References

1. L. V. Rybin, S. V. Osintseva, P. V. Petrovskii, M. I. Rybinskaya, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1994, **479**, S25.
2. M. I. Rybinskaya, L. V. Rybin, S. V. Osintseva, F. M. Dolgushin, A. I. Yanovskii, and Yu. T. Struchkov, *Izv. AN, Ser. khim.*, 1995, 159 [*Russ. Chem. Bull.*, 1995, **44**, 154 (Engl. Transl.)].

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Alkyne—vinylidene coupling on a triosmium cluster. Formation of $Os_3(CO)_9\{\mu_3\text{-}C(SiMe_3)=C(Me)C=C(SiMe_3)R\}$complexes ($R$ = Me or Bu^n) containing an osmacyclobutene moiety

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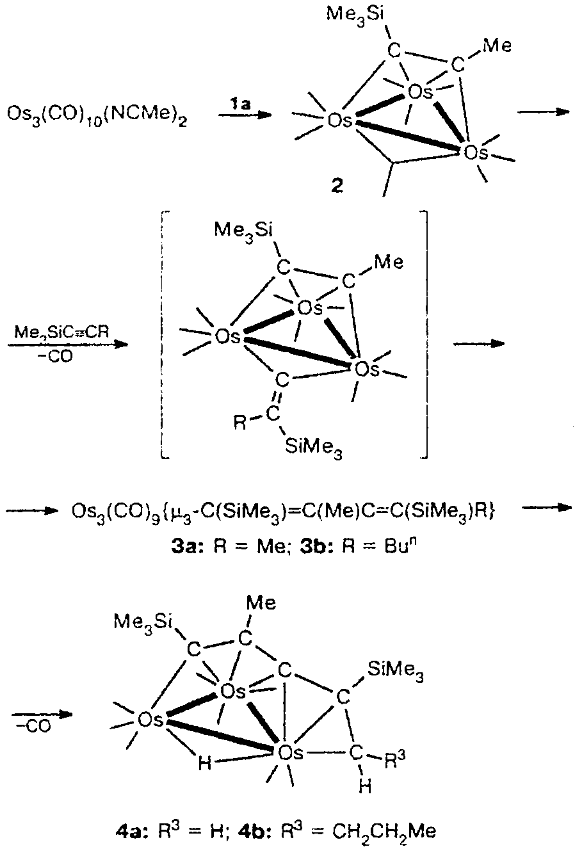
In connection with elucidating the mechanism of the dimerization of $Me_3SiC{\equiv}CMe$ (**1a**) and of its codimerization with alkynes $R^1C_2R^2$ on ruthenium and osmium clusters[1] we followed in detail the transformations of two silyl alkyne molecules on an Os_3 cluster under mild conditions. In the work we succeeded in isolating the reaction key intermediate, a red complex (**3a**). The ^1H and ^{13}C NMR spectra ($CDCl_3$, −45 °C, signals with relative intensity of 1, except as otherwise specified, δ_C, ppm: 0.57 (3 C), 2.47 (3 C), 29.67, 33.25, 51.53, 71.87, 126.33, 127.08, 170.15, 170.78, 173.11, 174.94, 175.77 (3 C), 177.86, 181.55) of cluster **3a** are temperature dependent. This is consistent with several dynamic processes occurring in the system.

A comparison of the spectroscopic data for clusters **2**—**4a** and related clusters shows that the second **1a** molecule in the coupling undergoes rearrangement by a 1,2-shift of the Me_3Si group. In principle, the organic ligands of cluster **3a** can be bound to the Os_3 cluster in two modes, **A** and **B**. A type **A** structure with a metallacyclobutene moiety has never been observed in cluster chemistry. In contrast, a type **B** structure has been found for the cluster $Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}PPh_2)\{\mu_3\text{-}CH{=}C(Pr^i)C{=}CH_2\}$, which contains bridged hydride and phosphide ligands.[2]

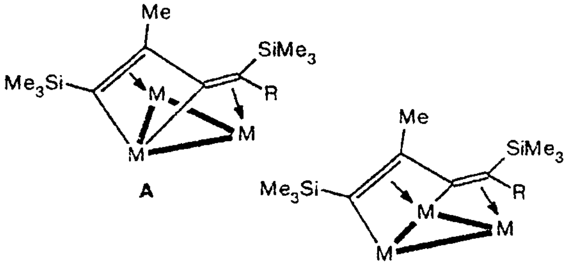


2

$\longrightarrow Os_3(CO)_9\{\mu_3\text{-}C(SiMe_3)=C(Me)C=C(SiMe_3)R\} \longrightarrow$

3a: R = Me; **3b**: R = Bu^n

4a: R^3 = H; **4b**: R^3 = CH_2CH_2Me



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In addition, in the case under consideration, *i.e.*, with three terminal CO groups at each osmium atom in cluster **3a** (IR spectroscopic data), only structure **A** has the 18e configuration at each metal atom. However, this uniform electron distribution is by no means a necessary condition for stability of triangular clusters.

The final structure of **3a** could be elucidated by X-ray diffraction analysis, however, we did not succeed in growing an appropriate crystal of this compound. To overcome this difficulty we synthesized cluster **3b** by reaction of **2** with alkyne $Me_3SiC{\equiv}CBu^n$ (**1b**). The spectroscopic similarity of **3a** and **3b** suggests that these complexes are identical in structure.

As shown by an X-ray diffraction study, molecule **3b** (space group $P2_12_12_1$, $Z = 4$, 2717 observed reflections, $R = 0.0448$) is composed of the Os_3 triangle with three terminal CO groups coordinatively bound to each metal atom. The organic ligand formed by alkyne-vinylidene coupling is linked to the Os_3 framework following the **A** pattern.

Metallacyclobutenes are known to be intermediates in reactions of carbene complexes with alkynes.[3] Therefore, the formation of type **A** clusters in the reaction under study indicates that the coupling of two hydrocarbon species may be preceded by alkyne-vinylidene rearrangement of the second alkyne molecule in the metal atom coordination sphere.

The synthesis, structure, and stereodynamic behavior of **3a** and **3b** will be detailed in the next publication.

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References

1. A. A. Koridze, N. M. Astakhova, P. V. Petrovskii, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1994, **481**, 247.
2. D. Nucciarone, N. J. Taylor, A. J. Carty, A. Tiripicchio, M. Tiripicchio Camellini, and E. Sappa, *Organometallics*, 1988, 7, 118.
3. M. F. Semmelhack, R. Tamura, W. Schnatter, and J. Springer. *J. Am. Chem. Soc.*, 1984, **106**, 5363.

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Transformations of β-D-xylofuranosyl nucleosides. The effective synthesis of 2′,3′-dideoxy-2′,3′-didehydrothymidine

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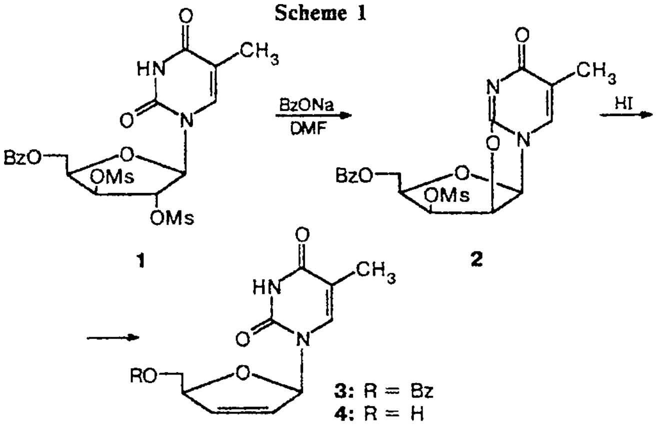
It is known that certain 2′,3′-didehydronucleosides possess high antiviral activity.[1,2] We showed earlier that heating 1-(2′-*O*-tosyl-3′,5′-di-*O*-benzoyl-β-D-xylofuranosyl)thymine with NaI leads to a mixture of 2,2′-anhydronucleoside and 5′-*O*-benzoyl-2′,3′-dideoxy-2′,3′-didehydrothymidine (in 30% yield).[3]

We continued the search for efficient methods of introducing a double bond at position 2′,3′ of the sugar moiety and found (Scheme 1) that the reaction of 2,2′-anhydro compound **2** with HI in anhydrous 1,2-dimethoxyethane at 20 °C for 8 h leads to 2′,3′-didehydronucleoside **3** in 93% yield.

The protecting group in compound **3** was removed with MeONa in methanol. The yield of 2,3′-dideoxy-2′,3′-didehydrothymidine (**4**) was 87%.

Scheme 1



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