NaH, 1 h, 0 °C) gave *exclusively* the *E* isomer **18** (80%), which, after quantitative deacetylation into **19**, was stereo- and regiospecifically mercuriocyclized into the chloromercurio compound **20** (80%). Demercuration (86%) and catalytic hydrogenolysis gave the pure β-linked disaccharide **22** (82%), which is the repeating disaccharide unit[15] of the K antigen of *Neisseria meningitidis* 29e. Application of this strategy to the synthesis of various KDO-containing oligosaccharides is under way in our laboratory.

Acknowledgment. We thank Dr. J.-Y. Lallemand (Gif-Sur-Yvette, France) for ^{13}C NMR spectra.

Supplementary Material Available: Spectral information, elemental analyses, and physical constants for new compounds (4 pages). Ordering information is given on any current masthead page.

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Intramolecular Cyclotrimerization of Macrocyclic and Acyclic Triynes with Group 6 Metal Carbonyls. The Formation of Fulvene and Benzene[1]

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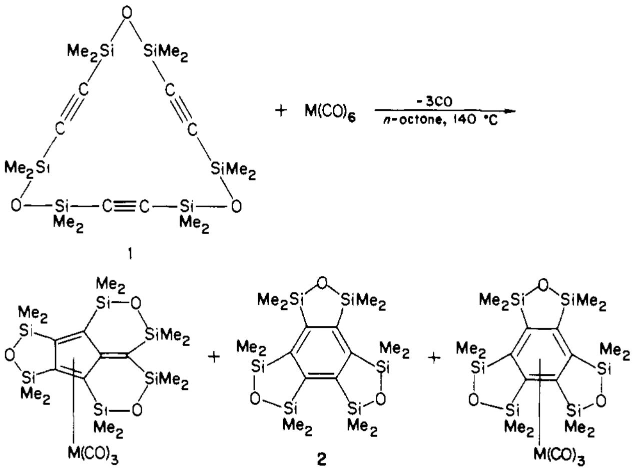
The transition-metal-catalyzed trimerization of alkynes has attracted organic chemists for a long time and several mechanisms and intermediates have been proposed for respective metals, triacetylene complexes (M = Cr, Ni),[2] metallacyclopentadienes (M = Co, Ir),[3] and halogenohexatrienyl metal complexes (M = Pd).[4] Herein we report a novel intramolecular trimerization of macrocyclic and acyclic triynes.



	4	2	3
a, M=Cr	49.7%	29.1%	trace
b, M=Mo	84.7%	0	0
c, M=W	18.1%	2.0%	0

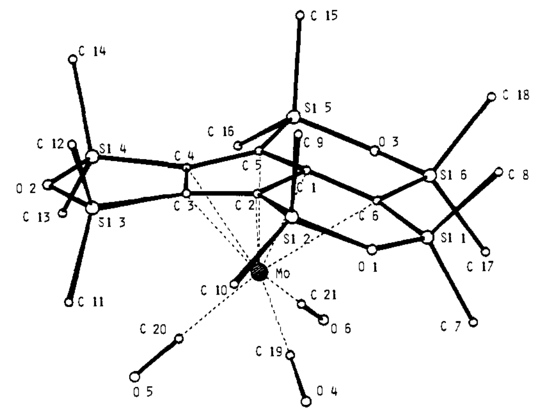
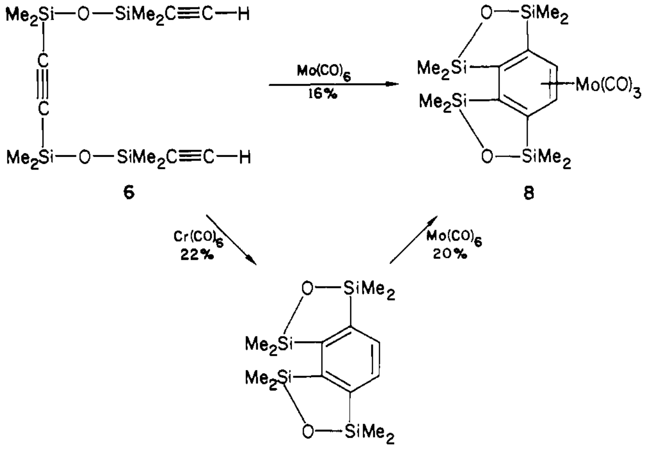


Figure 1. Perspective view of **4b** together with numbering of atoms.

Dodecamethyl-4,9,14-trioxa-3,5,8,10,13,15-hexasilacyclopentadeca-1,6,11-triyne (**1**) undergoes thermal intramolecular cyclotrimerization to the corresponding benzene derivative **2** in low yield,[5] but when **1** was heated in the presence of group 6 transition-metal carbonyls [M(CO)$_6$, M = Cr, Mo, and W], both black to black-violet crystalline complexes **4** and an intramolecular cycloadduct, **2**, were obtained in addition to a trace amount of the corresponding (arene)metal tricarbonyl complexes **3**.



The formation of **2** was indeed catalyzed by the metal complexes, because, in the absence of metal complexes, **1** did not isomerize under such mild conditions. The arene complex **3b** was obtained in good yield by the independent reaction of **2** with Mo(CO)$_6$. However, neither **3a** (M = Cr) nor **3c** (M = W) was obtained by the reaction of **2** with the corresponding metal carbonyls under the same conditions. Interestingly, the main products of the reaction accompanied by the intramolecular trimerization of acetylenes are not benzene complexes but fulvene complexes. Although several fulvene complexes have been prepared by direct complexation of the preformed hydrocarbon with group 6 metal carbonyls, this is the first synthesis of fulvene complexes from acetylenes.[6]

The molecular structure of **4b**, determined by the X-ray diffraction analysis (final *R* value = 0.0656) of the single crystal at room temperature, is given in Figure 1.[7] The Mo complex

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(1) Chemistry of Organosilicon Compounds. 193.

(2) (a) Schrauzer, G. N. *Chem. Ber.* **1961**, *94*, 1403. (b) Herwig, W.; Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1959**, *81*, 6203. (c) Zeiss, H. H.; Tsutsui, M. *Ibid.* **1961**, *83*, 825.

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(4) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.

(5) Sakurai, H.; Eriyama, Y.; Hosomi, A.; Nakadaira, Y. *Chem. Lett.* **1984**, 595.

(6) (a) Andrianov, V. G.; Struchkov, Y. T.; Setkina, V. N.; Zdanovichi, V. I.; Zhakaeva, A. Z.; Kursanov, D. M. *J. Chem. Soc., Chem. Commun.* **1975**, 117. (b) Lubke, B.; Edelmann, F.; Behrens, U. *Chem. Ber.* **1983**, *116*, 11 and references cited therein. (c) For a review of fulvene, see: Yates P. *Adv. Alicyclic Chem.* **1968**, *2*, 59.

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4b was thermally stable, but the decomplexation with trimethylamine *N*-oxide or by irradiation with a high-pressure mercury lamp in the presence of triphenylphosphine gave the liberated fulvene **5** in low yield.

In contrast to the above results, intramolecular cyclotrimerization of 3,3,5,5,8,8,10,10-octamethyl-4,9-dioxa-3,5,8,10-tetrasiladodeca-1,6,11-triyne (**6**), the corresponding acyclic triyne to **1**, gave a benzene derivative, **7**, in the reaction with $Cr(CO)_6$. The reaction of **6** with $Mo(CO)_6$ afforded a complex (**8**), which was also obtained by the reaction of **7** and $Mo(CO)_6$.

The mechanism and further extension of the reaction will be reported later.

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

Registry No. 1, 91269-65-7; **2**, 53170-83-5; **3a**, 93304-56-4; **3b**, 93304-57-5; **4a**, 93304-58-6; **4b**, 93304-59-7; **4c**, 93304-60-0; **5**, 497-20-1; **6**, 93304-55-3; **7**, 53170-80-2; **8**, 93304-61-1; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: Physical and spectroscopic data of all new compounds and tables of atomic parameters, anisotropic temperature parameters, list of distances, list of angles, and observed and calculated structure factors for **4b** (26 pages). Ordering information is given on any current masthead page.

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(7) Several interesting facts can be pointed out. The Mo atom has a distorted octahedral configuration and is bonded to six carbons of the fulvene ligand and three carbonyl groups. Similar to previously reported structure of diphenylfulvene complex,[6a] the C1–C6 double bond of **4b** is inclined by 30.47° to the planar cyclopentadiene ring in spite of a presumed loss of conjugation. An increased bond length of C1–C6 (1.447 Å) from values of diphenylfulvene complex (1.40 Å) or parent uncoordinated fulvene (1.349 Å)[8] should be noted. For a fulvene–$Cr(CO)_3$, an analysis of the bending of the exocyclic methylene group has been discussed recently by Hoffmann and his co-workers with the extended Hückel method.[9] The OC–Mo–CO bond angles (81.3°, 83.6°, and 97.5°) are unequal, while the respective Mo–CO bond lengths are approximately equal (1.99, 2.01, and 2.03 Å). The effect of substituents of the fulvene ligands on the details of the structure has been reported recently.[6b]

(8) (a) A value obtained by microwave spectroscopy: Barton, P. A.; Brown, R. D.; Burden, F. R.; Domaille, P. J.; Kent, J. E. *J. Mol. Spectrosc.* **1972**, *43*, 401. (b) Bond lengths and ^{13}C NMR of several fulvenes and their metal complexes have been discussed: Watts, W. *J. Organomet. Chem.* **1981**, *220*, 165.

(9) Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591.

Preparation and Some Chemistry of a Molecule Containing a μ-η^2,η^2-$NHNH^{2-}$ and a μ-η^1,η^1-NH_2NH_2 Ligand Bound between Two Tungsten(VI) Centers

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It is now thought that a pivotal intermediate in the reduction of dinitrogen by nitrogenase may be a complex of molybdenum containing an NHNH ligand.[1] There are only two structurally characterized molecules containing the NHNH unit. In $[Cr(CO)_5]_2(\mu$-η^1,η^1-NHNH)[2] the NHNH ligand appears to be most like diimide, and the metal therefore Cr(0), while in W(η^5-C_5Me_4-*t*-Bu)$(CCMe_3)I]_2$ (μ-η^1,η^1-NHNH)[3] it appears to be a 1,2-hydrazido^{2-} ligand, and the metal therefore W(6+). Here we report a molecule containing the hitherto unknown μ-η^2,η^2-$NHNH^{2-}$ ligand, as well as a μ-η^1,η^1-NH_2NH_2 ligand, that we think raises some interesting new questions concerning the chemistry of molecular nitrogen and partially reduced molecular nitrogen bound to relatively high oxidation state Mo or W centers.

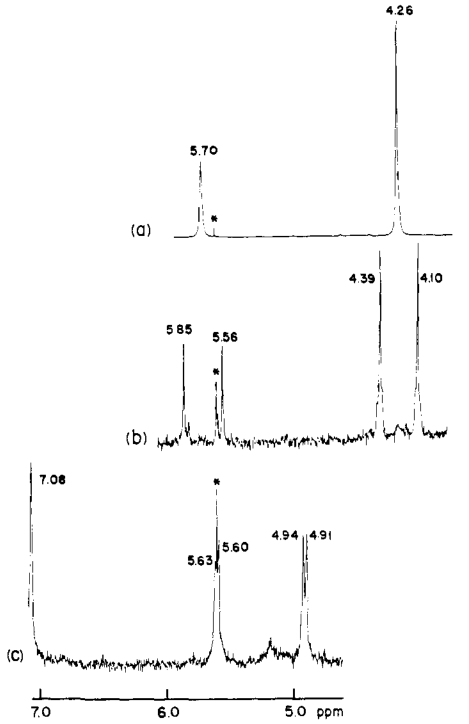

Figure 1. Signals for protons attached to nitrogen atoms in (a) **1** in acetone-d_6, (b) **1** prepared from $^{15}N_2H_4$, and (c) **2** in acetone-d_6 (* unidentified impurity).

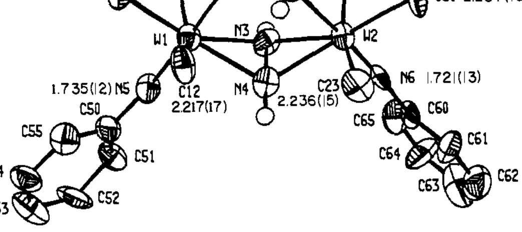

Figure 2. View of $[W(NPh)Me_3]_2(\mu$-η^1,η^1-$NH_2NH_2)(\mu$-η^2,η^2-NHNH) (hydrogen atoms included on nitrogen atoms only; ORTEP II, 40% ellipsoids). The included bond lengths refer to W–C or W═N bonds. Others can be found in the text or in the complete table in the supplementary material.

Addition of methyllithium to $W(NPh)Me_3Cl$[4] in ether at −30 °C generates what we believe to be thermally unstable, yellow $W(NPh)Me_4$ (cf. $W(NPh)(CH_2SiMe_3)_4$[4]). Addition of 1 equiv of hydrazine to a solution of $W(NPh)Me_4$ generated in this fashion yields a yellow solution from which a pale yellow solid (**1**) can be isolated in ~80% yield.[5] The ^1H NMR spectrum of **1** in acetone–d_6 shows (inter alia) two signals in the ratio of 1:2 at 5.70

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(5) Methyl lithium (10 mL, 1.14 M, 5.6 mmol) was added to a saturated solution of 2.0 g (5.6 mmol) of $W(NPh)Me_3Cl$ in ether at −30 °C. The resulting yellow solution was warmed until LiCl precipitated (at approximately −25 °C). The solution was then cooled again to −30 °C and transferred via cannula to a solution containing 0.18 mL (5.6 mmol) of anhydrous (98%) N_2H_4 in 50 mL of ether. The reaction was stirred at −30 °C for 20 min and then warmed to room temperature. The solution was filtered and the salts were washed with ether. The solvent was removed in vacuo leaving 1.60 g (80%) of yellow **1**. The compound can be recrystallized from dichloromethane by adding toluene. These crystals contain 0.5 equiv of toluene by ^1H NMR.

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