Carbocations Forming from the Reaction of Alkylbenzenes with $TaCl_5$–CH_2Cl_2: Isolation and X-Ray Structures

Euro Solari,[a] Carlo Floriani,*[a] Angiola Chiesi-Villa[b] and Corrado Rizzoli[b]

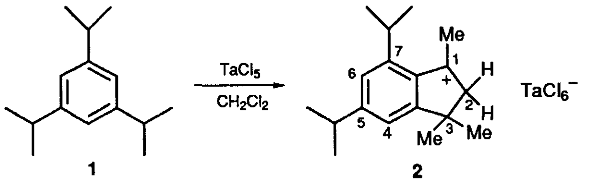
[a] *Section de Chimie, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland*
[b] *Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy*

Tantalum pentachloride–methylene chloride system performs C–C and C–H bond cleavages on alkylbenzenes producing the 5,7-diisopropyl-1,3,3-trimethylindan-1-yl cation from 1,3,5-triisopropylbenzene, and the 9,10-dihydro-9-anthryl cation from both 1,2,4,5-tetramethylbenzene and 1,2,3,5-tetramethylbenzene both having $TaCl_6^-$ as a counteranion, and they have been characterized by X-ray analysis.

The C–H and C–C bond activation has been approached in organometallic chemistry by the use of electron-rich unsaturated species.[1] The organic approach,[2] making use of superacids has been far less common in organometallic chemistry.[3] Very acidic metal halides are able to bind aromatic hydrocarbons and make them electrophilic, the binding of arenes by MCl_4 (M = Ti, Zr, Hf) being a significant example.[4] Within this context we explored the reaction of $TaCl_5$ with alkylbenzenes. To ensure the absence of any kind of impurities, $TaCl_5$ was recrystallized from n-octane under nitrogen several times. Reactions of $TaCl_5$ in benzene with a variety of alkylbenzenes produce labile arene complexes,[5] which are under investigation.[6] The same reaction carried out in CH_2Cl_2 as a solvent gave a totally different result.

By reacting a CH_2Cl_2 solution of 1,3,5-$Pr^i_3C_6H_3$ with $TaCl_5$ at room temperature for 12 hours a copious microcrystalline yellow solid was obtained. Its crystallization from CH_2Cl_2 gave crystals suitable for X-ray analysis.

The yield of compound **2** in Scheme 1 is never higher than 50% based on $TaCl_5$. Formation of **2**, which is a very stable compound, requires an isopropyl group migration from a second molecule of **1**, followed by the cyclization to the indanyl carbocation. Although we do not know the mechanism, we can exclude the halogen abstraction from CH_2Cl_2 which would imply the formation of MeCl, which was not observed. We suppose that, as in the reaction of $TiCl_4$ in the presence of arene,[4a] the autoionization of $TaCl_5$ is responsible



Scheme 1

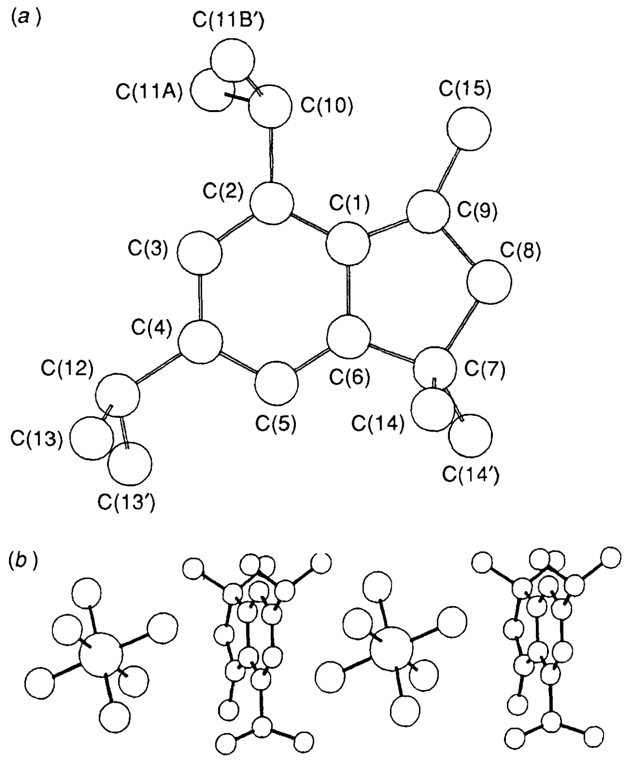
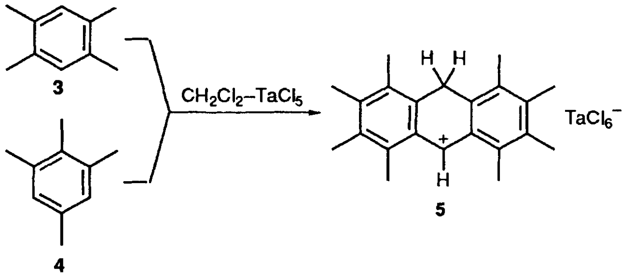


Fig. 1 (*a*) A Pluto drawing for the carbocation in compound **2**. Bond distances (Å) and angles (°): C(1)–C(2), 1.399(19); C(1)–C(6), 1.456(18); C(1)–C(9), 1.381(23); C(2)–C(3), 1.374(19); C(3)–C(4), 1.382(18); C(4)–C(5), 1.403(20); C(5)–C(6), 1.346(21); C(6)–(7), 1.506(20); C(7)–C(8), 1.580(22); C(8)–C(9), 1.498(24); C(9)–C(15), 1.443(28); C(6)–C(1)–C(9), 109.0(10); C(2)–C(1)–C(9), 131.6(11); C(5)–C(6)–(7), 128.0(12); C(1)–C(6)–(7), 111.7(10), C(6)–C(7)–C(8), 101.8(10); C(7)–C(8)–C(9), 106.3(11); C(8)–C(9)–C(1), 111.2(13); C(8)–C(9)–C(15), 112.5(13); C(1)–C(9)–C(15), 136.3(15). Prime indicates a transformation of $1 - x, y, z$. (*b*) A projection of the structure of compound **2** showing the running of the ions along the *a* axis.

for the formation of $TaCl_6^-$. We have been unable so far, however, to identify the other tantalum species. We can rule out any HCl content in the recrystallized $TaCl_5$ from n-octane. The indanyl cation in **2** is shown in Fig. 1(*a*)† and the NMR



Scheme 2

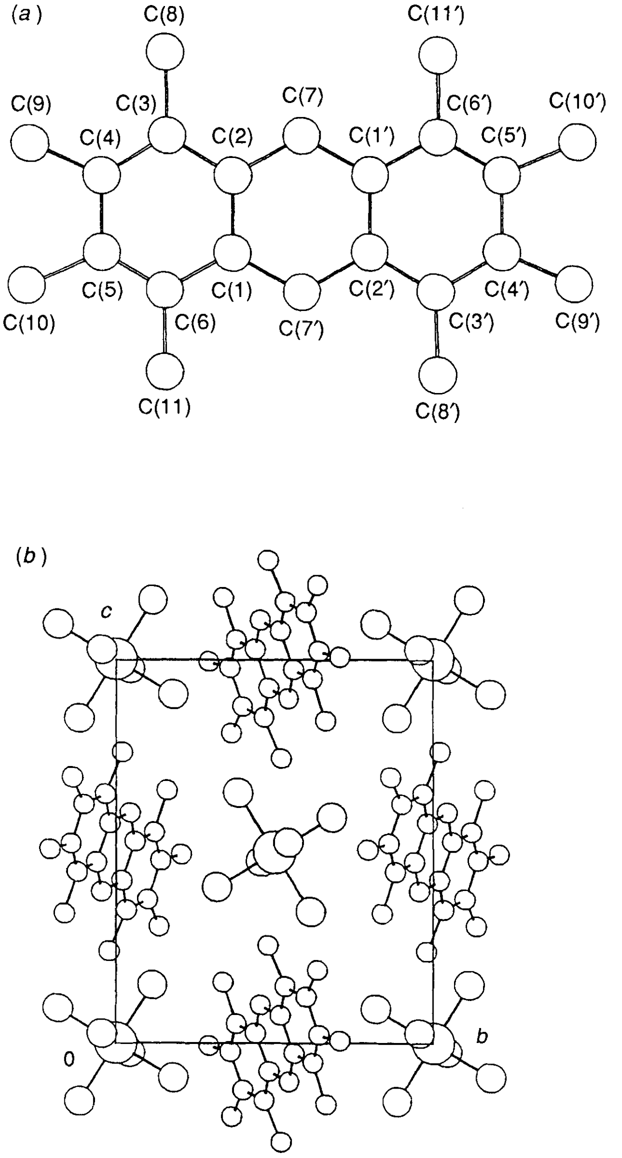


Fig. 2 (*a*) A Pluto drawing for the carbocation in compound **5**. Bond distances (Å) and angles (°): C(1)–C(2), 1.396(20); C(1)–C(6), 1.405(19); C(1)–C(7′), 1.454(20); C(2)–C(3), 1.421(19); C(2)–C(7), 1.451(17); C(3)–C(4), 1.341(19); C(4)–C(5), 1.390(29); C(5)–C(6), 1.411(23); C(6)–C(1)–C(7′), 118.6(13); C(2)–C(1)–C(7′), 120.6(13); C(2)–C(1)–C(6), 120.8(12); C(1)–C(2)–C(7), 119.0(12); C(1)–C(2)–C(3), 119.3(12); C(3)–C(2)–C(7), 121.7(12); C(1′)–C(7)–C(2), 120.4(12). Prime indicates a transformation of $1 - x, 1 - y, -z$. (*b*) A projection of the structure of compound **5** onto the plane perpendicular to the [100] axis.

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† *Crystal data*: Compound **2**, $C_{18}H_{27}Cl_6Ta$, $M = 634.1$, orthorhombic, space group *Cmca*, $a = 10.186(1)$, $b = 15.259(2)$, $c = 30.848(4)$ Å, $U = 4794.6(1.0)$ Å^3, $Z = 8$, $D_c = 1.757$ g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 52.09 cm^{-1}, crystal dimensions 0.15 × 0.21 × 0.48 mm. The structure was solved using SHELX-86 and anisotropically refined by full-matrix least-squares. For 1241 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Philips PW 1100 diffractometer in the range $6° < 2\theta < 46°$ the R value is 0.040 ($R_w = 0.042$). The C(11) methyl carbon was found to be statistically distributed over two positions (A and B) which were isotropically refined along with their site occupation factors resulting in 0.5171 and 0.4829 for A and B, respectively. The hydrogen atoms, except for those associated with C(11), were directly located from a difference map and introduced in calculations as fixed contributors.

Compound **5**, $C_{22}H_{27}Cl_6Ta$, $M = 685.1$, monoclinic, space group $P2_1/c$, $a = 8.558(3)$, $b = 10.722(4)$, $c = 13.304(4)$ Å, $\beta = 103.16(3°)$, $U = 1188.7(7)$ Å^3, $Z = 2$, $D_c = 1.914$ g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 52.60 cm^{-1}, crystal dimensions 0.03 × 0.21 × 0.61 mm. The structure was solved and refined as above. For 1327 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Nonius CAD4 diffractometer in the range $6° < 2\theta < 56°$, corrected for absorption, the R value is 0.050 ($R_w = 0.053$). The hydrogen atoms excepting those associated with one independent C(7) bridging carbon were put in geometrically calculated positions and introduced in refinement as fixed contributors.

For both compounds all calculations were carried out using SHELX-76. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

spectrum‡ does not show changes in solution. The ion packing is shown in Fig. 1(*b*) along the *a* direction, showing some short C(9)···Cl [3.461(3) Å] contacts. The two fused rings in the cation, as required by symmetry, are coplanar [see Fig. 1(*a*)]. The C–C bond trend may suggest other canonical forms, having the positive charge mainly on C(4) and C(2), for the carbocation in agreement with a rather long C(1)–C(6) bond [1.456(18) Å] and short C(5)–C(6) [1.346(1) Å] and C(1)–C(9) [1.382(23) Å] distances. Reaction of **2** with D_2O gave, as expected for a substituted benzylic cation,[2a] the corresponding 1,2-tetradeuterio form of the indene.§

In order to prove the effectiveness of CH_2Cl_2–$TaCl_5$ system in the C–H and C–C bond activation, we reacted under the same conditions 1,2,4,5-tetramethylbenzene and 1,2,3,5-tetramethylbenzene (Scheme 2). Both gave an abundant red-violet crystalline solid **5** as the major product in a yield of 45% based on the $TaCl_5$ used. Compound **5** is very stable and it was recrystallized from CH_2Cl_2. A minor yellow crystalline product (5%) is also formed. It is a different carbocation having $TaCl_6^-$ as a counteranion.[6] Its characterization is still incomplete. The structural characterization by NMR‡ and X-ray analysis† of **5** agrees with the proposed formula and localization of the positive charge [Fig. 2(*a*)]. The asymmetric unit contains two halves of the anion and the cation, each one lying on a centre of symmetry. This requires a statistical distribution of CH_2 and CH. The C(2)–C(7) and C(1)–C(7′) remarkably have single bond character, while the two benzene rings maintain their aromaticity. The whole cation is nearly planar. Packing is different along the three crystallographic axes, in the *b* and *c* directions the packing being determined by the intercalation of anions and cations at contact distances of 3.45–3.70 Å [Fig. 2(*b*)].

Formation of the same carbocation **5** from both durene and isodurene and the presence of eight peripheral carbons for two benzene rings, is the consequence of the very high reactivity of a so far undefined carbocation initially generated by the $TaCl_5$–CH_2Cl_2 system and rearranging to the most stable one.[2c]

Although the mechanism is not yet clear, the use of $TaCl_5$ in CH_2Cl_2 seems to be an extremely efficient system for producing carbocations from alkylarenes selectively, in a good yield, and isolable in a crystalline form.

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‡ ^1H NMR data of **2** (δ, CD_2Cl_2, room temperature): 1.49 (s, 6 H, *gem*-Me_2); 1.39 (d, 6 H, Pr^i); 1.44 (s, 6 H, Pr^i); 3.22 (m, 1 H, Pr^i); 3.76 (m, 1 H, Pr^i); 3.39 (s, 3 H, Me); 3.74 (s, 2 H, CH_2); 7.49 (d, 1 H, arene); 7.55 (d, 1 H, arene, J_{HH} 1.1 Hz). ^1H NMR data of **5** (δ, CD_2Cl_2, room temperature): 2.40 (s, 6 H, Me); 2.66 (s, 6 H, Me); 2.68 (s, 6 H, Me); 2.91 (s, 6 H, Me); 4.48 (s, 2 H, CH_2); 7.56 (s, 1 H, CH).

§ All the compounds have spectroscopic and analytical data in agreement with their assigned structures.

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