

Preliminary communication

PREPARATION AND REACTIONS OF TRIHALOGENO(PENTAMETHYLCYCLOPENTADIENYL)RUTHENIUM(IV)

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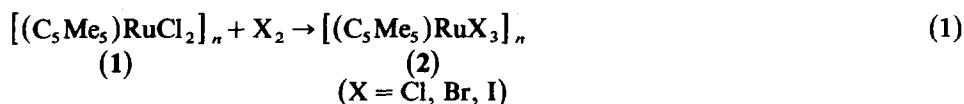
Summary

The reaction of $[(C_5Me_5)RuCl_2]_m$ with halogen (Cl_2 , Br_2 , and I_2) in dichloromethane gives trihalogenoruthenium(IV) complexes, $[(C_5Me_5)RuX_3]_n$ ($X = Cl, Br,$ and I), (**2**) in excellent yields. The Ru^{IV} complexes formulated as $(C_5Me_5)RuX_3(L)$ (**3**) are formed in the reaction of complex **2** with triphenylphosphine or carbon monoxide in dichloromethane, while treatment of complex **2** with triphenylphosphine or pyridine in ethanol exclusively affords Ru^{III} complexes, $(C_5Me_5)RuX_2(L)$ (**4**).

Although the development of the rich stoichiometric and homogeneous catalytic chemistry of the late transition metal elements in high oxidation states has been expected in comparison with that of high valent complexes of early transition metal elements, there have been only several reported examples of Group VIII B metal complexes in high oxidation states. Ruthenium(IV) organometallic complexes so far reported have been synthesized via oxidative addition of a hydrogen or halogen molecule to ruthenium(II) complexes [1]. We have recently reported the preparation of allylruthenium(IV) complexes [2]. We describe here a novel and facile synthetic route to ruthenium(IV) complexes containing only a C_5Me_5 group and halogen as auxiliary ligands and a number of complexes derived from them.

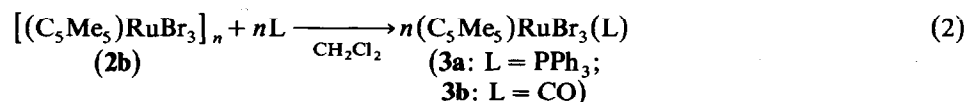
Treatment of an oligomeric ruthenium(III) complex, $[(C_5Me_5)RuCl_2]_m$ (**1**) (0.867 g, 2.82 mmol) [3], with bromine (1.2 ml, 23.4 mmol) in dichloromethane (15 ml) at ambient temperature for 5 h gave on work-up a tribromoruthenium(IV) complex $[(C_5Me_5)RuBr_3]_n$ (**2b**) in 89% yield as purple microprisms. In a similar manner, the corresponding trichloro- and triiodo-ruthenium(IV) complexes, $[(C_5Me_5)RuCl_3]_n$ (**2a**) and $[(C_5Me_5)RuI_3]_n$ (**2c**), were obtained by treatment of **1** with excess Cl_2 or I_2 , respectively (eq. 1). When the dichlororuthenium(III) complex **1** was treated with

1 equiv. of I_2 , the mixed trihalogeno complex, $[(C_5Me_5)RuCl_2I]_n$ (**2d**), was obtained in a 77% yield.

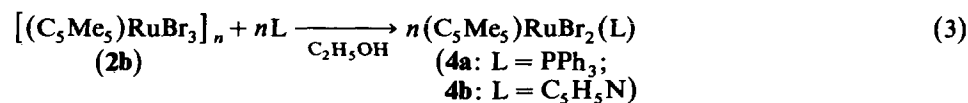


Trihalogenoruthenium(IV) complexes **2a–2d** were characterized on the basis of microanalytical data and IR spectra. **2a**: brown-black powder, 91%; m.p. > 280°C; IR (KBr): 2901, 1464, 1423, 1366, 1078, 1008, 998 and 333 cm^{-1} . Found: C, 34.59; H, 4.38; Cl, 30.11. $C_{10}H_{15}Cl_3Ru$ calcd.: C, 35.05; H, 4.41; Cl, 31.04%. **2b**: purple microprisms, 89%; M.p. > 280°C; IR (KBr): 2988, 2950, 2905, 1476, 1369, 1076, and 1003 cm^{-1} . Found: C, 24.77; H, 3.16; Br, 50.71. $C_{10}H_{15}Br_3Ru$ calcd.: C, 25.23; H, 3.18; Br, 50.36%. **2c**: brown-black powder, 87%; m.p. 181°C; IR (KBr): 2942, 2877, 1472, 1447, 1421, 1372, 1073, and 1006 cm^{-1} . Found: C, 19.27; H, 2.45; I, 58.30. $C_{10}H_{15}I_3Ru$ calcd.: C, 19.47; H, 2.45; I, 61.70%. **2d**: brown-black powder, 77%; m.p. > 280°C; IR (KBr): 2954, 2904, 1472, 1423, 1371, 1074, 1009, and 610 cm^{-1} . Found: C, 27.61; H, 3.48; Cl + I, 45.64. $C_{10}H_{15}Cl_2IRu$ calcd.: C, 27.67; H, 3.51; Cl + I; 45.57%. Poor solubility of the trihalogenoruthenium complexes **2a–2d** in most of organic solvents suggests that **2a–2d** have an oligomeric structure bridged by halogen atoms.

Upon treatment of tribromide **2b** with a two-electron donor such as triphenylphosphine or carbon monoxide in dichloromethane, coordinative addition occurred to give electronically saturated (18e) ruthenium(IV) complexes (eq. 2). **3a**: dark brown microprisms, 55%; m.p. 184°C; IR (KBr): 3047, 2966, 2800, 1586, 1480, 1436, 1371, 1185, 1121, 1090, 1015, 742, 723, 695, and 344 cm^{-1} ; 1H NMR ($CDCl_3/TMS$): δ 1.57 (15H, s), and 7.3–7.8 ppm (15H, m); ^{31}P $\{^1H\}$ NMR ($CDCl_3/external PPh_3$) δ 35.2 ppm. Found: C, 46.27; H, 3.97. $C_{28}H_{30}Br_3PRu$ calcd.: C, 45.55; H, 4.10%. **3b**: red-purple microprisms, 54%; m.p. 156°C; IR (KBr): 2972, 2925, 2047, 1470, 1423, 1373, 1204, 1004, and 486 cm^{-1} . Found: C, 27.07; H, 2.84. $C_{11}H_{15}OBr_3Ru$ calcd.: C, 26.21; H, 3.00%.

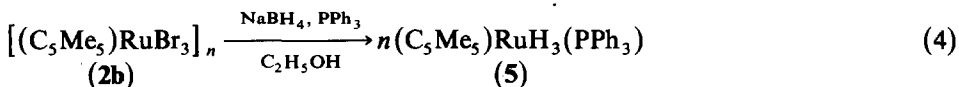


On the other hand, treatment of **2b** with PPh_3 in ethanol at ambient temperature for 1 d led to the exclusive formation of a stable paramagnetic ruthenium(III) complex, $(C_5Me_5)RuBr_2(PPh_3)$ (**4a**) accompanied by the oxidation of ethanol to afford acetaldehyde (eq. 3). The pyridine analogue of complex **4a**, $(C_5Me_5)RuBr_2(C_5H_5N)$ (**4b**), was similarly obtained by the reaction of **2b** with pyridine in ethanol (eq. 3). **4a**: brown needles, 93%; m.p. 213°C; IR (KBr): 3051, 2979, 2956, 2905, 1585, 1570, 1481, 1435, 1373, 1090, 1018, 747, 700, 529, and 490 cm^{-1} ; μ_{eff} 1.77 B.M. Found: C, 50.80; H, 4.78. $C_{28}H_{30}Br_2PRu$ calcd.: C, 51.08; H, 4.59%. **4b**: brown-red microprisms, 33%; m.p. 230°C; IR (KBr): 3046, 2976, 2952, 2910, 1594, 1479, 1444, 1377, 1209, 1061, 1021, 774, and 703 cm^{-1} ; μ_{eff} 1.98 B.M. Found: C, 38.05; H, 3.75. $C_{15}H_{20}Br_2NRu$ calcd.: C, 37.91; H, 4.24%.



Effective magnetic moments of 1.77 and 1.98 B.M. for complexes **4a** and **4b**, respectively, show that these are paramagnetic complexes with d^5 configuration.

Tribromide **2b** reacted with excess NaBH_4 (5.0 equiv.) in dry ethanol in the presence of PPh_3 (1.3 equiv.) to give a trihydride complex, $(\text{C}_5\text{Me}_5)\text{RuH}_3(\text{PPh}_3)$ (**5**), in an 18% yield (eq. 4). **5**: pale brown prisms; m.p. 136°C ; IR (KBr): 3052, 2972,



2896, 1974 (Ru–H), 1960 (Ru–H), 1479, 1434, 1375, 1091, 758, 744, 699, 538, and 514 cm^{-1} ; ^1H NMR ($\text{C}_6\text{D}_6/\text{TMS}$): δ -9.72 (3H, d, $J(\text{P-H})$ 20.5 Hz), 1.84 (15H, d, $J(\text{P-H})$ 1.3 Hz), 7.0–7.7 (15H, m) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6/\text{external PPh}_3$): δ 79.3 ppm. Found: C, 66.68; H, 6.67. $\text{C}_{28}\text{H}_{33}\text{PRu}$ calcd.: C, 67.05; H, 6.63%. The ^1H NMR and IR parameters of **5** resemble those of the C_5H_5 analogue of **5**, $(\text{C}_5\text{H}_5)\text{RuH}_3(\text{PPh}_3)$ [1i,j]. While the trihydride **5** is thermally stable both in the solid state and in solution under an atmosphere of argon, irradiation of **5** in C_6D_6 solution with ultraviolet light causes H/D exchange reaction between solvent and coordinated triphenylphosphine. The molecular structure of **5** by X-ray diffraction and further details of the photochemical reactions of **5** will be discussed elsewhere.

References

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