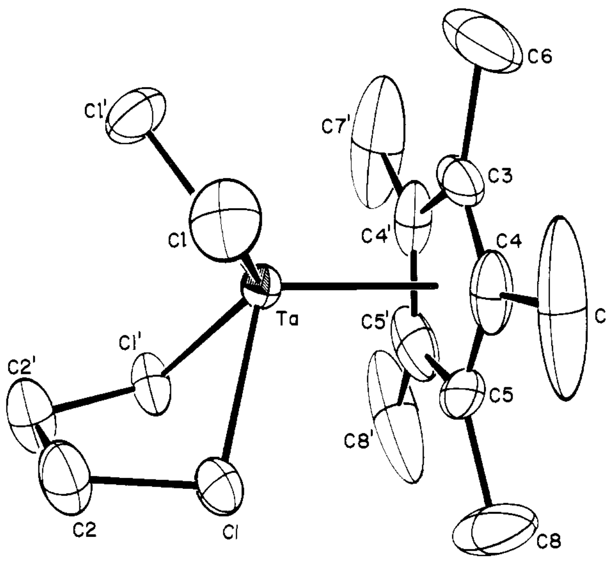

Figure 1. Stereochemistry of the $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ molecule, showing the "opened envelope" configuration of the tantallacyclopentane ring. The molecule has crystallographic C_s symmetry. (Hydrogen atoms were not located.)

$$\begin{tikzcd}
Ta(C_5Me_5)(CH_2CMe_3)C\ell_2 \arrow[r, "\frac{1}{2}ZnEt_2"] & Ta(C_5Me_5)(CH_2CMe_3)(C_2H_5)C\ell_2 \arrow[d, "-CMe_4"] & \\
Ta(C_5Me_5)(C_4H_8)C\ell_2 & Ta(C_5Me_5)(C_2H_4)C\ell_2 \arrow[l, "C_2H_4"'] & \text{(Equation 1)}
\end{tikzcd}$$

$$\begin{tikzcd}
Ta(C_5Me_5)(MeCH{=}CH_2)C\ell_2 \quad + & CH_2{=}CH(CH_2)_3CH{=}CH_2 \arrow[d, "-MeCH{=}CH_2"] & \\
 & Ta(C_5Me_5)(C_7H_{12})C\ell_2 & \text{(Equation 2)}
\end{tikzcd}$$

Single-crystal X-ray diffraction studies on the tantallacyclopentane derivatives $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ and $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$ have now been undertaken; our results are as follows.

The complex $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ crystallizes in the centrosymmetric orthorhombic space group *Pnam* with a = 10.0736 (18) Å, b = 11.2834 (20) Å, c = 13.5239 (24) Å, V = 1537.2 (5) Å^3, ρ(calcd) = 1.91 g cm^{-3} for mol wt 443.19 and Z = 4. Diffraction data were collected via a coupled 2θ (counter)-θ (crystal) scan technique using a Syntex P2$_1$ diffractometer and were corrected for absorption. All nonhydrogen atoms were located and refined, the final discrepancy indices being R_F = 5.7% and R_{wF} = 3.9% for all 1850 independent reflections (*none rejected*) with 4° < 2θ < 55° (Mo Kα radiation). The molecular geometry is shown in Figure 1. The molecule lies on a crystallographic mirror plane which contains atom C(3), C(6) and Ta; there is substantial librational motion of the $\eta^5\text{-}C_5Me_5$ ligand which prevents the determination of the hydrogen atoms' positions. The tantallacyclopentane ring has an unusual "opened envelope" conformation, the angle between the strictly planar C(1)-Ta-C(1′) and C(1)-C(2)-C(2′)-C(1′) systems being 116.26°. [Note that this conformation is in strict contrast to the puckered δ or λ conformation found in other saturated systems (e.g.,

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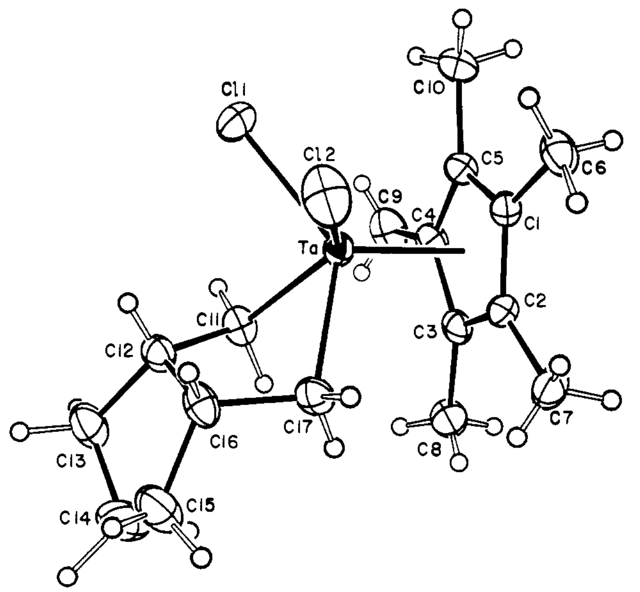

Figure 2. Stereochemistry of the $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$ molecule. Note the "opened envelope" configuration of the TaC_4 ring and the pseudobicyclo[3.3.0]octane system formed by cyclizing the incoming 1,6-heptadiene molecule.

M(en) chelate complexes) and to that found[2] in the PtC_4H_8 ring.] Distances within the five-membered ring follow: Ta-C(1) = Ta-C(1′) = 2.217 (8), C(1)-C(2) = C(1′)-C(2′) = 1.552 (11), and C(2)-C(2′) = 1.553 (12) Å. The C(1)-Ta-C(1′) angle is 72.45 (28)°; other angles are Ta-C(1)-C(2) = Ta-C(1′)-C(2′) = 97.57 (48) and C(1)-C(2)-C(2′) = C(1′)-C(2′)-C(2) = 110.12 (67)°. Distances within other portions of the molecule include tantalum-chlorine = 2.366 (2) and Ta-C(cyclopentadienyl) = 2.371 (10)-2.428 (8) Å.

The high degree of thermal motion in this molecule, taken in conjunction with the crystallographically required C_s symmetry (which could force an unusual conformation on the TaC_4H_8 system) led us to extend our crystallographic investigations to the complex $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$ from eq 2.

This complex crystallizes in the monoclinic space group $P2_1/n$ with a = 9.2051 (13) Å, b = 13.6233 (24) Å, c = 14.1436 (26) Å, β = 96.63 (13)°, V = 1761.8 (5) Å^3, ρ(calcd) = 1.82 g cm^{-3} for mol wt 483.25 and Z = 4. Diffraction data (Mo Kα) were collected as above and the structure was refined to R_F = 4.4% and R_{wF} = 3.4% for 3116 independent reflections with 4° < 2θ < 50° (*none rejected*). All atoms (including all hydrogen atoms) were located; the resulting structure is shown in Figure 2.

The TaC_7H_{12} system defines a bicyclic tantallabicyclo[3.3.0]octane framework, consisting of fused five-membered rings. The bicyclic system has an exo,cis-exo configuration relative to the tantalum atom. Although there is no crystallographically dictated symmetry, the molecule possesses approximate C_s symmetry. The tantallacyclopentane ring again has the "opened envelope" conformation, the angle between the planar C(11)-Ta-C(17) system and the approximately planar (root-mean-square deviation, 0.038 Å) C(11)-C(12)-C(16)-C(17) system being 122.64°.

Distances within the tantallacyclopentane ring are as follows: Ta-C(11) = 2.191 (6), Ta-C(17) = 2.200 (6), C(11)-C(12) = 1.528 (9), C(17)-C(16) = 1.539 (9), C(12)-C(16) = 1.562 (9) Å. Angles are C(17)-Ta-C(11) = 71.47 (25), Ta-C(11)-C(12) = 101.61 (41), C(11)-C(12)-C(16) = 109.02 (53), C(12)-C(16)-C(17) = 108.89 (53), and C(16)-C(17)-Ta = 104.03 (42)°. Other distances within the molecule include Ta-Cl(1) = 2.375 (2) and Ta-Cl(2) = 2.362 (2) Å, and Ta-C(cyclopentadienyl) = 2.378 (5)-2.469 (6) Å.

The two molecules are characterized by the "opened envelope" conformation for the tantallacyclopentane ring and have their two C(α)-C(β) bonds essentially perpendicular to the $\eta^5\text{-}C_5Me_5$ ring. It is worth noting that $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ readily dissociates[5] in solution, yielding the olefin complex $Ta(\eta^5\text{-}C_5Me_5)(C_2H_4)Cl_2$, in which the carbon atoms of the ethylene ligand lie *parallel* to the $\eta^5\text{-}C_5Me_5$ ring.[7]

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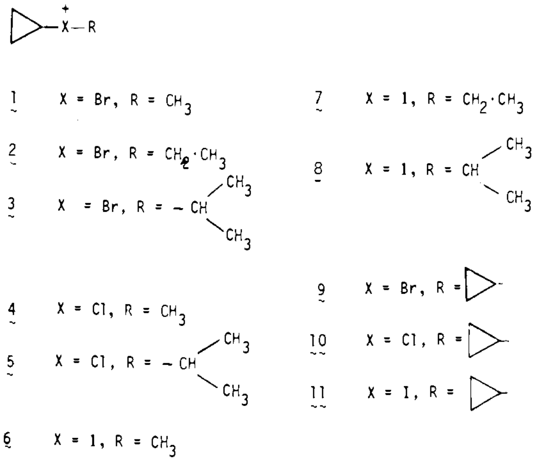
Onium Ions. 21.[1] Cyclopropylhalonium Ions

Sir:

Cyclopropylhalonium ions are one of the major missing class of halonium ions not yet observed despite extensive study on dialkyl-, arylalkyl-, and diarylhalonium ions.[2] Dence and Roberts[3] were the first to attempt the preparation of the cyclopropylphenyliodonium ion from phenyliodo dichloride and cyclopropyllithium. However, they were unable to isolate the corresponding iodonium ion or any product derived from it. We report now the first preparation and NMR spectroscopic observation of a series of cyclopropylhalonium ions.

The series of alkylcyclopropylhalonium ions **1–8** were prepared by reacting cyclopropyl halides with ethyl and methyl



fluoride–antimony pentafluoride complexes or isopropyl hexafluoroantimonate in SO_2 or SO_2ClF solutions at −78 °C.

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