

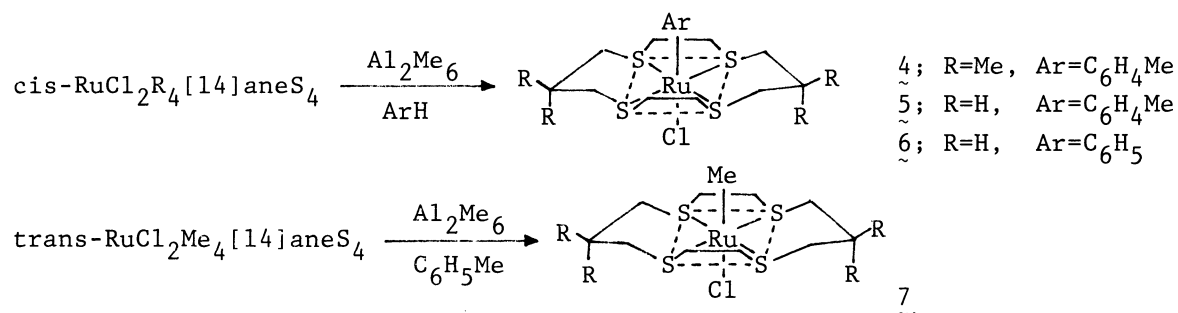
Methyl and Aryl Ru(II) Complexes of Crown Thioethers,  $R_4[14]aneS_4$  ( $R=Me, H$ ).  
 Remarkable Geometrical Effect on Intermolecular  $C(sp^2)-H$  Bond  
 Activation by cis- and trans- $RuCl_2R_4[14]aneS_4-Al_2Me_6$

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A reaction of cis- $RuCl_2R_4[14]aneS_4$  ( $R=Me, H$ ) with  $Al_2Me_6$  in aromatic hydrocarbons proceeds through an intermolecular  $C(sp^2)-H$  bond activation affording trans- $RuAr(Cl)R_4[14]aneS_4$  ( $Ar=C_6H_4Me, C_6H_5$ ), while a similar reaction of trans isomer gives trans- $RuMe(Cl)Me_4[14]aneS_4$ .

In quadridentate crown thioether complexes of transition metals, the ring size of the macrocycles plays an important role in determining chemical and physical properties of the complexes.<sup>1)</sup> Recently we have shown that the nucleophilicity of square planar Rh(I) complexes of 1,4,8,11-tetrathiacyclotetradecane ( $[14]aneS_4$ ) and 6,6,13,13-tetramethyl analogue ( $Me_4[14]aneS_4$ ) is also affected by the conformation of the rings.<sup>2)</sup> Now we found that two geometrical isomers of the corresponding Ru(II) complexes, cis- $RuCl_2R_4[14]aneS_4$  (1,  $R=Me$ ; 2,  $R=H$ <sup>3)</sup>) and trans- $RuCl_2Me_4[14]aneS_4$  (3), react quite differently with  $Al_2Me_6$  in aromatic hydrocarbons affording aryl and methyl complexes, respectively.

A starting material 1 was prepared by treating  $RuCl_2(PPh_3)_3$  with  $Me_4[14]aneS_4$  in toluene ( $60^\circ C, 3 h$ ) ( $\nu(Ru-Cl)$  245, 260  $cm^{-1}$ ). On heating in chlorobenzene ( $100^\circ C, 24 h$ ) 1 isomerized into the corresponding trans-isomer 3 ( $\nu(Ru-Cl)$  295  $cm^{-1}$ ). A reaction of 1 with an equimolar amount of  $Al_2Me_6$  in toluene at  $-20^\circ C$  for 15 min and subsequent decomposition of organoaluminum compounds with  $H_2O$  at the same temperature gave trans- $RuC_6H_4Me(Cl)Me_4[14]aneS_4$  (4)<sup>4)</sup> as pale yellow crystals (48%) rather than an expected methyl complex. The compound 4 was also obtained by treating 1 with  $MeMgBr$  under the similar conditions. The generality of inter-



molecular  $C(sp^2)$ -H activation with  $cis\text{-RuCl}_2R_4[14]aneS_4\text{-Al}_2Me_6$  system was confirmed by the formation of  $trans\text{-RuAr(Cl)[14]aneS}_4$  (**5**,  $Ar=C_6H_4Me$ ; **6**,  $Ar=C_6H_5$ )<sup>4)</sup> from the reaction of **2** with  $Al_2Me_6$  in the respective aromatic hydrocarbons. The ratio of m- and p-tolyl isomers of **5** was 4. In sharp contrast to the facile formation of the aryl complexes from **1** and **2**, a reaction of trans-isomer **3** with  $Al_2Me_6$  in toluene under the similar conditions produced a pale yellow methyl complex,  $trans\text{-RuMe(Cl)Me}_4[14]aneS_4$  (**7**)<sup>4)</sup> as the sole isolable product (38%). The  $^1H$  NMR spectra of **4-7** indicate that the organic and chloro ligands are mutually trans and  $R_4[14]aneS_4$  assumes all up conformation with chair and envelope forms for two  $RuSCH_2CH_2CH_2S$  and  $RuSCH_2CH_2S$  rings, respectively. We are currently studying the mechanism of  $C(sp^2)$ -H activation by the present system to elucidate the remarkable geometrical effect. Suffice it to say that the  $C(sp^2)$ -H activation takes place through an intermediacy of Ru(II) species and its mechanism probably differs from those mediated by 16-electron Ru(0) fragments such as  $Ru(Me_2PCH_2CH_2PMe_2)_2$ ,<sup>5a)</sup>  $Ru(CH_2=CH_2)(PPh_3)_3$ ,<sup>5b)</sup> and  $Ru(PR_3)(\eta^6\text{-arene})$ .<sup>5c)</sup>

This work is partly supported by Grant-in-Aid for Scientific Research (No. 60470048 and 61125004) from the Ministry of Education, Science, and Culture.

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- 4) Satisfactory elemental analyses and mass spectra were obtained for all new compounds.  $^1H$  NMR( $\delta$ , J in Hz,  $CDCl_3$ ): **4**; 1.04 and 1.17(s,  $SCH_2CMe_2$ ), 2.64 and 4.01(d,  $J=11.0$ ,  $SCH_2CMe_2$ ), 2.81-3.41(m,  $SCH_2CH_2S$ ), 2.19(s,  $MeC_6H_4$ ), 6.33-6.93(m, Ar). **5**; 1.80(dtt,  $J_{gem}=-16.48$ ,  $J_{vic}=1.80$ , 12.80,  $SCH_2CH_2CH_2S$ ), 2.48(dtt,  $J_{gem}=-16.48$ ,  $J_{vic}=1.53$ , 5.80,  $SCH_2CH_2CH_2S$ ), 3.03(ddd,  $J_{gem}=-10.68$ ,  $J_{vic}=1.80$ , 5.80,  $SCH_2CH_2CH_2S$ ), 4.01(ddd,  $J_{gem}=-10.68$ ,  $J_{vic}=1.53$ , 12.80,  $SCH_2CH_2CH_2S$ ), 2.85 and 3.15(m,  $J_{gem}=-12.27$ ,  $J_{vic}=5.54$ , 7.69,  $SCH_2CH_2S$ ), 2.19(s, p- $MeC_6H_4$ ), 2.23(s, m- $MeC_6H_4$ ), 6.53, 6.76, 6.95, and 6.96(m, m- $MeC_6H_4$ ), 6.72 and 7.04(d, p- $MeC_6H_4$ ). **6**; 1.80(dtt,  $J_{gem}=-16.48$ ,  $J_{vic}=1.84$ , 12.82,  $SCH_2CH_2CH_2S$ ), 2.50(dtt,  $J_{gem}=-16.48$ ,  $J_{vic}=1.53$ , 5.80,  $SCH_2CH_2CH_2S$ ), 3.05(ddd,  $J_{gem}=-10.68$ ,  $J_{vic}=1.84$ , 5.80,  $SCH_2CH_2CH_2S$ ), 4.02(ddd,  $J_{gem}=-10.68$ ,  $J_{vic}=1.53$ , 12.82,  $SCH_2CH_2CH_2S$ ), 2.86 and 3.16(m,  $J_{gem}=-12.32$ ,  $J_{vic}=5.56$ , 7.52,  $SCH_2CH_2S$ ), 6.72(dt,  $J=1.22$ , 7.32, p-H), 6.86(dd,  $J=7.32$ , 7.93, m-H), 7.17(dd,  $J=1.22$ , 7.93, o-H). **7**; 1.06 and 1.17(s,  $SCH_2CMe_2$ ), 2.67 and 3.89(d,  $J=11.0$ ,  $SCH_2CMe_2$ ), 2.84-3.39(m,  $SCH_2CH_2S$ ), -0.55(s, RuMe).
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(Received January 20, 1988)