FORMATION OF A STABLE ARENONIUM ION IN THE REACTION OF A SUPERACID, $HGeCl_3$, WITH 1,3,5-TRIMETHOXYBENZENE

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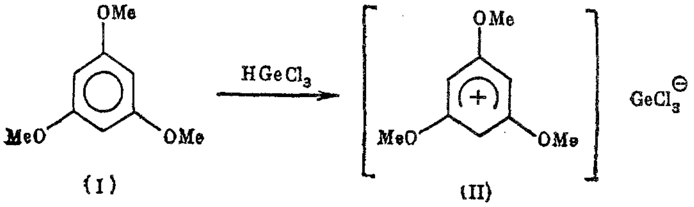
In previous work, we detected the capacity of $HGeCl_3$, which is considered to be a superacid [1, 2], to form a stable iminium salt with the trichlorogermyl anion upon reaction with triphenylamine [3] and a cyclohexenyl carbocation, which is longlived at −50°C, with the same anion in the reaction with 1,3-diethoxybenzene [4].

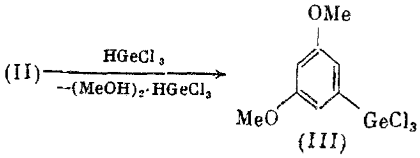
In the present work, we provide the first direct experimental evidence for the formation of σ-complexes in the hydrogermylation of aromatic compounds with trichlorogermane, which we postulated as early as 1965 [5]. The reaction of excess $HGeCl_3$ with 1,3,5-trimethoxybenzene (I) (3:1 mole ratio) in CD_2Cl_2 at 20°C gave the quantitative formation of lightly colored arenonium ion (II), which is stable under these conditions for ~1 h.



PMR spectrum of (II) in CD_2Cl_2 at 20°C (δ, ppm): 3.96 br. s (2H, CH_2), 4.11 br. s (6H, 2MeO), 4.40 br. s (3H, MeO), 6.16 br. s (2H, 2CH). ^{13}C NMR spectrum in CD_2Cl_2 at 20°C (δ, ppm): 38.9 (CH_2), 59.8 (2MeO), 61.7 (MeO), 95.7 (2CH), 183.0 (2C), 192.6 (C). UV spectrum in CH_2Cl_2 at 20°C: λ_{max} 352 nm, ε 7400.

In contrast to the IR spectrum of (I), the low-frequency band at 2840 cm^{-1} in the C—H stretching region becomes the strongest. This band may be attributed to vibrations of the CH_2 group.

Upon maintenance of the reaction for 12 h at 20°C, (II) is completely converted to 1,3-dimethoxy-5-trichlorogermylbenzene (III).



Product (III) and a complex, $(MeOH)_2 \cdot HGeCl_3$, which was separated as an immiscible layer, were fully characterized.

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SOLID-PHASE CONDENSATION OF COORDINATED γ-PICOLINE AND PYRIDINE IN PLATINUM(IV) COMPLEXES

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Heating of salts $(AH)_2[PtCl_6]$ (A = pyridine (Py) and γ-picoline (γ-Pic) in the solid phase gives dehydrohalogenation with coordination of amines at the metal atom known as the Anderson rearrangement [1].

We are the first to establish that the thermolysis of these salts in the solid phase and in melts gives the condensation of the coordinated ligands with the formation of chelate complexes of platinum(II), $[Pt(A\text{-}A)Cl_2]$, where A-A = 2,2'-dipyridyl in the case when A = Py (I) and 4,4'-dimethyl-2,2'-dipyridyl in the case when A = γ-Pic (II). The yield of the dipyridyl complexes exceeds 50% for (II) (230°C) and 30% for (I) (280°C). The composition and structure of the products obtained were established by elemental analysis and PMR spectroscopy. The convergent synthesis of the complexes directly from K_2PtCl_4 and the corresponding dipyridyl was carried out in aqueous solution in order to support the results obtained. The spectral data for products (I) and (II) and the corresponding synthesized complexes proved identical. PMR spectra of the products in $(CD_3)_2SO$ at 100 MHz (δ, ppm): (I): 9.50 d (1H, $^3J_{HH}$ = 6.1, $^3J_{PtH}$ = 40 Hz, H^6), 8.3 m (2H, $H^3 + H^4$), 7.7 m (1H, H^5); (II): 9.17 d (1H, $^3J_{HH}$ = 6.1, $^3J_{PtH}$ = 40 Hz, H^6), 8.39 s (1H, H^3), 7.61 d (1H, $^3J_{HH}$ = 6.1, H^5), 2.42 s (3H, CH_3).

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