Letters to the Editor

Direct synthesis of *exo-nido*-osmacarboranes and molecular structure of *exo-nido*-5,6,10-[$Cl(PPh_3)_2Os$]-5,6,10-μ-$(H)_3$-10-H-7,8-$Me_2C_2B_9H_6$

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Among *exo-nido*-metallacarboranes of platinum metals, which play an important role in the chemistry of metallacarboranes and homogeneous catalysis,[1] osmium complexes have not been known to date. Only recently, we have obtained[2] osmacarborane as the by-product, to which the *exo-nido*-structure was assigned on the basis of ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data. In this work, the direct syntheses of *exo-nido*-osmacarborane complexes (*exo-nido*-[$Cl(PPh_3)_2Os$]-7,8-$C_2B_9H_{12}$ (**3**) and *exo-nido*-[$Cl(PPh_3)_2Os$]-7,8-Me_2-7,8-$C_2B_9H_{10}$ (**4**) in 78% and 85% yields, respectively) were performed by the reactions of $OsCl_2(PPh_3)_3$ (**1**) with *nido*-undecaborate salts [*nido*-7,8-R_2-7,8-$C_2B_9H_{10}]^-K^+$ (**2a**, R = H; **2b**, R = Me) in benzene.

The direction of reaction of complex **1** with salts **2a,b** depends substantially on the experimental conditions. Unlike the conditions previously used for the synthesis of *closo*-3,1,2-[$(PPh_3)_2$OsHX-1,2-$R_2C_2B_9H_9$] (**5a—c**, **a**: R = H, X = Cl; **b**: R = X = H; **c**: R = Me, X = H) (refluxing of the reagents in ethanol[2]), the reaction of **1** with **2a,b** in benzene at 22 °C for 3.5 h affords only *exo-nido*-osmacarboranes **3** and **4**, respectively. It is noteworthy that when the time of the reaction of **1** with **2a** is increased to 24 h, a mixture of *exo-nido*- (**3**) and *closo*-isomers (**5a**) in the 3 : 1 ratio is formed, which suggests that the irreversible *exo-nido* → *closo*-rearrangement proceeds under mild conditions. The rearrangement of **3** into **5a** was performed quantitatively on refluxing of isomer **3** in benzene for 0.5 h. The rearrangement of complex **4** into the corresponding *closo*-isomer **5d** (R = Me, X = Cl) under the same conditions does not occur, which agrees well with the data obtained previously for *exo-nido*-ruthenacarborane complexes.[3]

According to the data of ^1H and ^{31}P NMR spectroscopy, the *exo-nido*-complexes **3** and **4** obtained are mixtures of isomers (~1 : 1) with the symmetrical (s) and asymmetrical (as) structures. ^1H NMR (solvent), δ: **3** (CD_2Cl_2): 6.0—6.25 (m, 60 H, $Ph^{s,as}$), 2.34 (s, 1 H, CH^{as} of carborane), 2.27 (s, 2 H, CH^s of carborane), 2.20 (s, 1 H, CH^{as} of carborane), −1.52 (q*, 2 H, $H(10)^{s,as}$), −4.78, −7.72, −15.32 (q*, 3 H, BH^{as}...Os), −5.52 (q*, 2 H, BH^s...Os), −14.64 (q*, 1 H, BH^s...Os); **4** ($CDCl_3$), 7.24—6.93 (m, 60 H, $Ph^{s,as}$), 1.44 (s, 3 H, Me^{as}), 1.40 (s, 3 H, Me^{as}), 1.39 (s, 6 H, Me^s), −1.20 (q*, 2 H, $H(10)^{s,as}$), −5.40, −8.23, −15.70 (q*, 3 H,

* Quadruplet-like signal.

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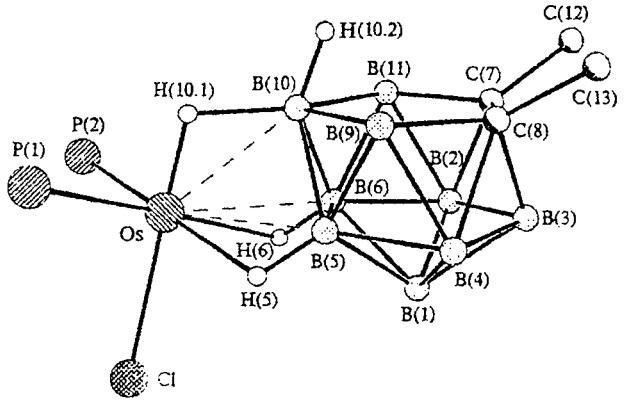

Fig. 1. Molecular structure of complex **4** (phenyl groups of triphenylphosphine ligands and hydrogen atoms, which do not participate in bonding with the osmium atom, are not presented for clarity). Main bond lengths (Å): Os—Cl 2.406(1), Os—P(1) 2.312(1), Os—P(2) 2.309(1), Os—B(5) 2.376(5), Os—B(6) 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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