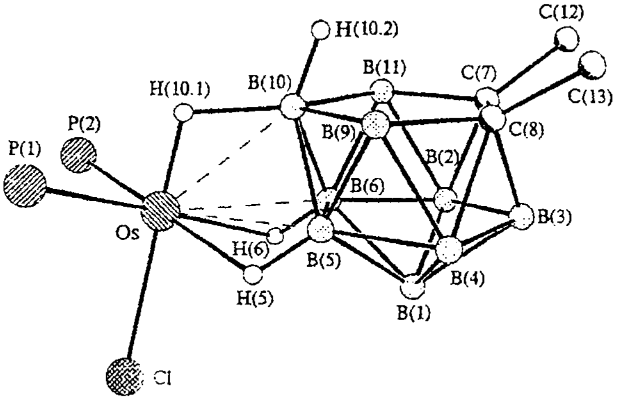

Fig. 1. Molecular structure of complex **4** (phenyl groups of triphenylphosphine ligands and hydrogen atoms, which do not participate in bonding with the osmium atom, are not presented for clarity). Main bond lengths (Å): Os—Cl 2.406(1), Os—P(1) 2.312(1), Os—P(2) 2.309(1), Os—B(5) 2.376(5), Os—B(6) 2.379(5), Os—B(10) 2.275(5), Os—H(5) 1.90(6), Os—H(6) 1.97(6), Os—H(10.1) 1.79(5), B(5)—H(5) 0.98(6), B(6)—H(6) 1.10(6), B(10)—H(10.1) 1.46(6), B(10)—H(10.2) 1.07(5).

BH^{as}...Os), −6.30 (q*, 2 H, BH^{s}...Os), −16.2 (q*, 1 H, BH^{s}...Os). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2), δ: **3**, 0.23 (br.s, 1 P, P^{as}), −0.21 (br.s, 2 P, P^{s}), −2.38 (br.s, 1 P, P^{as}); **4**, 0.42 (br.s, 1 P, P^{as}), −0.21 (br.s, 2 P, P^{s}), −2.8 (br.s, 1 P, P^{as}).

The X-ray diffraction analysis was carried out for symmetrical isomer **4** (Fig. 1) (λMo, 8819 reflections with $I > 2\sigma(I)$, R = 0.045, $Z = 2$; space group $P\bar{1}$, all hydrogen atoms of the carborane ring were located objectively and refined in the isotropic approximation). The XDA confirmed the *exo-nido*-structure of **4** and the fact that it belongs to the rare group of metallacarborane complexes[4,5] in which three B—H fragments of the *nido*-carborane ligand participate in the formation of three two-electron three-centered (agostic) bonds with the metal atom.

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Reaction of levoglucosenone with a stabilized sulfur ylide

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Among sulfur ylides, only dimethylsulfonium methylide $Me_2S^{+-}CH_2$ was studied in the reaction with levoglucosenone **1**. The attack of the reagent occurs only on the carbonyl group of levoglucosenone to form the corresponding epoxide[1] (this ylide reacts similarly with other α,β-unsaturated ketones[2]). It is known that stabilized ylides of the $Me_2S^{+-}CHCOR$ type react with α,β-unsaturated ketones to form cyclopropanes, but not epoxides, *i.e.*, the attack of the reagent is directed on the C=C bond.[3] In the case of levoglucosenone, this could result in the formation of chiral cyclopropanes.

In fact, in this work, we obtained cyclopropane **3** by the reaction of **1** with dimethylsulfonium phenacylide $Me_2S^{+-}CHCOPh$ (generated *in situ* by the addition of Et_3N to sulfonium salt **2**), and the reaction is stereospecific:

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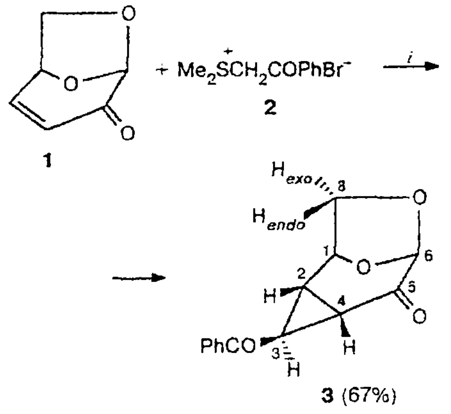

i. Et_3N, EtOH, 40—50 °C, 10 min

It is of special interest that not only the two centers, which were initially present in a molecule of **1** (C(2) and C(4)), but also the center present in salt **2** (C(3)) have the defined absolute configurations in compound **3**. The configurations of the atoms of the cyclopropanic fragment of compound **3** were established from the ^{1}H NMR spectrum. The three-membered cycle is closed from the side opposite to the anhydro bridge ("from the bottom"), as indicated by the value of the coupling constant $J_{1,2}$ = 1.5 Hz.[4] As follows from the values of the coupling constants $J_{2,3} = J_{3,4}$ = 4.1 Hz and $J_{2,4}$ = 7.8 Hz, the H(3) proton is in the *trans*-position to the H(2) and H(4) atoms (as is known, in cyclopropanes the coupling constants of *cis*-protons are greater than those of *trans*-protons).

(1*S*,2*S*,3*S*,4*S*,6*R*)-3-Benzoyl-7,9-dioxatricyclo[4.2.1.0^{2,4}]-nonan-5-one (3), m.p. 119—120 °C (EtOH). ^{1}H NMR (300 MHz, acetone-d_6), δ: 2.27 (ddd, 1 H, H(2), *J* = 7.8, 4.1, 1.5 Hz); 2.36 (br.dd, 1 H, H(4), *J* = 7.8, 4.1 Hz); 3.63 (t, 1 H, H(3), *J* = 4.1 Hz); 3.88 (dd, 1 H, H_{exo}(8), *J* = 7.1, 4.7 Hz); 4.17 (d, 1 H, H_{endo}(8), *J* = 7.1 Hz); 4.98 (s, 1 H, H(6)); 5.11 (br.d, 1 H, H(1), *J* = 4.7 Hz); 7.56 (t, 2 H); 7.67 (t, 1 H); 8.10 (d, 2 H) (all Ph). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 25.41 (C(2)); 27.23, 30.07 (C(3) and C(4)); 69.08 (C(8)), 71.66 (C(1)); 100.13 (C(6)); 129.24, 129.84, 134.65, 137.44 (all C_{Ph}); 195.56, 196.04 (C(5) and COPh).

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(Alk-1-ynyl)fluorocarbenes — a new class of carbenic intermediates: generation from 3-substituted 1,1,3-tribromo-1-fluoropropanes by treatment with bases and cycloaddition to alkenes

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We have previously suggested new methods for generating (alk-1-ynyl)chloro- and (alk-1-ynyl)bromocarbenes from the corresponding 1,1-dihaloalk-2-ynes[1—5] and 3-substituted 1,1,1,3-tetrahalopropanes by the action of bases.[6] Therefore, it was of interest to evaluate the possibility of preparing unknown (alk-1-ynyl)fluorocarbenes by a similar approach, since the introduction of fluorine into polyhalomethanes (alkanes) makes their dehydrohalogenation substantially difficult and, in some cases, completely rules out the generation of fluorocarbenes by this method.[7]

For this purpose, we studied the action of bases on 1,1,3-tribromo-3-organyl-1-fluoropropanes **1**. As it turned out (Scheme 1), the reaction with Bu^tOK in hexane at 20 °C (method *i*) or with KOH in the presence of benzyltriethylammonium chloride in CH_2Cl_2 at 20 °C

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