Structural characterization of the anionic halfsandwich complex [Li(TMEDA)$_2$][Mo(η^5-C$_5$H$_5$)(CO)$_3$] and its reactivity towards stannanes and distannanes

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ABSTRACT

The crystal structure of the molybdenum half sandwich alkali salt [Li(TMEDA)$_2$][Mo(η^5-C$_5$H$_5$)(CO)$_3$] shows the occurrence of a separated ion pair in the solid state. Furthermore, the crystal structures of the long known organotin complexes [Mo(η^5-C$_5$H$_5$)(SnMe$_3$)(CO)$_3$], [{Mo(η^5-C$_5$H$_5$)(CO)$_3$}$_2$SnMe$_2$] and [Mo(η^5-C$_5$H$_5$)(SnMeCl$_2$)(CO)$_3$] have been recorded. The chlorination of [Mo(η^5-C$_5$H$_5$)(SnMe$_3$)(CO)$_3$] with SnCl$_4$ is presented as an improved synthetic access to [Mo(η^5-C$_5$H$_5$)(SnMeCl$_2$)(CO)$_3$]. Finally, the reaction of Li[Mo(η^5-C$_5$H$_5$)(CO)$_3$] with ^{t}Bu$_2$(Cl)Sn–Sn(Cl)^{t}Bu$_2$ leads to the novel molybdenum distannane complex [Mo(η^5-C$_5$H$_5$){Sn^{t}Bu$_2$-Sn(Cl)^{t}Bu$_2$}(CO)$_3$], which is fully characterized by NMR, elemental and X-ray analysis.

1. Introduction

Alkali metal salts M′[(η^5-C$_5$H$_5$)M(CO)$_n$] (M′ = alkali metal, M = transition metal) are the main precursors to a wide range of half sandwich complexes with covalent metal-metal and metal-element bonds. Although they are known in great variety, only a few have been characterized by X-ray diffraction analysis so far, including e.g. [Na(TMEDA)][(η^5-C$_5$H$_5$)Fe(CO)$_2$] or K[(η^5-C$_5$H$_5$)-Fe(CO)$_2$] [1–3]. Most of the structurally authenticated ionic species are characterized by coordinating ligands like crown ethers or other chelating donors at the cation, thus forming ion pairs in the crystal. Only in the case of potassium as countercation, a donor-free species is known, which forms a two-dimensional network in the solid state [2].

Due to their distinct nucleophilic character, these anionic complexes undergo salt elimination reactions with organic, organometallic and inorganic halides. The outstanding preparative versatility of this route has led to a vast range of organometallic species so far, most of which have been obtained from group 13 [4–15] and group 14 precursors [16–20].

In this report we focus on the alkali salt molybdenum complexes M[Mo(η^5-C$_5$H$_5$)(CO)$_3$] (M = Li, Na, K) (**1**) and their reactions with organotin halides. The former compounds have been known for over fifty years, and were initially reported as intermediates

in the synthesis of the hydride [Mo(η^5-C$_5$H$_5$)H(CO)$_3$] [21], and are commonly obtained by deprotonation of the latter or by reduction of the corresponding dimer, [Mo(η^5-C$_5$H$_5$)(CO)$_3$]$_2$. They are stable in inert atmosphere for an extensive period of time but show pyrophoric behavior towards air. While even commercially available as the sodium salt, an X-ray diffraction study has not been obtained so far on any complex M[Mo(η^5-C$_5$H$_5$)(CO)$_3$]. Various stannane complexes of molybdenum have been synthesized by reaction of organotin halides with this anion, leading not only to mono- but di- and even tri-nuclear tin compounds [22,23]. Mostly due to their early discovery in the sixties, the crystal structures of these were generally not established.

Here we report the preparation of [Li(TMEDA)$_2$][Mo(η^5-C$_5$H$_5$)-(CO)$_3$] (**1a**), its structural characterization by X-ray diffraction and its use for the synthesis of the new molybdenum distannane complex [Mo(η^5-C$_5$H$_5$)Sn^{t}Bu$_2$-Sn(Cl)^{t}Bu$_2$(CO)$_3$] (**5**). Additionally, we present the crystal structures of the well-known molybdenum monostannane complexes [Mo(η^5-C$_5$H$_5$)(SnMe$_3$)(CO)$_3$] (**2**), [{Mo(η^5-C$_5$H$_5$)(CO)$_3$}$_2$SnMe$_2$] (**3**) and [Mo(η^5-C$_5$H$_5$)(SnMeCl$_2$)-(CO)$_3$] (**4**) and report an alternative synthesis for the latter compound (see Fig. 1).

2. Results and discussion

Suspending Li[Mo(η^5-C$_5$H$_5$)(CO)$_3$] (**1**) in TMEDA, filtering the mixture through glass wool and cooling the solution down to

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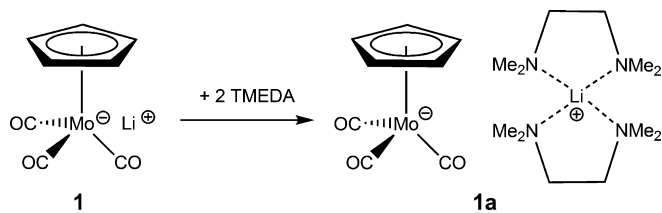
Fig. 1. Preparation of **1a** from **1**.

−30 °C gave $[Li(TMEDA)_2][Mo(\eta^5-C_5H_5)(CO)_3]$ (**1a**) as light yellow crystals.

The structure of **1a** in the solid state is shown in Fig. 2. It consists of two fully separated ions, as indicated e.g. by the large Mo–Li distance (6.375 Å), which is due to the sterical shielding and coordinative saturation of the lithium cation by two TMEDA molecules. The geometry of the anion is that of an undistorted three-legged piano-stool with almost identical Mo–C(O) bond lengths and Cp_{Cent}–Mo–C(O) angles for all three CO moieties. The Mo atom adopts a symmetrical position with respect to the C_5H_5-ligand as indicated by five almost identical Mo–C separations of 2.385(2)–2.398(3) Å. The two bidentate TMEDA ligands complexing the lithium ion are arranged almost perpendicular to each other, which was observed for other $[Li(TMEDA)_2]^+$ fragments before. Likewise, the Li–N distances (2.103(4)–2.155(6) Å) as well as the acute intra- (e.g. N11–Li–N21) and obtuse intermolecular (e.g. N11–Li–N12) angles of about 88° and 116.9(2)–124.9(2)°, respectively, match those in $[Li(TMEDA)_2]I$ (2.09(3)–2.13(2) Å; 88(1)°; 119(1)–124(2)°) [24].

Although the synthesis of $[Mo(\eta^5-C_5H_5)(SnMe_3)(CO)_3]$ (**2**) was already published in 1965 by Patil and Graham [25,26], the structure of this archetypal Mo-stannyl complex in the solid state remained unknown. By slow evaporation of a saturated solution of **2** in hexane suitable single crystals for X-ray diffraction were obtained. The molecule shows a four-legged piano-stool geometry with a large Mo–Sn distance of 2.8546(3) Å which is comparable to that of related molybdenum stannyl complexes such as $[\{Fe(\eta^5-C_5H_5)(CO)_2\}_2\{Mo(\eta^5-C_5H_5)(CO)_3\}SnCl]$ [22]. The $SnMe_3$ ligand adopts a staggered conformation with respect to the $[Mo(\eta^5-C_5H_5)(CO)_3]$ fragment as indicated by a dihedral angle Cp_{Cent}–Mo–Sn–C6 of 175.39°. This orientation together with the large Mo–Sn separation allows for rather acute Sn–Mo–C(O) angles of 68.48(6) and 69.42(8)° compared to the (O)C–Mo–C(O) angles of (79.30(9) and 81.18(9)°). The coordination sphere around the tin atom displays angles from 106.97(7) to 112.40(7)°, whereby the small deviation from the ideal tetrahedral geometry is presumably caused by packing effects within the unit cell (see Fig. 3).
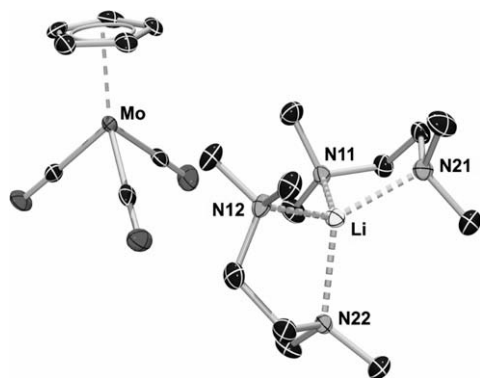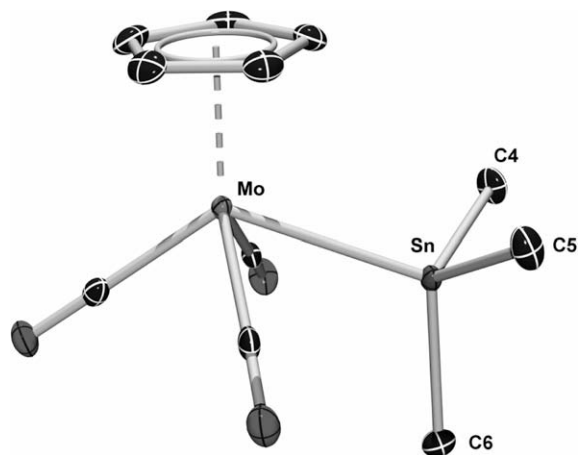

Fig. 3. Structure of **2** in the crystal (ellipsoids at 50% probability).
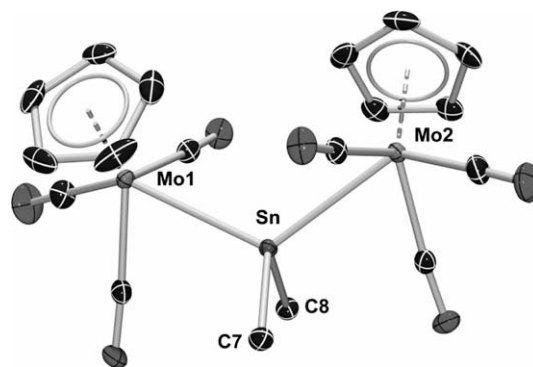

Fig. 4. Structure of **3** in the crystal (ellipsoids at 50% probability).

In accordance with a known procedure [26], reaction of two equivalents of **1** with Me_2SnCl_2 leads to the binuclear stannyl complex $[\{Mo(\eta^5-C_5H_5)(CO)_3\}_2SnMe_2]$ (**3**). Crystals of the latter suitable for X-ray diffraction were obtained from hexane at −30 °C (see Fig. 4). In the solid state, the two half sandwich fragments are arranged almost perpendicular to each other, as indicated by a dihedral angle of 82.00° between the Cp ring planes. The Mo–Sn distances (2.8792(3) and 2.8944(4) Å) are similar to the Mo–Sn distance of the mononuclear complex **2**. However, the sterical demand of the two half sandwich fragments imposes a significant distortion from tetrahedral coordination for the tin atom as reflected by the large Mo1–Sn–Mo2 angle of 120.289(3)° and the therefore diminished C7–Sn–C8 angle of 105.67(9)°.

Earlier attempts to obtain the dichlorostannyl complex $[Mo(\eta^5-C_5H_5)(SnMeCl_2)(CO)_3]$ (**4**) directly from **1** and $MeSnCl_3$ in equimolar amounts did not lead to a single product, but a mixture of mono-, di- and tri-nuclear species [27]. Subsequently, Bichler et al. were able to obtain **4** by chlorination of **2** with HCl/pentane, however, under rather harsh conditions (120 °C/8 h) and without providing information as to the yield of this synthesis [28]. Based on our previous work on corresponding tungsten chlorostannyl complexes [16], we obtained **4** upon reaction of **2** with $SnCl_4$ as chlorinating agent according to Fig. 5. After mixing the reagents in benzene at ambient temperature, an immediate color change from light yellow to orange indicated the fast progress of the chlorination and the chlorostannyl species **4** was obtained after work up in 58% yield, as an analytically pure, yellow solid.

Suitable single crystals for X-ray diffraction were grown at −30 °C from toluene (see Fig. 6). Similar to **2**, the stannyl group
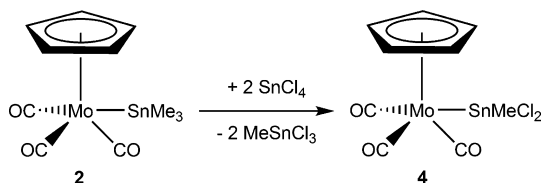

Fig. 2. Structure of **1a** in the crystal (ellipsoids at 50% probability).

Fig. 5. Synthesis of **4** by chlorination of **2** with $SnCl_4$.

in **4** adopts a staggered conformation with respect to the $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$-fragment as indicated by the dihedral angle Cp_{Cent}–Mo–Sn–C4 of 174.91°. The most noticeable difference is the Mo–Sn distance of 2.71997(19) Å, which is significantly shorter by more than 13 pm as in **2**. The higher steric demand of the methyl group together with its decreased electronegativity compared to the adjacent chlorine atoms imposes a notable deviation from tetrahedral geometry for the tin center, as indicated by two large C4–Sn–Cl angles of 101.06(7) and 101.32(8)° and a smaller Cl1–Sn–Cl2 angle of 97.185(18)°.

Treatment of **1** with one equivalent of 1,2-dichlorotetra^{t}butyl-distannane $^tBu_2(Cl)Sn$–$Sn(Cl)^tBu_2$ yielded in the new molybdenum distannane complex $[Mo(\eta^5\text{-}C_5H_5)Sn^tBu_2\text{-}Sn(Cl)^tBu_2(CO)_3]$ (**5**) (see Figs. 7 and 8).

Compared to the starting material $^tBu_2(Cl)Sn$–$Sn(Cl)^tBu_2$, the signals of the ^{t}butyl groups in the ^1H NMR and ^{13}C NMR spectra of **5** are generally downfield shifted. This shift is more pronounced for the butyl groups geminal to the molybdenum atom, but rather small for the terminal Sn^tBu_2Cl group. This effect is caused by the substitution of one chlorine atom in the precursor by the less electronegative molybdenum, as observed before [29]. In consistence with this, the J_{Sn} coupling constants in ^1H and ^{13}C NMR spectra of **5** are decreased in comparison to the values found for the distannane $^tBu_2(Cl)Sn$–$Sn(Cl)^tBu_2$. Due to the ^tBu-groups, **5** shows a very good solubility in non polar solvents like pentane or hexane. Remarkably, upon treatment of $^tBu_2(Cl)Sn$–$Sn(Cl)^tBu_2$ with two equivalents or even a large excess of the anion **1**, only the signals
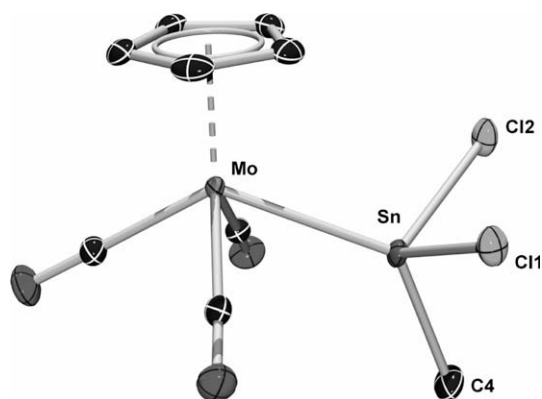
Fig. 6. Structure of **4** in the crystal (ellipsoids at 50% probability).

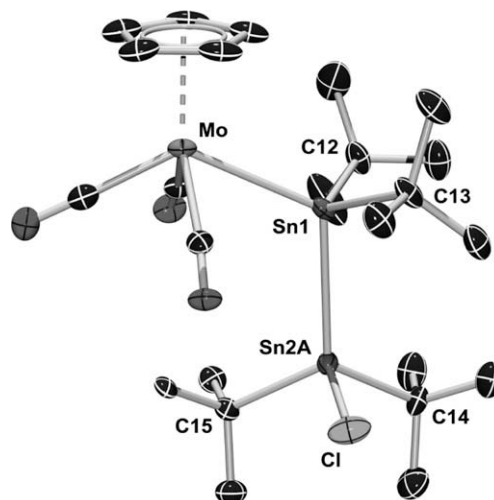**Fig. 7.** Preparation of the novel molybdenum distannane **5**.

Fig. 8. Structure of **5** in the crystal (ellipsoids at 50% probability).

associated with **5** could be detected in the reaction mixture and the substitution of the second chloride by molybdenum did not occur. This finding may be explained by steric restraints, in particular the significant change of the geometry of the tin center brought about by substitution of chlorine by the $[Mo\text{-}(\eta^5\text{-}C_5H_5)(CO)_3]$-moiety, as observed in the crystal structure of **5** (Fig. 8). In $^tBu_2(Cl)Sn$–$Sn(Cl)^tBu_2$, the sterical demand of the large ^{t}butyl groups results in small Cl–Sn–C angles of 101.01(13)–103.15(12)° and large C–Sn–C angles of 115.69(18)° and 117.61(17)° [30]. Due to the bulky $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$-fragment in **5**, the geometry around the tin atom Sn1 is nearly tetrahedral, as indicated by three almost identical angles between Mo and the ^{t}butyl groups of 109.39(3)–111.38(3)°. This strain also leads to an enlargement of the C12–Sn1, C13–Sn1 and Sn2A–Sn1 bonds by approximately 4 pm each compared to $^tBu_2(Cl)Sn$–$Sn(Cl)^tBu_2$. The geometry of the terminal tin atom Sn2A, however, is not affected by the substitution, as bond lengths and angles do not differ from those of the starting material.

3. Experimental

All manipulations were performed under an inert atmosphere of argon or *in vacuo* using standard Schlenk techniques or in a glove box. Solvents were dried according to standard procedures or by using a MBraun solvent purification system (SPS) and stored under argon over molecular sieves. C_6D_6 was degassed using three freeze-pump-thaw cycles and stored over molecular sieves. IR spectra were recorded as solutions between KBr plates on a Bruker Vector 22 FT-IR-spectrometer. NMR spectra were recorded on a Bruker 300 Avance spectrometer (^1H, ^{13}C: internal standard TMS, ^{119}Sn: external standard $SnMe_4$). Elemental analyses (C, H) were obtained from a Vario Micro (Elementar Analysensysteme). Li $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ [16], $^tBu_2(Cl)Sn$–$Sn(Cl)^tBu_2$ [30], $[Mo(\eta^5\text{-}C_5H_5)\text{-}(SnMe_3)(CO)_3]$ [25] and $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2SnMe_2]$ [26] were prepared according to the literature procedures. All other chemicals were obtained commercially and used without further purification. Melting points were measured on a Mettler Toledo DSC823.

3.1. Synthesis of $[Mo(\eta^5\text{-}C_5H_5)(SnMeCl_2)(CO)_3]$ (**4**) by excessive chlorination of **2** with $SnCl_4$

A solution of 160 mg (0.40 mmol) **2** in 10 mL benzene was treated with 235 mg (106 µl, 0.90 mmol) $SnCl_4$. Upon addition, the color of the solution changed immediately from yellow to orange.

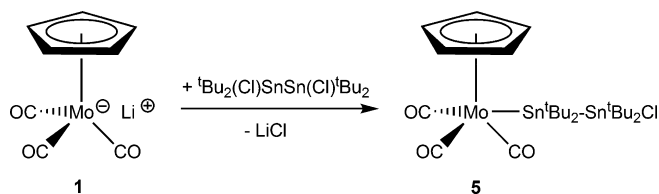After stirring for 1 h the solvent and remaining $SnCl_4$ were removed *in vacuo* and the remaining solid was dried thoroughly. The residue was washed with pentane (2×3 mL) and evaporated to dryness.

Yield 97 mg (0.23 mmol, 58%). Yellow powder. M.p. 116 °C. Single crystals suitable for X-ray diffraction were grown at −30 °C from toluene.

^{1}H NMR (300.1 MHz, C_6D_6): δ = 4.57 (s, 5H, Cp), 1.11 (s, 3H, $^2J_{HSn}$ = 45.4, 43.5 Hz, Me) ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = 227.4, 222.9 (s, CO), 91.3 (s, Cp), 13.5 (s, $^1J_{CSn}$ = 279, 267 Hz, Me) ppm. ^{119}Sn NMR (111.9 MHz, C_6D_6): δ = 367 (s, Sn) ppm. IR (dichloromethane): $\tilde{v}_{C=O}$ = 2032, 1968, 1937 cm^{-1}. Anal. Calc. for $C_9H_8Cl_2MoO_3Sn$ (449.71): C, 24.04; H, 1.79. Found: C, 23.46; H, 1.86%.

3.2. Synthesis of [$Mo(\eta^5\text{-}C_5H_5)Sn^tBu_2\text{-}Sn(Cl)^tBu_2(CO)_3$] (**5**)

484 mg (0.90 mmol) of $^tBu_2(Cl)Sn–Sn(Cl)^tBu_2$ were added to a suspension of 250 mg (0.99 mmol) Li[$Mo(\eta^5\text{-}C_5H_5)(CO)_3$] in 15 mL of ether. After 1 h stirring at ambient temperature the solvent was removed and the residue was extracted with hexane (2×15 mL). The combined extracts were filtered over a celite pad and the solvent was evaporated *in vacuo*.

Yield 535 mg, 0.72 mmol, 80%. Yellow powder. M.p. 106 °C. Single crystals suitable for X-ray diffraction were grown at −30 °C from hexane. ^{1}H NMR (300.1 MHz, C_6D_6): δ = 4.89 (s, 5H, Cp), 1.52 (s, 18H, $^3J_{HSn}$ = 73.4, 70.2 Hz, $^4J_{HSn}$ = 6.5 Hz, $^tBu_2$), 1.50 (s, 18H, $^3J_{HSn}$ = 73.4, 70.2 Hz, $^4J_{HSn}$ = 5.4 Hz, $^tBu_2$) ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = 231.6, 226.6 (s, CO), 89.7 (s, Cp), 39.1 (s, 2×$C_{quart.}$), 34.8 (s, $^2J_{HSn}$ = 9 Hz, CH_3), 31.7 (s, $^2J_{HSn}$ = 16 Hz, CH_3) ppm. ^{119}Sn NMR (111.9 MHz, C_6D_6): δ = 197 (s, Mo–Sn), 99 (s, Sn) ppm. IR (dichloromethane): $\tilde{v}_{C=O}$ = 1995, 1924, 1897 cm^{-1}. Anal. Calc. for $C_{24}H_{41}ClO_3MoSn_2$ (746.39): C, 38.62; H, 5.54. Found: C, 38.04; H, 5.55%.

Supplementary material

CCDC 696044, 696042, 696043, 696045 and 696041 contain the supplementary crystallographic data for **1a**, **2**, **3**, **4** and **5**. 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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