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The first example of a dinitrosylmolybdenum alkylidene complex: synthesis, spectroscopic characterization and metathesis activity

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Abstract

The first spectrally characterized example of a stable dinitrosylmetal ethylidene complex, $[(AlCl_2)_2(\mu\text{-O-i-Pr})_2Mo(NO)_2(=CHMe)]$, is reported. This complex is the product of transformation of the adduct $[(EtAlCl_2)_2(\mu\text{-O-i-Pr})_2Mo(NO)_2\}$ to a dialkyl complex followed by α-hydrogen elimination. The ethylidene complex is an active catalyst for olefin metathesis.

Among the many synthesized and characterized transition-metal carbene complexes (hetero-atom-stabilized and non-hetero-atom-stabilized), only a few nitrosylmetal carbene complexes have been reported [1]. They are mostly (cyclopentadienyl)metal mononitrosyl complexes. Only one example of a group 6 metal dinitrosyl complex possessing carbene-type ligands has been obtained and described in the literature to date [2] — a dinitrosylchromium complex with the heteroatom-stabilized carbene ligands: $[Cp(NO)_2)Cr{=}C(OR)NHMe]^+$ (R = Me, Et). The other transition-metal carbene complexes recognized possess only heteroatom-stabilized carbene ligands, too [3].

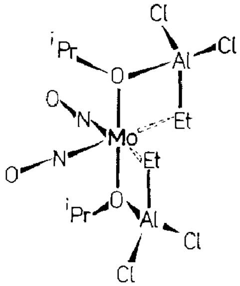
The dinitrosyl complexes of group 6 metals (especially Mo) with alkylaluminiums form highly active catalysts for olefin metathesis [4]. Quite recently it was discovered that the intermediates and carbene catalysts preserve the $cis\text{-}\{Mo(NO)_2\}^6$ fragment [5]. In this paper we describe the synthesis of the first example of a dinitrosylmolybdenum non-hetero-atom-stabilized carbene complex $[(AlCl_2)_2\text{-}(\mu\text{-O-i-Pr})_2Mo(NO)_2(=CHMe)]$ together with its spectroscopic (^1H NMR, IR) characterization and metathesis activity. This carbene complex results from the sequential reaction of $\{Mo(NO)_2(O\text{-i-Pr})_2\}_n$ with $EtAlCl_2$ followed by intramolecular transformations:

$$\underset{(1)}{\{Mo(NO)_2(O\text{-i-Pr})_2\}_n} \xrightarrow{EtAlCl_2} \underset{(2)}{[(EtAlCl_2)_2(\mu\text{-O-i-Pr})_2Mo(NO)_2]} \qquad (1)$$

$$\mathbf{2} \rightarrow \underset{(\mathbf{3})}{[(\mathrm{AlCl_2})_2(\mu\text{-O-i-Pr})_2\mathrm{Mo(NO)_2(Et)_2}]} \xrightarrow{-\mathrm{EtH}}$$

$$\underset{(\mathbf{4})}{[(\mathrm{AlCl_2})_2(\mu\text{-O-i-Pr})_2\mathrm{Mo(NO)_2({=}CHMe)}]} \qquad (2)$$

Both complexes, **2** and **4**, previously determined by IR in solution [5], were isolated as analytically pure precipitates [6*]. **2** [7a*] is a green precipitate reacting with oxygen and moisture. Its IR spectrum [7b*] displays two ν(NO) bands typical for *cis*-$\{\mathrm{Mo(NO)_2}\}$. The character of this spectrum in the ν(OR) region indicates bridge coordination of the alkoxy ligands. Its ^{1}H MNR spectrum [7c*] exhibits $\mathrm{CH_3}$ and CH resonances of alkoxy ligands and $\mathrm{CH_3}$ and $\mathrm{CH_2}$ resonances of joined aluminium alkyl ethyl groups. The interaction between $\mathrm{EtAlCl_2}$ and **1** (tetramer [4c]) is followed by cleavage of the Mo–O–Mo bridge bonding of the alkoxy ligands and the formation of new Mo–O–Al bond (also realized by the uptake of $\mathrm{EtAlCl_2}$ to the terminal alkoxy ligands). The bond breaking most likely occurs in the *trans* positions towards the NO groups. In the known mononitrosyl-alkoxy complexes, the M–O distances in the bridge alkoxy ligands are much longer in these positions [8]. The following structure of **2** seems to be the most probable:



Transformation of **2** into **3** and α-hydrogen elimination lead to the formation of **4** (reaction 2). This complex was isolated as a green precipitate [9a*]. It appears moderately stable to dry air in the solid state for a short time, but is sensitive to air and moisture in solution. In the solid state, it may be stored indefinitely at room temperature in an inert atmosphere. **4** is soluble in PhCl and $\mathrm{CH_2Cl_2}$, but after some time a brown precipitate of the same quantitative composition separated out. It could be regarded as the polymeric form of **4**, i.e. $\{(\mathrm{AlCl_2})_2(\mu\text{-O-i-Pr})_2\mathrm{Mo(NO)_2}({=}\mathrm{CHMe})\}_n$ (**4a**). The IR spectra of **4** [9b*] and **4a** [10*] in the ν(NO) region are characteristic for a *cis*-dinitrosyl molybdenum complex of electronic structure $\{\mathrm{Mo(NO)_2}\}^6$, i.e. the same as that of complexes **1** and **2**. Hence the carbene ligand in complex **4** is nucleophilic in nature. The α-hydrogen atoms of the alkyl ligand could be quite acidic and removal of one of them left a nucleophilic carbene ligand [11]. The carbene α-proton in the ^{1}H NMR spectrum of **4** (in $\mathrm{CD_2Cl_2}$ at 25 °C) gives a quartet at 7.15 ppm (1H). This spectrum also exhibits a doublet at δ 1.00 ppm (3H) for the methyl protons of the carbene ligand and methyl (δ 1.16 ppm, d,

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* Reference number with asterisk indicates a note in the list of references.

12H) and methyne (δ 4.22 ppm, q, 2H) resonances of the isopropoxy ligands. The nucleophilicity of the carbene α-carbon was preserved only for high-oxidation-state carbene complexes [12]. **4** is the first example of a carbene-metal complex in a low oxidation state with a nucleophilic carbene group. Coordination of such a group is possible owing to the presence of strong π-acceptor NO ligands in the coordination sphere. Investigations of the electronic structure of this model complex, carried out by the extended Hückel method [5], revealed that the coordination of the carbene ligand in the Mo–NO bonding plane (xy), realized from the side opposite to the NO ligands, required the smallest amount of activation energy. The conditions most favourable for the formation of $\pi C_{carbene} \rightarrow Mo$ bonding are also present. The calculations revealed that the H–C–Me plane of the carbene ligand lies horizontally in the plane of the *cis*-$\{Mo(NO)_2\}$ fragment [13]. The strong electron-withdrawing effect due to the presence of NO ligands could stop rotation around the Mo–carbene bond in **4**. This rotation could also be inhibited by the bulky structure of the isopropoxy ligands.

4 in PhCl is an active catalyst for olefin metathesis. It converts 10^3 mol.equiv. of pent-2-ene into but-2-ene and hex-3-ene after about 2 h. The activity of **4** declines with time, because of the precipitation of **4a**.

Complex **2** also displayed moderate catalytic activity in PhCl solution, undoubtedly because of its intramolecular transformation into **4** at room temperature. The ^1H NMR spectrum of **2** (in CD_2Cl_2 at 25 °C) confirmed this transformation. Addition of $AlCl_3$ in PhCl to a solution of **2** in PhCl makes the activity of this system comparable to that of **4**.

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6 **1** was prepared as described in [4c]. All reactions were carried out under an atmosphere of dry Ar using dried and purified solvents and reagents.

7 (a) **2** was precipitated under addition of hexane $EtAlCl_2$ solution to **1** toluene solution cooled to −60 °C (Mo/Al 1/2). The product was filtered off, washed with hexane and dried in vacuo. (Found: Mo, 18.21; Al, 10.09; N, 5.11; C, 22.82; Cl, 26.77; H, 4.85. $Mo(NO)_2(O\text{-}i\text{-}Pr)_2(EtAlCl_2)_2$ calcd.: Mo, 18.17; Al, 10.22; N, 5.31; C, 22.75; Cl, 26.86; H, 4.62%); (b) in Nujol mull (Specord 75 IR): ν_s(NO) 1836s; ν_{as}(NO) 1723 vs; ν(O-i-Pr) 1175 sh, 1160m, 1100br, 1025w, 978m, 925w; (c) in CD_2Cl_2 at −30 °C (Tesla BS576A, δ relative to Me_4Si): $\delta(CH_3(^iPr))$, 1.25(d, 6H); $\delta(CH(^iPr))$, 4.25(q 1H); $\delta(CH_3(Et))$, 0.98(t, 3H); $\delta(CH_2(Et))$, −0.03(q, 2H).

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9 (a) To **1** in PhCl cooled to about −5 °C, $EtAlCl_2$ in PhCl (Mo/Al 1/3) was added slowly. The solution was heated to room temperature. After 1/2 h, the solution was reduced to 1/2 volume (in vacuo, at room temperature) and from this solution **4** was precipitated with pentane and hexane at −40 °C. The product was filtered off, washed with hexane and pentane, and dried in vacuo. (Found: Mo, 19.21; Al, 10.90; N, 5.40; C, 19.40; Cl, 28.55; H, 3.97. $Mo(NO)_2(O\text{-}i\text{-}Pr)_2(AlCl_2)_2(CHMe)$ calcd.: Mo, 19.27; Al, 10.83; N, 5.63; C, 19.29; Cl, 28.48; H, 3.64%); (b) in Nujol mull: ν_s(NO) 1848vs; ν_{as}(NO) 1744vs; ν(O-i-Pr) 1168m, 1150m, 1100m, 1025sh, 985m, 962m, 925sh cm^{-1}.

10 In Nujol mull: ν_s(NO) 1822vs; ν_{as}(NO) 1720vs; ν(O-i-Pr) 1175sh, 1158m, 1100br, 1025w, 975m, 940m cm^{-1}.
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