Tetrahedron Letters,Vol.25,No.19,pp 1991-1994,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

SYNTHESES AND CHEMICOPHYSICAL PROPERTIES OF MACROCYCLIC COMPOUNDS CONTAINING A RUTHENOCENE UNIT

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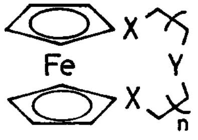
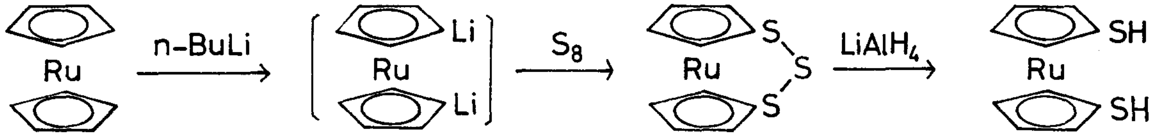
Summary: Synthesis and extraction ability of macrocyclic compounds containing ruthenocene as an integral part of the macrocyclic skelton are reported. Also, the complexes of the 1,n-dithiaoxa[n]ruthenocenophanes with transition metal cations were isolated.

Synthesis of a number of crown ethers was first reported by Pedersen twenty years ago.[1] Since that time, a large number and a variety of macrocyclic polyethers have been prepared and their cation complexing abilities have been studied extensively.[2] Recently, syntheses and metal cation complexing ability of macrocyclic compounds containing a ferrocene unit as an integral part of the macrocyclic skelton have been reported.[3] The ferrocenophanes have received much attention because the iron atom of a ferrocene nucleus may play a role as a coordinatable heteroatom. We have previously reported that polythia[n]- (**1**), polyoxa[n]- (**2**), and oxathia[n]ferrocenophanes (**3**) exhibited a considerably enhanced binding with transition metal cations, compared with the corresponding ring-membered crown ethers.[4,5] We will here report the syntheses and chemicophysical properties of novel-typed crown ethers, 1,n-dithiaoxa[n]ruthenocenophanes (**10**).



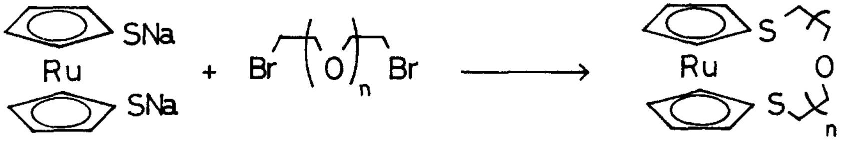
1 : X = Y = S
2 : X = Y = O
3a : X = S, Y = O
3b : X = O, Y = S

The 1,n-dithiaoxa[n]ruthenocenophanes (**10a-c**) were obtained as follows. The reaction of 1,1'-dilithioruthenocene (**5**), which was prepared from ruthenocene (**4**) and n-butyllithium in the presence of TMEDA, with sulfur gave 1,2,3-trithia[n]ruthenocenophane (**6**) in 43% yield. Reduction of **6** with $LiAlH_4$ in boiling ether afforded a 94% yield of ruthenocene-1,1'-dithiol (**7**). Disodium ruthenocene-1,1'-dithiolate (**8**), which was prepared from the reaction of **7** with aqueous sodium hydroxide in ethanol, was allowed to react with dihalide (**9a**) in



4 5 6 7

aqueous ethanol using high dilution conditions to give 1,16-dithia-4,7,10,13-tetraoxa[16]ruthenocenophane (**10a**) as pale yellow crystals in 17% yield. In the same manner, the reaction of **8** with the dihalide (**9b**) and (**9c**) also gave 1,13-dithia-4,7,10-trioxa[13]ruthenocenophane (**10b**) and 1,10-dithia-3,7-dioxa[10]-ruthenocenophane (**10c**) in 48 and 23% yield, respectively. The structures of the new compounds (**6**, **7**, and **10a-c**) were determined on the basis of their elemental analyses, IR, electronic, mass, ^{1}H-NMR and ^{13}C-NMR spectra.[6]



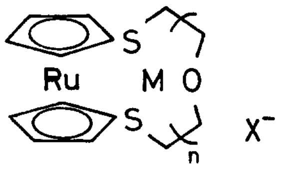
8

9a : n = 4
b : n = 3
c : n = 2

10a : n = 4
b : n = 3
c : n = 2

The extraction ability of **10a-c** with alkali, alkaline-earth and transition metal cations was measured by the Pedersen's method.[7] It was found that **10a-c** showed little or no extraction ability with alkali and alkaine-earth metal cations, while they showed relatively high extraction ability with transition metal cations. For a silver cation, **10a-c** have an excellent extraction ability (99%), compared with the corresponding dithiaoxa[n]ferrocenophanes.[4a] However, **10a-c** showed selectivity toward Hg^{2+} and Tl^+ [**10b** (95%), **10c** (95%) and **10a** (30%) for Hg^{2+}; **10a** (87%), **10b** (33%), **10c** (2%) for Tl^+]. It is noteworthy that these results were supported by the electronic spectral study. For example, a hypsochromic shift (10 nm) and a decreased absorbance (15-19%) in the absorption peak at 320 nm (a spin-allowed d-d transition band)[8] were observed on complexing of silver nitrate to **10a-c** in aqueous methanol (H_2O:MeOH=1:1), but not in the case of alkali metal nitrates. The electronic spectral changes are similar to those of the complexing of 1,n-dithiaoxa[n]ferrocenophanes (**3a**) with metal nitrates.[4]

The complexes of **10** with $HgCl_2$ and $AgNO_3$, (**11a**) and (**11b**), respectively, were isolated. These complexes showed higher melting points than the metal-free lignads (**10a-c**) and were confirmed by microanalysis to be 1:1 complexes. Their ^{1}H-NMR and electronic spectra provided further information about the structure of the complex (**11a**). In the ^{1}H-NMR spectrum (CD_3CN) of **11a**, the signals of



11a : n = 4, M = Hg^{2+}
X = Cl$_2$
11b : n = 3, M = Ag$^+$
X = NO$_3$

methylene protons next to a sulfur atom, α-, and β-ring protons of ruthenocene nucleus were shifted downfield only +0.19, +0.03, and -0.03 ppm, compared with those of **10a**, respectively. On the other hand, the ^{1}H-NMR spectrum of the complex Cp$_2$Ru·HgCl$_2$ (**12**)[9] in CD$_3$CN shows a signal at δ 5.31 corresponding to the Cp ring protons. The downfield shift of the Cp ring protons of **12**, compared with those of **4**, is about +0.7 ppm. Hence, the difference in the chemical shifts between the free ligand (**10a**) and the complex (**11a**) seems to be attributable to complexation of Hg^{2+} cation into the crown ether part of the ligand, although a possibility of the direct coordination of the incorporated Hg^{2+} to the Ru atom of ruthenocene nucleus cannot be ruled out. The above explanation was supported by the electronic spectral study. The complex **11a** in acetonitrile exhibits no charge-transfer absorption of the type Cp$_2$Ru$\rightarrow$HgCl$_2$ at 280 nm,[9] although the absorption band at 320 nm showed a hypsochromic shift (10 nm) and a decrease of its absorbance (4%).

Further studies on the synthesis of the related ruthenocenophanes are in progress.

References and footnotes

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6. All new compounds gave satisfactory elemental analyses and spectral data. Selected physical and spectral data for **6**, **7**, **10a-c**, and **11a-b** are as follows.
   6: m.p. 183.5-184.0°C, MS (m/e) 326 (M$^+$+1, 20%) and 325 (M$^+$, 100%), ^{1}H-NMR (CDCl$_3$) δ 4.48 (m, 4H), 4.87 (m, 4H).
   7: m.p. 116.8-117.8°C, MS (m/e) 396 (M$^+$+1, 25%) and 325 (M$^+$, 100%), ^{1}H-NMR

(CDCl$_3$) δ 2.25 (s, SH, 2H), 4.47 (t, J=1.8 Hz, H$_\alpha$, 4H), and 4.66 (t, J=1.8 Hz, H$_\beta$, 4H).

10a: m.p. 46.2-48.0°C, MS (m/e) 499 (M^++1, 28%) and 498 (M^+, 100%), ^{1}H-NMR (CD$_3$CN) δ 4.74 (t, J=1.7 Hz, H$_\alpha$, 4H), 4.61 (t, J=1.7 Hz, H$_\beta$, 4H), 3.63 (t, J=6.3 Hz, $OC\underline{H}_2CH_2S$, 4H), 3.51 (s, $OC\underline{H}_2C\underline{H}_2O$, 12H), 2.86 (t, J=6.3 Hz, $SC\underline{H}_2CH_2O$, 4H). ^{13}C-NMR (CD$_3$CN) δ 88.1 (C$_b$), 77.3 (C$_\alpha$), 72.6 (C$_\beta$), 71.5 (OCH$_2$), 71.3 (OCH$_2$), 70.9 (OCH$_2$), 39.6 (SCH$_2$). UV (CH$_3$CN): 320 nm (ε 472).

10b: m.p. 38.5-39.2°C, MS (m/e) 455 (M^++1, 25%) and 454 (M^+, 100%), ^{1}H-NMR (CD$_3$CN) δ 4.76 (t, J=1.7 Hz, H$_\alpha$, 4H), 4.61 (t, J=1.7 Hz, H$_\beta$, 4H), 3.61 (t, J=6.3 Hz, $SCH_2C\underline{H}_2O$, 4H), 3.59 (s, $OC\underline{H}_2C\underline{H}_2O$, 8H), 2.87 (t, J=6.3 Hz, $SC\underline{H}_2CH_2O$, 4H). ^{13}C-NMR (CD$_3$CN): δ 89.2 (C$_b$), 77.0 (C$_\alpha$), 72.3 (C$_\beta$), 71.4 (OCH$_2$), 71.2 (OCH$_2$), 70.5 (OCH$_2$), 39.0 (SCH$_2$). UV (CH$_3$CN) 320 nm (ε 472).

10c: m.p. 101.0-101.5°C, MS (m/e) 411 (M^++1, 23%) and 410 (M^+, 100%), ^{1}H-NMR (CD$_3$CN) δ 4.79 (t, J=1.7 Hz, H$_\alpha$, 4H), 4.62 (t, J=1.7 Hz, H$_\beta$, 4H), 3.65 (s, $OC\underline{H}_2C\underline{H}_2O$, 4H), 3.73 (t, J= 6.3 Hz, $SCH_2C\underline{H}_2O$, 4H), 3.14 (t, J=6.3 Hz, $SC\underline{H}_2CH_2O$, 4H). ^{13}C-NMR (CD$_3$CN): δ 90.4 (C$_b$), 77.1 (C$_\alpha$), 72.0 (C$_\beta$), 71.5 (OCH$_2$), 70.8 (OCH$_2$), and 39.6 (SCH$_2$). UV (CH$_3$CN) 320 nm (ε 472).

11a: m.p. 172.0-173.0°C, ^{1}H-NMR (CD$_3$CN) δ 4.93 (t, J=1.8 Hz, H$_\alpha$, 4H), 4.64 (t, J= 1.8 Hz, H$_\beta$, 4H), 3.68 (t, J=6.0 Hz, $OC\underline{H}_2CH_2S$, 4H), 3.52 (s, $OC\underline{H}_2C\underline{H}_2O$, 4H), 2.83 (t, J=1.8 Hz, $SC\underline{H}_2CH_2O$, 12H). UV (CH$_3$CN) 310 nm (ε 455).

11b: m.p. 157.0-157.5°C, ^{1}H-NMR (CD$_3$CN) δ 4.91 (t, J=1.8 Hz, H$_\alpha$, 4H), 4.77 (t, J=1.8 Hz, H$_\beta$, 4H), 3.72 (t, J=6.3 Hz, $SCH_2C\underline{H}_2O$, 4H), 3.68 (s, $OC\underline{H}_2C\underline{H}_2O$, 8H), 3.08 (t, J=6.3 Hz, $SC\underline{H}_2CH_2O$, 4H). UV (CH$_3$CN) 310 nm (383).

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(Received in Japan 30 January 1984)