Isolation of a Co-ordinated Ketol Intermediate in the Hydrolysis of PF_6^- Initiated by the Labile Cations $[Ru(\eta^6\text{-arene})(acetone)_3]^{2+}$; *X*-Ray Crystal Structure of Acetone(4-hydroxy-4-methylpentan-2-one)-(η^6-mesitylene)ruthenium Bistetrafluoroborate

By MARTIN A. BENNETT,* TREVOR W. MATHESON, GLEN B. ROBERTSON, WILLIAM L. STEFFEN, and TERENCE W. TURNEY
(*Research School of Chemistry, The Australian National University, Canberra, A.C.T., Australia* 2600)

Summary Formation of the tri-μ-difluorophosphato complexes $[Ru_2(\mu\text{-}PO_2F_2)_3(\eta^6\text{-arene})_2][PF_6]$ from $[Ru(\eta^6\text{-arene})(acetone)_3][PF_6]_2$ proceeds *via* di-cations $[Ru(\eta^6\text{-arene})(4\text{-hydroxy-4-methylpentan-2-one})(acetone)]^{2+}$; the mesitylene complex has been isolated as its BF_4^- salt and characterised by single crystal *X*-ray analysis.

MAITLIS and his co-workers[1–4] have shown that labile, synthetically useful tris(acetone) species $[M(\eta^5\text{-}C_5Me_5)(OCMe_2)_3]^{2+}$ (M = Rh, Ir) can be generated *in situ* by the action of $AgPF_6$ on $[MCl_2(\eta^5\text{-}C_5Me_5)]_2$. We find that analogous arene ruthenium(II) cations $[Ru(\eta^6\text{-arene})(OCMe_2)_3]^{2+}$ (**1**) are formed in solution from the reaction of $AgPF_6$ or $AgBF_4$ with $[RuCl_2(\eta^6\text{-arene})]_2$[5] in dry acetone, and that the salts can be isolated at temperatures below 0 °C as thermally labile, yellow microcrystalline solids. Although satisfactory analytical data could not be obtained, spectroscopic data show unequivocally the presence of three co-ordinated acetone molecules, *e.g.* $[Ru(\eta^6\text{-}C_6Me_6)(OCMe_2)_3][PF_6]_2$: ^1H n.m.r. ($[^2H_6]$-Me_2SO) δ 2·07 (s, 18H, C_6Me_6) and 2·98 (s, 18H, Me_2CO); i.r. (Nujol) 1665 cm^{-1} [ν(C=O)].

The normally inert anion in the $[Ru(\eta^6\text{-arene})(OCMe_2)_3][PF_6]_2$ salts undergoes partial hydrolysis at room temperature over a period of 2 h to give mainly mesityl oxide and the tri-μ-difluorophosphato complexes $[Ru_2(\mu\text{-}PO_2F_2)_3(\eta^6\text{-arene})_2][PF_6]$ (**2**) in high yield, *e.g.* for arene = C_6Me_6: ^{31}P n.m.r. ($[^2H_6]$-Me_2CO)† δ_P −13·1 (t, 3P, $^1J_{PF}$ 951 Hz, PO_2F_2), and −144·5 (septet, 1P, $^1J_{PF}$ 708 Hz, PF_6); ^{19}F n.m.r. ($[^2H_6]$-Me_2CO) δ_F‡ −63·0 (d, 6F, PO_2F_2) and −67·9 (d, 6F, PF_6); i.r. (Nujol) 1300(s), 1146(s) [$\nu(PO_2)$], 869(s), 852(s), 836(s) [ν(PF)], 558(s) [δ(PF)], and 486(s) [δ(POF)] cm^{-1}. A similar reaction occurs more slowly (54 °C; 18 h) in the case of $[Rh(\eta^5\text{-}C_5Me_5)(OCMe_2)_3][PF_6]_2$,[1,3] and the reaction of $[MnCl(CO)_5]$ with $AgPF_6$ is reported to give $[Mn(O_2PF_2)(CO)_5]$.[6] The first step in our system seems to involve an aldol condensation between two acetone molecules. Thus, $[Ru(\eta^6\text{-}C_6H_3Me_3)(OCMe_2)_3][BF_4]_2$ isomerises rapidly at room temperature to give a complex $[Ru(\eta^6\text{-}C_6H_3Me_3)(OCMe_2)\{Me_2C(OH)CH_2COMe\}][BF_4]_2$ (**3**) containing bidentate 4-hydroxy-4-methylpentan-2-one, which reacts with NH_4PF_6 to give (**2**) (arene = mesitylene) quantitatively. The structure of (**3**) has been elucidated by single crystal *X*-ray analysis.

---

† In p.p.m. relative to external 85% H_3PO_4, downfield being taken as positive.

‡ In p.p.m. relative to $CFCl_3$, measured using C_6F_6 as external reference; downfield is taken as positive.

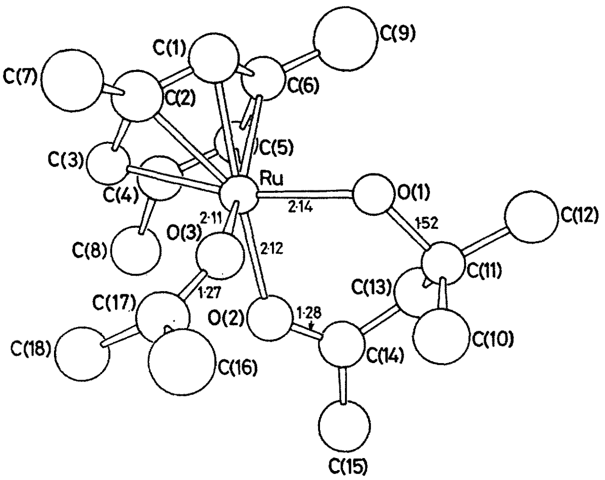

FIGURE. Molecular structure of $[Ru(\eta^6$-mesitylene)(4-hydroxy-4-methylpentan-2-one)(acetone)]$[BF_4]_2$.

Crystal data: $C_{18}H_{30}B_2F_8O_3Ru$, $M = 569·2$, monoclinic, space group $P2_1/c$, with $a = 8·217(3)$, $b = 16·727(7)$, and $c = 17·431(8)$ Å, $\beta = 94·60(4)°$, $Z = 4$, $D_c = 1·580$ g ml^{-1}, $D_m = 1·579$ g ml^{-1}, $\mu = 7·35$ cm^{-1}, Mo-K_α radiation. The 3763 observed reflections $[I > 3\sigma(I)]$ having $2\theta \leqslant 60°$ were measured with a fully automated Philips PW1100-20 diffractometer. The structure was solved by straightforward application of the heavy atom method and refined to a current R value of 0·127 employing isotropic thermal parameters on all atoms. One of the BF_4^- groups appears to be disordered.§

The ruthenium atom is bound approximately symmetrically to the six aromatic carbon atoms of the mesitylene ligand (Ru–C bond lengths 2·16—2·20 Å), to the oxygen of an acetone ligand (Ru–O 2·11 Å), and to both oxygen atoms of the pentanone (Ru–O 2·12 and 2·14 Å). That the two oxygen atoms of the pentanone are different is evident from the C–O bond distances. The C(11)–O(1) (alcoholic oxygen) distance of 1·52 Å is significantly longer than the C(14)–O(2) (ketonic oxygen) bond length of 1·28 Å and the C(17)–O(3) bond distance of 1·27 Å for the acetone ligand. Furthermore, the six angles around C(11) range from 105·7 to 113·9° and are all close to the ideal tetrahedral angle of 109·5°, whereas the C(13)–C(14)–C(15), C(13)–C(14)–O(2), and C(15)–C(14)–O(2) bond angles of 102·9, 122·1, and 116·9° respectively indicate that C(14) is trigonally hybridised.

The O-donors in complexes (**1**)—(**3**) are readily substituted by other ligands, *e.g.* Me_2SO, pyridine, MeCN, PhCN, or $P(OMe)_3$ to give $[Ru(\eta^6\text{-arene})L_3]^{2+}$ salts, and by both electron-withdrawing and -donating arenes in the presence of trifluoroacetic acid to give almost quantitative yields of dicationic mixed arene complexes $[Ru(arene^1)(arene^2)]Y_2$ ($Y = PF_6$ or BF_4; arene^1 = C_6H_6, $C_6H_3Me_3$, or C_6Me_6; arene^2 = C_6H_6, $C_6H_3Me_3$, C_6Me_6, PhOMe, PhCl, PhCOMe, $PhCO_2Me$, $PhNMe_2$, or naphthalene).

(*Received*, 19*th September* 1978; *Com.* 1010.)

---

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] S. J. Thompson, P. M. Bailey, C. White, and P. M. Maitlis, *Angew. Chem. Internat. Edn.*, 1976, **15**, 490.
[2] C. White, S. J. Thompson, and P. M. Maitlis, *J.C.S. Dalton*, 1977, 1654.
[3] C. White, S. J. Thompson, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **134**, 319.
[4] S. J. Thompson, C. White, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **136**, 87.
[5] R. A. Zelonka and M. C. Baird, *Canad. J. Chem.*, 1972, **50**, 3063; M. A. Bennett and A. K. Smith, *J.C.S. Dalton*, 1974, 233.
[6] F. L. Wimmer and M. R. Snow, *Austral. J. Chem.*, 1978, **31**, 267.