Synthesis and Diastereoselective Structural Change of a Photochromic Transition Metal Complex, (η^6-Spirobenzopyran)(tricarbonyl)chromium

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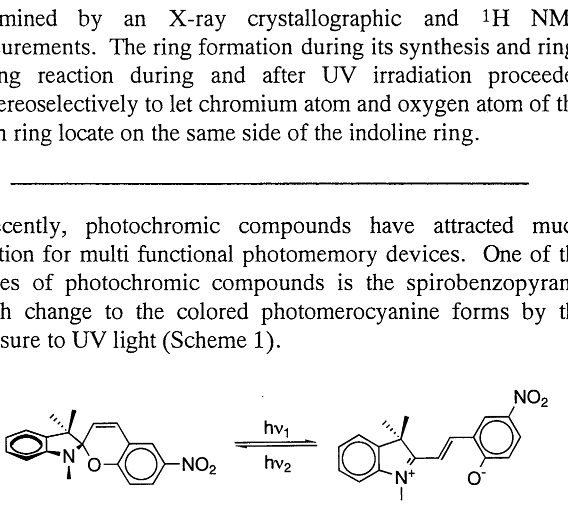
Photochromic transition metal complexes, (η^6-spirobenzopyran)$Cr(CO)_3$, were synthesized and the structure was determined by an X-ray crystallographic and ^1H NMR measurements. The ring formation during its synthesis and ring-closing reaction during and after UV irradiation proceeded diastereoselectively to let chromium atom and oxygen atom of the pyran ring locate on the same side of the indoline ring.

Recently, photochromic compounds have attracted much attention for multi functional photomemory devices. One of the classes of photochromic compounds is the spirobenzopyrans, which change to the colored photomerocyanine forms by the exposure to UV light (Scheme 1).

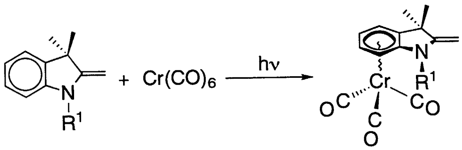


Scheme 1.

Successful efforts to use thermally reversible spiropyrans as optical information storage media have been made.[1,2] Because of its intrinsic property, however, information stored by photochromic compounds could be damaged on memory reading even by weak light exposure. In order to overcome this weakness, application of optical rotation is expected to be a good solution for non-destructive readout.[3] For the use of this technique, it is necessary to design chiral photochromic compounds and to perform their stereospecific transformation.

In this paper, we wish to report the synthesis of racemic but potentially resolvable spiropyrans having a chromium tricarbonyl unit. Due to the dual asymmetric units, that is the spiro carbon atom and the coordination site of chromium, this type of metal complexes can be a mixture of diastereomers.[4] The molecular structure of the major diastereomer of one of the compounds and the diastereoselective thermal and photochemical ring closure of the merocyanine forms are also reported.

N-Alkyl-3,3-dimethyl-2-methyleneindolines (**1**), which were easily prepared by the literature method from 2,3,3-trimethylindolenine,[5] were allowed to react with $Cr(CO)_6$ by exposure to 100W high pressure mercury lamp at 140°C to afford corresponding (η^6-*N*-alkyl-3,3-dimethyl-2-methyleneindoline)(tricarbonyl)-chromium (**2**) as shown in Scheme 2.

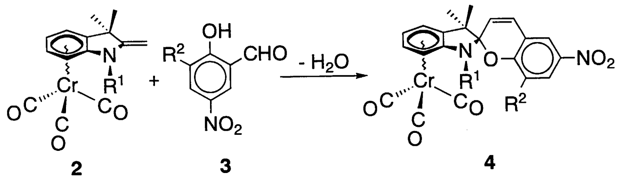


1 **2**

2a : $R^1 = CH_3$
2b : $R^1 = C_{18}H_{37}$

Scheme 2.

The structures of novel chromium tricarbonyl complexes **2** were assigned by ^1H NMR and IR spectra as follows.[6] For example, ^1H NMR spectrum of **2a** gave its aromatic protons at 4.70 (t), 4.81 (d), 5.51 (t) and 5.69 (d) ppm ($CDCl_3$), that is 1.40~2.05 ppm upfield from those of **1**, while the chemical shifts of methyl group on nitrogen and *exo*-methylene shifted only 0.12 and 0.28 ppm upfield, respectively. The IR spectrum of **2a** gave two ν(CO) bands at 1941 and 1845 cm^{-1}. As these data corresponds to typical (η^6-arene)chromium tricarbonyl structure,[6] complexes **2** were concluded to be (η^6-1-alkyl-3,3-trimethyl-2-methyleneindoline)$Cr(CO)_3$ having a piano-stool structure. (η^6-Spirobenzopyran)$Cr(CO)_3$ complexes (**4**) were obtained by the reaction of **2** with 5-nitrosalicylaldehyde derivatives (**3**) in the dark (Scheme 3). Their ^1H NMR and IR data also suggested the structures[7] shown in Scheme 3.



2 **3** **4**

2a : $R^1 = CH_3$
2b : $R^1 = C_{18}H_{37}$

3a : $R^2 = H$
3b : $R^2 = CH_2{=}C(CH_3)COOCH_2$

4a : $R^1 = CH_3$, $R^2 = H$
4b : $R^1 = CH_3$, $R^2 = CH_2{=}C(CH_3)COOCH_2$
4c : $R^1 = C_{18}H_{37}$, $R^2 = CH_2{=}C(CH_3)COOCH_2$

Scheme 3.

Of particular interest is that only one diastereomer (a pair of enantiomers) was obtained for both **4a** and **4b** from the reactions of **2a** with **3a** and **3b** at room temperature, respectively. However, the reaction of **2b** with **3b** gave a diastereomeric mixture, which was easily separated by column chromatography. We have observed that the C-O bond of spirobenzopyrans is cleaved at room temperature without exposure to light.[8] However, neither **4a** nor **4b** epimerized at room temperature in the dark. This fact indicates that they are thermodynamically favorable diastereomers. Indeed, the HPLC study showed that **4b** gave a 1/1 diastereomer mixture at 60 °C in benzene in the dark, indicating the equilibrium between diastereomers at this temperature. Contrary to **4a** and **4b**, **4c** gave a diastereomeric mixture at room temperature probably because of more steric

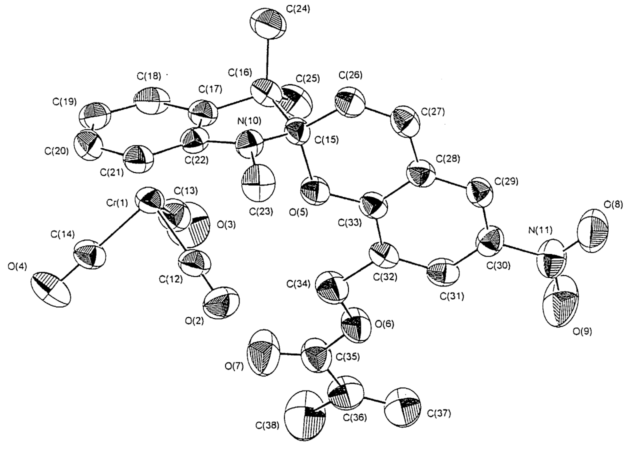


Figure 1. ORTEP drawing of **4b**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)-C(17), 2.284(6); Cr(1)-C(18), 2.241(7); Cr(1)-C(19), 2.210(7); Cr(1)-C(20), 2.189(7); Cr(1)-C(21), 2.233(7); Cr(1)-C(22), 2.297(7); O(5)-C(15), 1.493(9); O(5)-C(15)-N(10), 106.6(6); O(5)-C(15)-C(16), 107.6(5); O(5)-C(15)-C(26), 110.6(6); N(10)-C(15)-C(16), 103.8(5); N(10)-C(15)-C(26), 110.9(6); C(16)-C(15)-C(26), 116.7(6).

congestion.

The crystal structure of **4b** was determined by X-ray crystallographic analysis[9] and shown in Figure 1 as the ORTEP drawing. Figure 1 clearly shows that **4b** has the *endo* form in which the oxygen atom in benzopyran ring faces to the chromium atom in spite of the bulky methacryloxymethyl group. The distortion of benzopyran ring directing toward the chromium tricarbonyl moiety is probably due to the interaction between the chromium and oxygen atoms (3.76 Å).

Of particular interest is that the O(5)-C(15) bond distance of **4b** (1.49 Å) is almost identical to that found in the uncoordinated spirobenzopyran (1.49 Å), which is a little longer than typical C(sp^3)-O bond (1.42 Å).[10] It is expected that such a stretched C-O bond is easy to cleave upon UV irradiation.

The structures of **4** in solution were also investigated by ^{1}H NMR and ^{1}H-^{1}H NOESY measurements. It was confirmed that **4a**, **4b**, and the major species of **4c** were the *endo* form (2*S*, 3a*S* / 2*R*, 3a*R*), which means that oxygen atom in benzopyran ring faces to the chromium atom as shown by the crystal structure in the previous paragraph. This fact suggests that the Cr atom plays an important role in the ring closure process to form spirobenzopyran structure. The minor species of **4c** was independently confirmed to be the *exo* form also from NMR measurements.

These novel spirobenzopyrans bearing chromium complexes showed reversible color change due to photochromism (λ_{max} = 564 nm ($\tau_{1/2}$ = 0.7 min) for **4a**, 557 nm ($\tau_{1/2}$ = 3.4 min) for **4b**, 566 nm ($\tau_{1/2}$ = 10 min) for **4c** in acetone at 28 °C). During and after UV irradiation, only the major diastereomer (a pair of enantiomers) was observed for **4a** and **4b**, indicating that the stereochemical feature of these compounds was preserved.

In summary, new photochromic metal complexes, (η^6-spirobenzopyran)Cr(CO)$_3$ were synthesized. As the result of intramolecular metal-oxygen interaction, only one diastereomer (a pair of enantiomers) was obtained for **4a** and **4b**. The crystal structure of the major diastereomer was determined for **4b**. Because phenyl-chromium complex is thermally stable, these compounds are potentially resolvable into enantiomers.[11] The stereochemistry was confirmed to be retained during photochromic transformation. This may provide a new means of non-destructive readout using the change of optical rotation when this kind of chiral spiropyrans are used as the optical information storage media.

References and Notes

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6 Spectroscopic data for **2a**: yield 53 %; ^{1}H NMR (200 MHz, CDCl$_3$): δ1.34 (s, 3-CH_3, 3H), 1.50 (s, 3-CH_3, 3H), 2.92 (s, N-CH_3, 3H), 4.12 (s, 2-CH_2, 2H), 4.70 (t, ^3J = 6.2 Hz, 5-*H*, 1H), 4.81 (d, ^3J = 6.6 Hz, 7-*H*, 1H), 5.51 (t, ^3J = 6.4 Hz, 6-*H*, 1H), 5.69 (d, ^3J = 6.0 Hz, 4-*H*, 1H); FT-IR (KBr, cm^{-1}): 2971 (m, ν(C-H)), 2856 (m, ν(C-H)), 1941 (vs, ν_{asym}(C≡O)), 1845 (vs, ν_{sym}(C≡O)), 1552, 1490 (s, ν(C=C)$_{ring}$), 1316 (m, ν(C-N)), 671 (s, δ(C=C)$_{ring}$)

7 Spectroscopic data for **4b**: yield 68 %; ^{1}H NMR (400 MHz, CDCl$_3$): δ1.20 (s, 3-CH_3, 3H), 1.41 (s, 3-CH_3, 3H), 1.99 (s, CH$_2$=C(CH_3)CO-, 3H), 2.84 (s, N-CH_3, 3H), 4.90 (t, ^3J = 6.5 Hz, 5-*H*, 1H), 4.93 (d, ^3J = 6.7 Hz, 7-*H*, 1H), 5.47 (d, ^3J = 6.7 Hz, 4-*H*, 1H), 5.50 (t, ^3J = 6.8 Hz, 6-*H*, 1H), 5.56 (d, *J* = 14.9 Hz, 8'-CH_2-, 1H), 5.59 (d, *J*cis = 10.5 Hz, 3'-*H*, 1H), 5.63 (t, CH_2=C(CH$_3$)CO-, 1H), 5.66 (d, *J* = 14.5 Hz, 8'-CH_2-, 1H), 6.22 (s, CH_2=C(CH$_3$)-CO-, 1H), 6.91 (d, *J*cis = 10.2 Hz, 4'-*H*, 1H), 7.94 (d, ^4J = 2.7 Hz, 5'-*H*, 1H), 8.14 (d, ^4J = 2.6 Hz, 7'-*H*, 1H); FT-IR (KBr, cm^{-1}): 2967 (w, ν(C-H)), 2934 (w, ν(C-H)), 1943 (vs, ν_{asym}(C≡O)), 1861 (vs, ν_{sym}(C≡O)), 1725 (s, ν(C=O)), 1589 (w, ν(C=C)$_{ring}$), 1523 (m, ν_{asym}(N=O)), 1481 (m, ν(C=C)$_{ring}$), 1341 (s, ν_{sym}(N=O)), 1251 (m, ν(C-N)), 1155 (s, ν_{asym}(C-O-C)), 1084 (m, ν_{sym}(C-O-C)), 933 (m, δ(C-H)), 670 (m, δ(C=C)$_{ring}$), 636 (m, δ(C=C)$_{ring}$); MS (EI, 70 eV): m/z = 556 (M$^+$); Anal. Found: C, 58.18; H, 4.22; N, 4.91 %. Calcd for $C_{27}H_{24}O_8N_2Cr$: C, 58.28; H, 4.35; N, 5.04 %.

8 A. Miyashita, T. Kuwayama, M. Hirano, and H. Nohira, unpublished results.

9 Crystallographic data for **4b**: $C_{27}H_{24}O_8N_2Cr$, *Fw* = 556.50, monoclinic, space group $P2_1/n$, a = 19.188(5) Å, b = 12.078(3) Å, c = 11.214(3) Å, β = 98.25(2) °, V = 2572 Å^3, Z = 4, D_{calc} = 1.437 g/cm^3, $R(R_w)$ = 0.051 (0.053) for 4480 unique reflections.

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