FORMATION OF A LONG-LIVED CYCLOHEXENYL CARBOCATION STABILIZED BY THE TRICHLOROGERMYL ANION IN THE REACTION OF HGeCl₃ WITH 1,3-DIETHOXYBENZENE

s.	Ρ.	Kolesnikov, S. L. Povarov,	UDC 547.592.2-128.7:542.91:
A.	I.	Lutsenko, and O. M. Nefedov	547.565.2:546.289'131-128.2

The strong protonating properties of HGeCl₃ have permitted us to characterize this compound as a new superacid in organic chemistry [1, 2]. We have recently discovered the first stable organic salt of this acid, namely, and iminium salt [3]. Stable carbocations have not been observed in the reactions of HGeCl₃ since the GeCl₃ anion, which has medium nucleophilicity, readily recombines with these carbocations. The formation of carbocations was proposed, for example, in the reactions of HGeCl₃ with aromatic compounds, leading finally to tris- and bis-trichlorogermyl derivatives of cyclohexane or cyclohexene [1-4].

In the present work, we were the first to observe the formation of a long-lived cyclohexenyl cation stabilized by the $GeCl_3$ anion. The reaction of 1,3-diethoxybenzene with a large excess of HGeCl₃ at -50°C in CD₂Cl₂ leads to 1,3-diethoxy-5-trichlorogermylcyclohexenyl cation (I), which is stable under these conditions for many hours.



PMR spectrum of (I) at -50° C at CD₂Cl₂ (δ , ppm): 1.61 t (6H, 2Me), 3.29 m (4H, H², H³), 3.39 m (1H, H⁴), 4.77 m (4H, 2CH₂O), 6.37 (1H, H¹). ¹³C NMR spectrum of (I) at -50° C in CD₂Cl₂ (δ , ppm): 14.0 (2Me), 31.8 (2CH²H³), 34.8 (CH⁴), 73.1 (2CH₂O), 99.4 (CH¹), 198.9 (2C).

IR spectrum at -50°C in CH₂Cl₂ (v, cm⁻¹): 1530 (only band between 1450 and 2100). UV spectrum at -50°C: λ_{max} 432 nm.

Upon warming of the reaction mixture up to about 20°C, (I) undergoes the following transformations:



Products (III) and (IV) and the $(C_2H_5OH)_2 \cdot HGeCl_3$ complex, which separates as an immiscible layer, were fully characterized.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2874-2875, December, 1987. Original article submitted July 21, 1987.

LITERATURE CITED

- 1. S. P. Kolesnikov, I. V. Lyudkovskaya, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 1127 (1984).
- V. B. Kazanskii, O. M. Nefedov, A. A. Pankov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 698 (1983).
- S. P. Kolesnikov, S. L. Povarov, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 1453 (1986).
- 4. S. P. Kolesnikov, I. V. Lyudkovskaya, Z. G. Makarova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 492 (1985).

FORMATION OF NITROGEN OXIDES FROM THE NITROGEN LIGAND IN CIS-(Me₂PhP)₄Mo(N₂)₂ BY THE ACTION OF NITRONIUM SALTS

٧.	s.	Lenenko, P. Krencke, M. V	Waren, UDC 542.91:541.49:547.
V.	в.	Shur, and M. E. Vol'pin	1'13:546.175

We found that the reaction of cis- $(Me_2PhP)_4Mo(N_2)_2$ with nitronium salts in CH_2Cl_2 , CHCl₃, and sulfolane gives the rapid liberation of gas consisting of molecular nitrogen, N₂O, and NO. A study of this reaction using labelled cis- $(Me_2PhP)_4Mo({}^{15}N_2)_2$ and unlabelled nitronium tetrafluoroboride ${}^{14}NO_2BF_4$ in absolute sulfolane showed that the gaseous products formed under these conditions contain ${}^{15}N_2$ from the starting complex and ${}^{14}NO$, ${}^{14}N_2O$, and ${}^{14}N_2$ obtained as a result of the reduction of ${}^{14}NO_2BF_4$ due to Mo(O) electrons. Products corresponding to the attack of the nitrogen ligand by the nitronium cation are not found in the gas phase.

We have found, however, that if the reaction of cis- $(Me_2PhP)_4Mo({}^{15}M_2)_2$ with ${}^{14}NO_2BF_4$ is carried out in the presence of small amounts of water, labelled ${}^{15}N={}^{14}N=0$ and ${}^{15}NO$ as well as ${}^{15}N\equiv{}^{14}N$ appear in the gaseous products in addition to ${}^{15}N_2$, ${}^{14}N_2$, ${}^{14}N_2O$, and ${}^{14}NO_2$. The yield of these products depends on the amount of added water, reaching about 5 mole %relative to Mo (${}^{15}N={}^{14}N=O$: ${}^{15}N\equiv{}^{14}N$ ~ 20:2:1) when the [Mo]:NO_2BF_4:H_2O mole ratio is 1:6:24. The replacement of NO_2BF_4 by a nitrating mixture ([Mo]:HNO_3:H_2SO_4 = 1:6:12) enhances the yield of ${}^{15}N={}^{14}N=O$, ${}^{15}NO$, and ${}^{15}N\equiv{}^{14}N$ to 21 mole % (the mole ratio of these products was 17:1:3). The addition of water is not required in this case. Only trace amounts of ${}^{15}N={}^{14}N=O$, ${}^{15}N={}^{14}N$ are formed under the same conditions but in the absence of H_2SO_4.

These results indicate the possibility of involving the nitrogen ligand in cis- $(Me_2PhP)_4Mo(N_2)_2$ in a reaction with a nitronium cation to form nitrogen oxides. The protonation of the nitrogen ligand is apparently the first step in this reaction.

LITERATURE CITED

1. R. L. Richards, Advances in the Chemical Fixation of Nitrogen [Russian translation], Izd. Mir, Moscow (1983), p. 214.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow, and Central Isotope and Radiation Research Institute, Academy of Sciences of the German Democratic Republic, Leipzig. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, p. 2876, December, 1987. Original article submitted July 22, 1987.