Journal of Organometallic Chemistry, 415 (1991) 97–100
Elsevier Sequoia S.A., Lausanne
JOM 21911

Alkylidene dinitrosyl molybdenum complexes. Synthesis and characterization of ethylidene complexes of the type $[(Et_3Sn \cdot AlCl_3)_2(\mu\text{-}OR)_2Mo(NO)_2(=CHMe)]$

A. Keller
Institute of Chemistry, University of Wroclaw, 50-383 Wroclaw (Poland)

(Received March 6th, 1991)

Abstract

Reactions of dialkoxy dinitrosyl molybdenum complexes with Et_4Sn (alkylating agent) and $AlCl_3$ (Lewis acid) yield ethylidene dinitrosyl molybdenum complexes. They were isolated as polymeric species $\{(Et_3Sn \cdot AlCl_3)_2(\mu\text{-}OR)_2Mo(NO)_2(CHMe)\}_n$ (R = Me, Et, ^iPr) and ^1H NMR, IR and analytically characterized. These are new examples of low-valent nucleophilic alkylidene complexes.

The first examples of alkylidene complexes with low oxidation state and having nucleophilic =CHR ligands, i.e. $[(AlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2(CHR')]$ (R′ = Me, R = Me (**1**), Et (**2**), ^iPr (**3**); R′ = Et, R = Et (**4**) were obtained quite recently [1,2]. They are formed in the dicomponent systems: precatalyst–$EtAlCl_2$ (precatalyst: $\{Mo(NO)_2(OR)_2S\}_n$; R = Me, S = MeCN (**5**); R = Et, S = EtOH (**6**); R = ^iPr (**7**)). In such systems the aluminium alkyl plays a dual role—that of Lewis acid and alkylating agent. The alkylating agents could also be Et_4Sn [3] and/or Et_xSnCl_{4-x} [4], when $AlCl_3$ (Lewis acid) empties coordination sites on the central atom.

The dialkyl complexes formed in that way produce the appropriate alkylidene complexes by α-hydrogen elimination. Since $AlCl_3$ forms with Et_xSnCl_{4-x} adducts in 1 : 1 and 1 : 2 molar ratios [5], such ratios might be expected to be preserved in the subsequently formed intermediates and alkylidene complexes:

$$\mathbf{5,6,7} \xrightarrow{2AlCl_3} \underset{R = Me\ (\mathbf{8}),\ Et\ (\mathbf{9}),\ ^iPr\ (\mathbf{10})}{\left[(AlCl_3)_2(\mu\text{-}OR)_2Mo(NO)_2\right]} \xrightarrow{n Et_4Sn}$$

$$\left[\{(Et_4Sn)_n AlCl_3\}_2(\mu\text{-}OR)_2Mo(NO)_2\right] \rightarrow$$

$n = 1$: R = Me (**11**), Et (**12**), ^iPr (**13**)
$n = 2$: R = Me (**11′**), Et (**12′**), ^iPr (**13′**)

$$\left[\{(Et_4Sn)_n(AlCl_3 \cdot Et_3Sn)\}_2(\mu\text{-}OR)_2Mo(NO)_2(Et)_2\right] \xrightarrow[-EtH]{}$$

$n = 0$: R = Me (**14**), Et (**15**), ^iPr (**16**)
$n = 1$: R = Me (**14′**), Et (**15′**), ^iPr (**16′**)

$$\left[\{(Et_4Sn)_n(AlCl_3 \cdot Et_3Sn)\}_2(\mu\text{-}OR)_2Mo(NO)_2(CHMe)\right] \qquad (1)$$

$n = 0$: R = Me (**17**), Et (**18**), ^iPr (**19**)
$n = 1$: R = Me (**17′**), Et (**18′**), ^iPr (**19′**)

0022-328X/91/$03.50

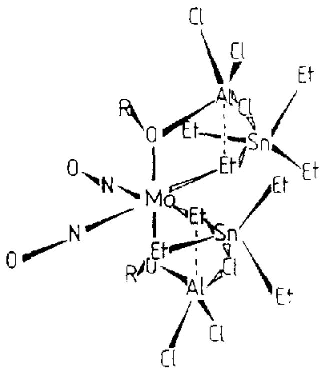

Fig. 1. The most probable structure of the adducts **11–13**.

The reactions of **5**, **6**, **7** with the $AlCl_3$–$(Et_4Sn)_n$ ($n = 1$ and/or 2) adducts are the most efficient in formation of **17–19** and **17′–19′** [3]. Undoubtedly the appropriate adducts **11–13** or **11′–11′** are formed, excluding **8–10** (reaction 1). Their most probably structure is presented in Fig. 1. It allows easy transformation to the dialkyl complexes **14–16**.

17–19 and **17′–19′** are green complexes, easily soluble in PhCl, and undergo polymerization, like **1–4** [1,2,6] but much faster, to produce polymeric species of the formula $\{(Et_2Sn \cdot AlCl_3)_2(\mu\text{-}OR)_2Mo(NO)_2(CHMe)\}_n$ (R = Me (**17a**), Et (**18a**), ^iPr (**19a**). They were isolated in this form and composition and were characterized analytically and spectrally.

17a, **18a** and **19a** are light-brown precipitates, sparingly soluble in PhCl and sensitive to air and moisture. They may be stored indefinitely at room temperature in an inert atmosphere. Their IR spectra (see Experimental Section) in the $\nu(OR)$ region point to a bridge coordination of the alkoxy ligands [7]. The $\nu(NO)$ frequencies, typical for a *cis*-$\{Mo(NO)_2\}^6$ core (the superscript denotes number of metal *d*-electrons) are lower than those of their monomeric counterparts, as in the polymeric species of **1–4** [1,2]. **17a–19a**, like the latter, undergo quantitative decomposition following the pattern:

$$\mathbf{17a},\ \mathbf{18a},\ \mathbf{19a} \xrightarrow{H_2O,\ HCl,\ O_2 \text{ or } H_2O_2} Mo^{VI} \text{ complex} + \underset{\text{ca. } 80\%}{-[CH(CH_3)CH(CH_3)]_n-} + \underset{\text{ca. } 20\%}{-[CH_2CH_2]_n-} \qquad (2)$$

The ^1H NMR spectra and the elemental analysis of the products of the reaction of **5–7** with $AlCl_3 + n\ Et_4Sn$ ($n = 1, 2, 3$) revealed the reaction

$$[(Et_3Sn \cdot AlCl_3)_2(\mu\text{-}OR)_2Mo(NO)_2(CHMe)] \rightleftharpoons [(Et_3Sn \cdot AlCl_3)(AlCl_2)(\mu\text{-}OR)_2Mo(NO)_2(CHMe)] + Et_3SnCl \qquad (3)$$

in the system where $1 \geqslant Al:Sn > 1/2$.

The ^1H NMR spectra of complexes isolated from the $1 \geqslant Al:Sn > 1/2$ indicate also that within the $(Et_3Sn \cdot AlCl_3)$ fragments there proceeds (to some extent) the exchange reaction, giving rise to the formation of $(Et_2SnCl \cdot EtAlCl_2)$ fragments ($\delta(CH_3CH_2Al) = 1.05$ ppm, t; $\delta(CH_3CH_2Al) = 0.05$ ppm, q).

The ^1H NMR spectra of **17a–19a** (see Experimental Section) were recorded in CD_3CN solutions at 30 ° C and −40 ° C.

The H_α chemical shift values of ethylidene ligands in ^1H NMR spectra of **17a** (δ(CH) = 7.50 ppm) and **18a** (δ(CH) = 7.45 ppm) are almost identical to those for **1** and **2** respectively [2], whereas for **19a** (δ(CH) = 7.33 ppm) this value exceeds by 0.2 ppm that for **5** [1,2]. Such H_α chemical shift values are characteristic for nucleophilic alkylidene ligands [1,2,8–10].

The ethylidene α-hydrogen in ^1H NMR spectra at 30 ° C of **17a** and **18a** gives a sharp singlet; at −40 ° C, **17a** and **18a** give a broad singlet and a quartet of a broad nature, respectively. In the spectrum of **19a** at 30 ° C this resonance is revealed as a considerably broadened singlet at 30 ° C and a quartet at −40 ° C. The nature of the methyl resonances of the ethylidene ligands was found to change with temperature, like the H_α resonances.

The ethylidene α-hydrogen migration is responsible for these phenomena [2]. The important factor which could facilitate (or inhibit) the migration is the nature of the anionic (alkoxy) ligands in the metal alkylidene complexes [2,11–13].

The ^1H NMR spectra of **17a–19a** exhibit also the resonances of the alkoxy ligands and of the Et_3Sn fragments. The latter ones, in which as in Et_3SnCl $\delta(CH_3CH_2Sn) = \delta(CH_3CH_2Sn)$, overlap the methyl resonances of ethoxy and isopropoxy ligands. The nature of these resonances is indicative of the appropriate dynamic exchange processes.

Experimental

All reactions were carried out under dry argon, with purified and dried reagents. **5**, **6** and **7** were prepared by published methods [14].

Instrumentation

IR: Specord M80; ^1H NMR: Tesla BS576A.

Synthesis of 17a, 18a and 19a

17a, **18a** and **19a** were prepared by the same method. To the solution of the starting complex (**5**, **6** and **7**) in PhCl (1×10^{-3} mol in 30 cm^3) the Et_4Sn (3×10^{-3} mol) was added. The solution was heated to 60 ° C. After about 30 min the solution was cooled to about −5 ° C and a solution of $AlCl_3$ in PhCl with Et_4Sn (Al : Sn = 1 : 2) in molecular ratio Mo : Al = 1 : 6 was added dropwise. The solution was heated to room temperature. After 2 h the desired product was precipitated with hexane from the reaction mixture. The product was filtered off, washed with PhCl and hexane and dried *in vacuo*.

Analysis

$MoAl_2Sn_2Cl_6N_2O_4C_{16}H_{40}$ calc.: Mo, 10.38; Al, 5.84; Sn, 25.68; Cl, 23.01; N, 3.03; C, 20.79; H, 4.36%. Found: Mo, 10.58; Al, 6.12; Sn, 25.01; Cl, 23.38; N, 2.83; C, 20.44; H, 4.91%.

$MoAl_2Sn_2Cl_6N_2O_4C_{18}H_{44}$ calc.: Mo, 10.07; Al, 5.67; Sn, 24.92; Cl, 22.33; N, 2.94; C, 22.70; H, 4.66%. Found: Mo, 10.88; Al, 6.08; Sn, 24.18; Cl, 22.79; N, 2.70; C, 23.11; H, 4.94%.

MoAl$_2$Sn$_2$Cl$_6$N$_2$O$_4$C$_{20}$H$_{48}$ calc.: Mo, 9.78; Al, 5.50; Sn, 24.21; Cl, 21.69, N, 2.86; C, 24.50; H, 4.93%. Found: Mo, 10.39; Al, 6.00; Sn, 23.84; Cl, 22.07; N, 2.91; C, 24.98; H, 5.38%.

Infrared data

IR data obtained in Nujol mulls.

17a: ν(NO), 1826vs, 1720vs; ν(OMe), 1090m, 1025s, 965m; other bands, 830m, 745m, 685s, 640br, 570m, 520m, 475sh.

18a: ν(NO), 1822vs, 1720vs; ν(OEt), 1150w, 1090m, 1025m, 970w; other bands, 850m, 745m, 650br, 565sh.

19a: ν(NO), 1823vs, 1720vs; ν(O^{i}Pr), 11170sh, 1155m, 1100m, 1025m, 970m, 940w; other bands, 840m, 740m, 650br, 560m,br.

^{1}H NMR data

^{1}H NMR data were obtained in CD$_3$CN at −40 °C relative to Me$_4$Si.

17a: δ((C*H*CH$_3$) 7.50(s,br); δ(CHC*H*$_3$) 0.90(s,br); δ(OCH$_3$) 2.55(s,br); δ(C*H*$_3$C*H*$_2$Sn) 1.26(s).

18a: δ(C*H*CH$_3$) 7.45(q,br); δ(CHC*H*$_3$) 0.93(d); δ(OC*H*$_2$CH$_3$) 4.40(br); δ(OCH$_2$C*H*$_3$) + δ(C*H*$_3$C*H*$_2$Sn) 1.27(s).

19a: δ(C*H*CH$_3$) 7.33(q); δ(CHC*H*$_3$) 0.94(d); δ(OC*H*CH$_3$) 4.32(br); δ(OCHC*H*$_3$) + δ(C*H*$_3$C*H*$_2$Sn) 1.27(s).

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