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Synthesis and Structure of Trisilane-1,3-diyl *ansa* Half-Sandwich Complexes of Group 6 Metals

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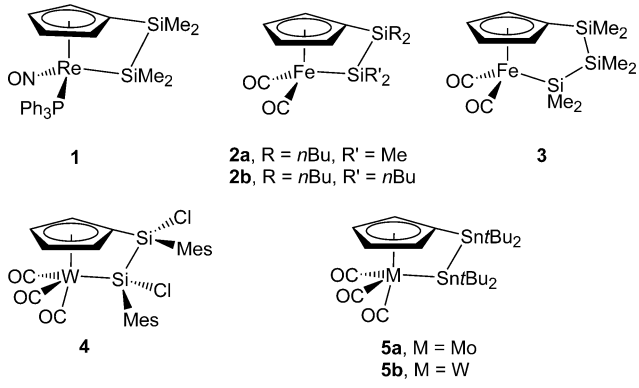
We present the synthesis and characterization of the first trisila-bridged *ansa* half-sandwich complexes of Group 6 transition metals in a one-step synthesis from dilithiated precursors Li[M(η^5-C_5H_4Li)(CO)$_3$] (M = W, Mo) by use of stoichiometric amounts of $Si_3Me_6Cl_2$ under dilute conditions. Variation of the reaction conditions leads to dinuclear trisila-bridged half-sandwich complexes, which were also characterized.

Introduction

In contrast to carbon-bridged *ansa* half-sandwich complexes, which have been intensively studied over the past decades,[1] the knowledge of other main-group bridging moieties is rather limited, despite their similar reactivity to [*n*]metallocenophanes, which have found widespread applications in catalysis, particularly for the polymerization of olefins.[2] Their propensity to undergo substitution, insertion and ring-opening polymerisation reactions are also of considerable interest.[3] The first *ansa* half-sandwich complex containing a heteroatom bridge between the η^5-cyclopentandienyl ligand and the central metal atom was reported by Gladysz et al. in 1988 by a two-step method in which the desired *ansa* half-sandwich complex **1** was obtained from a chloro(metallo)disilane precursor by deprotonation of the Cp ligand, followed by intramolecular nucleophilic substitution.[4] According to this route, Pannell et al. synthesized the corresponding iron complexes with SiR_2SiR_2 (**2a**,**b**) and $SiR_2SiR_2SiR_2$ (**3**) bridging moieties (Scheme 1).[5] We reported an efficient one-step protocol for various *ansa* half-sandwich complexes of molybdenum and tungsten containing silyl and stannyl bridges (**4**, **5a**,**b**), employing the dilithiated precursors **6a** and **6b**.[6] Based on this work, we developed access to trisila-bridged *ansa* half-sandwich complexes of molybdenum and tungsten under dilute conditions, which is presented here.



Scheme 1. Selected Si- and Sn-bridged *ansa* half-sandwich complexes.

Results and Discussion

The first approach to trisilanediyl *ansa* half-sandwich complexes was carried out in accordance to the successful synthesis of **4** and **5a**,**b**, thus treating the dimetallated half-sandwich complexes **6a**,**b** with 1,3-dichlorohexamethyltrisilane. However, this attempt led to an intermolecular reaction with a second metal complex, which yielded the dinuclear half-sandwich complexes of molybdenum and tungsten **7a** and **7b**, respectively, after protonation (Scheme 2). This different outcome might be attributed to the increased degree of flexibility of the trisilane in comparison to the previously employed disilanes and distannanes, respectively. By adapting the stoichiometry, **7a** and **7b** were accessible in good yields of 65 and 54%, respectively.

The ^{1}H NMR spectra of both compounds **7a**,**b** comprise two singlets for the $SiMe_2$ groups. Both Cp ligands show two multiplets at δ = 4.83 and 4.69 ppm for **7a** and at δ = 4.79 and 4.69 ppm for **7b**, respectively. The metal-bound

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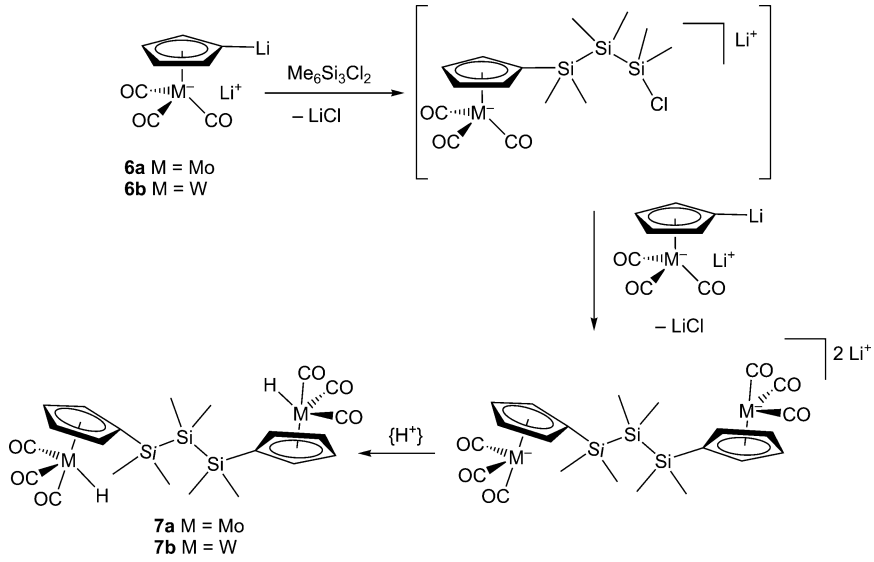
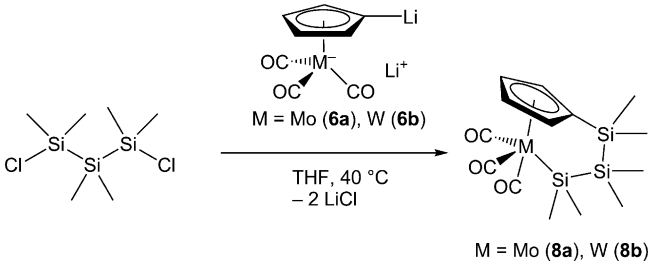


Scheme 2. Synthesis of dimeric half-sandwich complexes **7a** and **7b**.

hydrogen atom gives rise to a high-field shifted resonance at δ = –5.46 ppm for **7a** and at δ = –7.12 ppm for **7b** with a coupling constant of 15 Hz caused by the ^{183}W nucleus in case of the latter. Both compounds display two singlets in their ^{29}Si NMR spectra at δ = –20 and –38 ppm for **7a** and at δ = –20 and –48 ppm for **7b**, which are in full agreement with the proposed structure and symmetry. According to ^{29}Si-^{1}H correlation spectra, the high-field shifted signals of **7a**,**b** [δ(^{29}Si) = –38 and –48 ppm] can be assigned to the cyclopentadienyl-bound silyl groups.

Employing conditions of dilute solutions, that is decrease in concentration of the reactants by one order of magnitude, was believed to favor an intramolecular reaction and, thus, formation of the desired *ansa* half-sandwich complexes **8a** and **8b**. Indeed, both compounds became accessible under these conditions and were isolated in moderate yields of 30 and 15%, respectively, after sublimation in vacuo and recrystallization at –30 °C from pentane (Scheme 3).



Scheme 3. Synthesis of trisila-bridged *ansa* half-sandwich complexes of molybdenum and tungsten.

The ^{1}H NMR spectra of **8a** and **8b** show three singlets for the $SiMe_2$ groups and two multiplets for the Cp ligand, which indicates C_s symmetry in solution. Furthermore, ^{29}Si NMR spectra display three signals at δ = 13.0, 2.6 and –21.8 ppm for **8a** and at δ = –3.6, –3.8 and –20.5 ppm for **8b**, respectively. In accordance with previous results, the most deshielded resonance of each set might be ascribed to the metal-bound silicon centres.[7]

To obtain insight into the solid-state structure of the new complexes, single-crystal diffraction studies were carried out for **8a** and **8b** (Figures 1 and 2). Both compounds crystallize in the triclinic space group $P\bar{1}$. Two different molecules are present in the asymmetric unit of **8a** and **8b**, for which the structural parameters are almost identical. Thus, in the following we confine our discussion to one molecule for each compound.

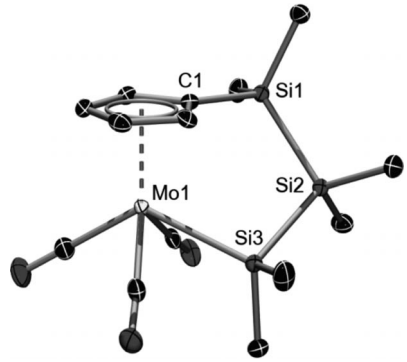


Figure 1. Molecular structure of **8a**. Ellipsoids are drawn at 50% probability. The second molecule of the asymmetric unit and the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo–Si3 2.6491(3), Si1–Si2 2.3599(2), Si2–Si3 2.3648(2); Si1–Si2–Si3 105.03(3); Si3–W–C1–Si1 43.85(8).

The Si–M and Si–Si bond lengths for **8a** (M = Mo) amount to 2.6491(3) and 2.3599(2) Å, respectively, whereas the corresponding values for **8b** (M = W) are very similar [2.6512(7) and 2.3586(2) Å] and fall in the range reported in the literature for comparable compounds.[7] Due to the relatively large trisila bridging moiety there is only little molecular strain present, as indicated by angles of 105.03(3)°

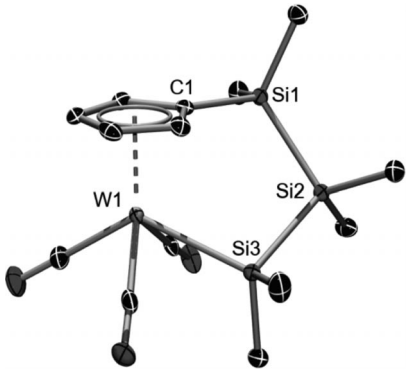


Figure 2. Molecular structure of **8b**. Ellipsoids are drawn at 50% probability. The second molecule of the asymmetric unit and the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:W–Si3 2.6512(7), Si1–Si2 2.3586(2), Si2–Si3 2.3652(2), Si1–Si2–Si3 105.151(3), Si3–W–C1–Si1 43.00(11).

for Si1–Si2–Si3 in **8a** and 105.51(3)° in **8b**. Furthermore, both compounds show only a moderate Si3–M–C_{ipso}–Si1 torsion of 43.85(8)° (**8a**) and 43.00(11)° (**8b**), respectively.

Conclusions

We were able to synthesize the first trisila-bridged *ansa* half-sandwich complexes **8a** and **8b** of group 6 metals by a one-step method. Furthermore, by modulating the reaction conditions it was also possible to synthesize the dinuclear half-sandwich complexes **7a** and **7b**.

Supporting Information (see footnote on the first page of this article): Experimental details and details on the crystallographic data.

CCDC-786157 and -786158 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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