Synthesis and properties of mono- and bis[2-(dimethylaminomethyl)]cymantrenyl derivatives of ytterbium

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The reaction of [2-(dimethylaminomethyl)]cymantrenyl]lithium with ytterbium diiodide affords [2-(dimethylaminomethyl)cymantrenyl]ytterbium iodide or bis[2-(dimethylaminomethyl)cymantrenyl]ytterbium depending on the ratio of the starting reactants. Reactions of these complexes with a series of electrophiles (H_2O, Me_3SiCl, MeCOCl, $HgCl_2$, PhCOCl) were studied and the corresponding derivatives of cymantrene were prepared in high yields.

Key words: [2-(dimethylaminomethyl)cymantrenyl]lithium; ytterbium diiodide; [2-(dimethylaminomethyl)cymantrenyl]ytterbium iodide; bis[2-(dimethylaminomethyl)cymantrenyl]ytterbium; electrophiles; derivatives of cymantrene.

To continue investigations in the field of the chemistry of metallocenyl derivatives of divalent lanthanides,[1] we prepared some cymantrenyl derivatives of divalent ytterbium, namely, those in which the ytterbium atom is located at the carbon atom next to the carbon atom of the cyclopentadienyl ring bearing a dimethylaminomethyl group, and studied their properties.

We found that [2-(dimethylaminomethyl)cymantrenyl]lithium[2] (**1**) reacts with ytterbium diiodide $YbI_2 \cdot (THF)_4$ in THF in the temperature range $-30 \div -20$ °C to afford a mixture of mono- (**2**) and disubstituted (**3**) derivatives.

$$\underset{\mathbf{1}}{(OC)_3MnC_5H_3(CH_2NMe_2)Li} + YbI_2 \cdot (THF)_4 \xrightarrow{a}$$

$$\longrightarrow \underset{\mathbf{2}}{(OC)_3MnC_5H_3(CH_2NMe_2)YbI} \xrightarrow{b}$$

$$\longrightarrow \underset{\mathbf{3}}{[(OC)_3MnC_5H_3(CH_2NMe_2)]_2Yb \cdot 2THF}$$

Reagents and conditions: *a*. THF, $-30 \div -20$ °C; *b*. $(OC)_3MnC_5H_3(CH_2NMe_2)Li$

The composition and structure of compounds **2** and **3** were determined by IR and NMR spectroscopy and X-ray fluorescence and elemental analyses.

It should be noted that compounds **2** and **3** possess unusual stability among metallocenyl derivatives of divalent lanthanides.[3] Their stabilization is apparently due to the intramolecular coordination of ytterbium by the nitrogen atom of the Me_2NCH_2 group.

Optimal conditions for preparing complexes **2** and **3** are: a THF—benzene (10:1) solvent mixture, a temperature of $-30 \div -20$ °C, and a stoichiometric ratio of the reagents. Under these conditions the yields of compounds **2** and **3** are as high as 70—80 %. The role of benzene is probably that the LiI formed in the reaction precipitates and, therefore, the formation of ate-complexes is ruled out.

Compound **2** was also prepared by the oxidative addition of zero-valent ytterbium to 1-iodo-2-(dimethylaminomethyl)cymantrene in THF. A fourfold excess of activated ytterbium was used in this reaction.

$$(OC)_3MnC_5H_3(CH_2NMe_2)I + Yb/Hg \longrightarrow$$

$$\longrightarrow \underset{\mathbf{2}}{(OC)_3MnC_5H_3(CH_2NMe_2)YbI}$$

The IR spectra of compounds **2** and **3** exhibit two intense bands in the region of stretching vibrations of carbonyl groups, at 1960—2050 cm^{-1}, which are due to the terminal CO ligands, and a ν(CO) band at

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Table 1. ^{1}H NMR spectra

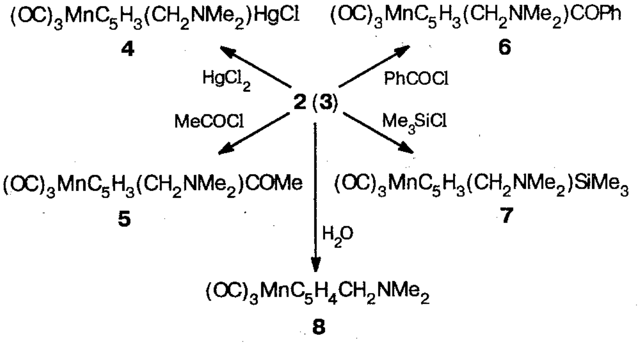
Compound	δ (C_4D_8O)		
	C_5H_5	CH_2	Me
$(OC)_3MnC_5H_5$	4.95		
$(OC)_3MnC_5H_4HgCl$	5.12; 4.88		
$(OC)_3MnC_5H_4CH_2NMe_2$	4.65; 4.62	2.82	1.99
$(OC)_3MnC_5H_3(CH_2NMe_2)I$	4.50; 4.37; 4.32	2.89	2.16
$(OC)_3MnC_5H_3(CH_2NMe_2)Li$	4.93; 4.85; 4.79	3.15; 3.77	2.36
$(OC)_3MnC_5H_3(CH_2NMe_2)YbI$	5.09; 5.02; 4.73	3.10; 3.68	2.38
$[(OC)_3MnC_5H_3(CH_2NMe_2)]_2Yb$	4.95; 4.88; 4.70	3.21; 3.81	2.30
$[(OC)_3MnC_5H_3(CH_2NMe_2)]_2Hg$	4.97; 4.89; 4.67	3.09; 3.54	2.24

1770 cm^{-1}, which should probably be assigned to vibrations of the CO group coordinatied with the lanthanide atom through an oxygen atom.

An examination of the ^{1}H NMR spectra of complexes **2** and **3** and their mercury-containing analog, $[(OC)_3MnC_5H_3CH_2NMe_2]_2Hg$, has shown that the introduction of metal-containing substituents into the *ortho*-position of dimethylaminomethylcymantrene exerts a deshielding effect on the protons of the cyclopentadienyl ligand (Table 1).

The nonequivalency of the methylene protons and the downfield displacement of the signals for the methyl and methylene protons in the spectra of Li, Yb, and Hg derivatives compared with those for $(OC)_3MnC_5H_4CH_2NMe_2$ points to additional interaction of these metals with the nitrogen atom of the Me_2NCH_2 group, which was confirmed for $[(OC)_3MnC_5H_3(CH_2NMe_2)]_2Hg$ by an X-ray structural investigation.[4]

The chemical transformations of compounds **2** and **3** under the action of the most commonly used electrophiles (H_2O, $HgCl_2$, Me_3SiCl, MeCOCl, and PhCOCl) have been studied.



Previously unknown disubstituted derivatives of cymantrene **4—7** were obtained. All of these compounds were isolated in high yields (60—80 %) and characterized by the data of elemental analysis and IR spectroscopy.

Experimental

The reactions were carried out in absolute solvents under argon. ^{1}H NMR spectra were recorded on a Bruker WP-200 SY spectrometer (200.13 MHz). Chemical shifts were measured relative to the high-field THF signal (1.85 ppm). IR spectra were measured on a Specord M-80 instrument. The X-ray fluorescence analysis was carried out on a VRA-2 instrument. $YbI_2 \cdot (THF)_4$ was prepared by the known procedure.[5]

[2-(Dimethylaminomethyl)cymantrenyl]itterbium iodide (2). 20 mL of a THF—C_6H_6 (10:1) mixture was added to compound **1** prepared from 0.76 g of $(OC)_3MnC_5H_4CH_2NMe_2$ and 2.8 mL of Bu^{n}Li (1.09 *N*), then a solution of 0.45 g of YbI_2 in 5 mL of THF was added at $-60 \div -70$ °C. The reaction mixture was stirred for 2 h and warmed up to the room temperature. The resulting turbid solution was allowed to settle and filtered. Complex **2** was precipitated by adding 50 mL of hexane. The precipitate was filtered off and dried under argon. According to X-ray fluorescence analysis, the Mn : Yb ratio was 1 : 1. IR (THF), ν/cm^{-1}: 2045, 1967, 1770 (the CO ligand).

Bis[2-(dimethylaminomethyl)cymantrenyl]itterbium (3). Complex **1** (from 0.76 g of $(OC)_3MnC_5H_4CH_2NMe_2$ and 2.8 mL of Bu^{n}Li (1.09 *N*)) was added at $-40 \div -50$ °C to a solution of compound **2** in 25 mL of THF—C_6H_6 (10:1) mixture prepared as described above. After stirring for 5 h the reaction mixture was left overnight. According to the procedure described above, 1.12 g (49 %) of compound **3** as a complex with THF was isolated. Found (%): C, 43.25; H, 4.70; Mn, 12.90. $C_{30}H_{38}Mn_2N_2O_8$. Calculated (%): C, 43.03; H, 4.58; Mn, 13.12. IR (THF), ν/cm^{-1}: 2048, 1965, 1770 (the CO ligand).

1-Chloromercuro-2-(dimethylaminomethyl)cymantrene (4). 0.8 g of $HgCl_2$ in 10 mL of THF was slowly added at

−60÷−70 °C to compound **2** prepared as described above. The reaction mixture was stirred for 1 h at −20÷−30 °C, warmed to room temperature, and treated with water. The organic layer was extracted with C_6H_6 and dried with $MgSO_4$. The solvent was removed and the residue was chromatographed on a column with SiO_2 (with benzene as the eluent) to give 1 g (73 %) of complex **4**. Found (%): C, 26.64; H, 2.06; N, 2.84; Mn, 11.0; Cl, 8.10; Hg, 39.89. $C_{11}H_{11}MnHgClNO_3$. Calculated (%): C, 26.62; H, 2.24; N, 2.82; Mn, 11.07; Cl, 7.15; Hg, 40.43. IR (C_6H_6), ν/cm^{-1}: 2048, 1940 (the CO ligand).

1-Acetyl-2-(dimethylaminomethyl)cymantrene (5). 0.6 mL of CH_3COCl was added at −60÷−70 °C to a THF solution of compound **2**. The reaction mixture was warmed up to −20÷−30 °C and stirred for 2 h. After hydrolysis, extraction with diethyl ether, and drying, the solvent was removed. The residue was chromatographed on a column with SiO_2 (with petroleum ether as the eluent) to give 0.52 g (68 %) of product **5**. Found (%): C, 51.80; H, 4.70; Mn, 19.20. $C_{13}H_{14}MnNO_4$. Calculated (%): C, 51.49; H, 4.66; Mn, 18.12. IR (C_6H_6), ν/cm^{-1}: 2025, 1930 (CO ligand); 1690 (the acetyl C=O).

Compound 6 was prepared and isolated in a similar way. Yield 0.51 g (59 %) of compound **6**. Found (%): C, 59.85; H, 4.80; N, 3.90; Mn, 15.39. $C_{18}H_{17}MnNO_4$. Calculated (%): C, 59.18; H, 4.42; N, 3.84; Mn, 15.04. IR (C_6H_6), ν/cm^{-1}: 2040, 1936 (the CO ligand), 1670 (the acetyl C=O).

1-Trimethylsilyl-2-(dimethylaminomethyl)cymantrene (7). 0.3 g of Me_3SiCl in 10 mL of THF was slowly added at 0 °C to compound **2**. The mixture was stirred for 4 h, the solvent was evaporated to afford 0.43 g (72 %) of product **7**. Found (%): C, 46.10; H, 5.65; Mn, 17.90. $C_{14}H_{20}MnNO_3Si$. Calculated (%): C, 46.06; H, 5.38; Mn, 17.30. IR (C_6H_6), ν/cm^{-1}: 2030, 1942 (the CO ligand).

Dimethylaminomethylcymantrene (8). Complex **2** prepared from 0.38 g of $(CO)_3MnC_5H_3(CH_2NMe)_2I$ and 0.8 g of Yb was dissolved in 125 mL of THF. At ~20 °C water was added dropwise. Extraction and drying gave 0.21 g (82 %) of compound **8**.

The preparation and isolation of compounds **4—8** in the reactions with complex **3** was carried out in a similar way.

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