

## Abstract

### Complexes with metals of Group 9 containing $[(C_5Me_4C_nF_{2n+1})M]$ fragment

Two types of tetramethylperfluoralkylcyclopentadienylrhodium(III) dimers  $[(C_5Me_4C_nF_{2n+1})RhCl_2]_2$  (**1a**:  $n = 4$ , **1b**:  $n = 6$ ) were reacted with series of trialkyl- and triarylphosphine ligands to give complexes of general formula  $[(C_5Me_4C_nF_{2n+1})Rh(PR'R_2)Cl_2]$  (**a**:  $n = 4$ , **b**:  $n = 6$ ; **2a**:  $R', R = Me$ ; **3a**:  $R', R = Et$ ; **4a**:  $R', R = Bu$ ; **5a**:  $R', R = i-Pr$ ; **6a**:  $R', R = Ph$ ; **7a**:  $R' = p-tol, R = Ph$ ; **8a**:  $R', R = p-tol$ ; **11b**:  $R', R = Me$ ). In most cases this ligand cleavage gave quantitatively the monomeric Rh(III) complexes of common piano-stool structure. Complex  $[(C_5Me_4C_4F_9)RhBr_2]_2$  (**9**) was obtained from **1a** by halogen exchange. This complex was then reacted in the same way as **1a** with  $P(p-tol)_3$  to give  $[(C_5Me_4C_4F_9)Rh\{P(p-tol)_3\}Br_2]$  (**10**).

The single-crystal X-ray structure of **5a** was determined. Some phosphine complexes (**2a** – **4a**, **6a**) were then reacted with  $PhMgCl$  and  $PhMgBr$  to give corresponding arylrhodium(III) complexes with general formula  $[(C_5Me_4C_4F_9)Rh(PR_3)PhCl]$  (**12**:  $R = Me$ ; **13**:  $R = Et$ ; **14**:  $R = Bu$ ; **15**:  $R = Ph$ ). All products were identified by their NMR spectra. All complexes with triarylphosphine ligands (**6a**, **7a**, **8a**, **10**, **15**) showed hindered rotation about the rhodium-phosphorus bond. The conformational dynamics was studied via variable temperature NMR spectroscopy in the temperature range of  $-40\text{ }^\circ\text{C}$  to  $30\text{ }^\circ\text{C}$ . Detailed study was carried out on **10** which allowed us to determine the Gibbs activation energy of rotation of this compound by the CT method.

## Keywords

(perfluoralkyl)tetramethylcyclopentadienyl ligands, rhodium(III) complexes, ligand cleavage, phosphines, hindered rotation, coalescence temperature