Relative stability of η^5-cyclopentadienyl(olefin)ruthenium cations: the first estimation of the nature of the Ru^{II}–olefin bond

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Abstract

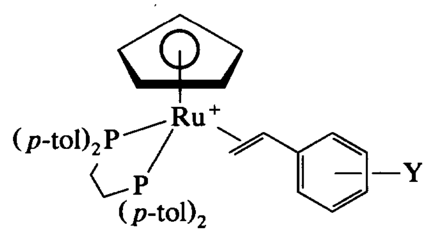
Relative stability in coordination of substituted styrene derivatives to $[Ru(\eta\text{-}C_5H_5)(dtpe)]^+$ (dtpe = 1,2-bis(di-*p*-tolylphosphino)ethane) was determined by NMR spectroscopy to reveal unusually weak substituent dependency of the stability.

Key words: Ruthenium; Olefin; Cyclopentadienyl; Bond nature

The nature of the metal–olefin bond has attracted much attention since the conception of the Dewar–Chatt–Duncanson model [1]. Measurement of the relative stability is the basic experimental method for examining this bond. The binding abilities of the Group 10 [2–7] and Group 11 [8] metals to various olefins have been determined, and these clearly reflected the trend of either distinctly electrophilic or nucleophilic character of most of the relevant metal centres [2,9]. Only in a limited number of cases did the palladium or platinum centre show an intermediate character [5,6].

In spite of the increasing interest in the role of cationic fragments of ruthenium(II), *e.g.* $[Ru(\eta\text{-}C_5H_5)L_2]^+$, as a Lewis acidic centre in synthetic transformations of olefins such as isomerization, ene-type addition, and Diels-Alder reactions [10], few studies have been focused on the nature of the bond between ruthenium(II) and olefin. Here we report the first examination of the nature of metal–olefin bond in η-cyclopentadienyl(olefin)ruthenium cations, which reveals an unusually weak substituent dependency of the stability.

The chloride, $Ru(\eta\text{-}C_5H_5)(dtpe)Cl$, was treated with silver tetrafluoroborate in the presence of styrene or *m*-nitrostyrene to give the cationic complexes $[Ru(\eta\text{-}C_5H_5)(dtpe)(CH_2{=}CHC_6H_5)](BF_4)$ (**1**) or $[Ru(\eta\text{-}C_5H_5)(dtpe)(CH_2{=}CHC_6H_4NO_2\text{-}m)](BF_4)$ (**2**) in good yields [11]. To **1** (or **2**) in a solution of CD_2Cl_2 was added a mixture of styrene (or *m*-nitrostyrene) and styrene derivative bearing one of the substituents listed in Table 1, and the solution was allowed to stand at 25°C until equilibration (15 h). The equilibrium constant K in competitive coordination depicted in eqn. 1



1: Y = H
2: Y = *m*-NO$_2$

TABLE 1. Equilibrium constants (K) for eqn. (1), according to which substituent occupies position Y

H	1	*m*-Me	1.31	*m*-Br	1.16
p-MeO	0.99	*m*-MeO	1.15	*m*-NO$_2$	0.71
p-Me	1.14	*m*-F	0.83	*o*-Me	0.13
p-Cl	0.82	*m*-Cl	0.91	*o*-Cl	0.17
p-NO$_2$	0.77				

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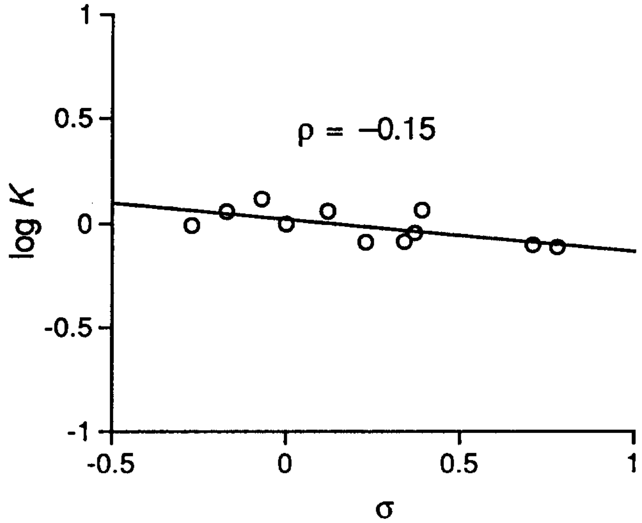
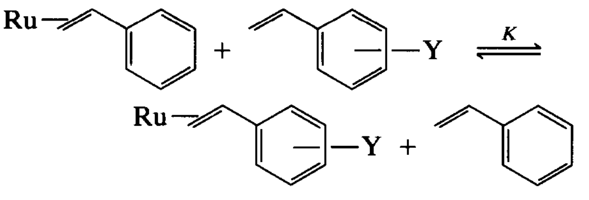


Fig. 1. Hammett plot for eqn. (1), in CD_2Cl_2 at 25°C.

was determined from the ^1H NMR spectra of the mixture. Reproducible K values were obtained upon changing the mixing ratio of the styrenes. The averaged K values are summarized in Table 1 and a plot of log K $vs.$ Hammett substituent constant is shown in Fig. 1.



(1)

Ru = $[Ru(\eta\text{-}C_5H_5)(dtpe)]^+$

Each K value in Table 1 deviated only slightly from unity ($\rho = -0.15$) except for the o-substituted styrene complexes, showing that the $[Ru(\eta\text{-}C_5H_5)(dtpe)]^+$ ion exhibits an unusually low electrophilic character for a cationic complex. Neither is it nucleophilic. This trend is quite different from those in $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(CH_2{=}CHC_6H_4Y)]^+$ ($\rho = -1.32$) [3a], $trans$-$PtCl_2(py)(CH_2{=}CHC_6H_4Y)$ ($\rho^+ = -0.82$) [3b], and $[Pd(\eta\text{-}C_5H_5)(PR_3)(CH_2{=}CHC_6H_4Y)]^+$ ($\rho = -0.94 \sim -1.44$) [4]. Furthermore, the dependency to substituents is lower than that in $M(\eta^3\text{-}CH_2CMeCH_2)(Ar)(CH_2{=}CHC_6H_4Y)$ (M = Pt, Ar = C_6F_5, $\rho = -0.38$; M = Pd, Ar = C_6HCl_4-2,3,5,6; $\rho = -0.25$), showing unusually weak dependency on the substituent for platinum(II) and palladium(II) complexes [5,6].

The theoretical study on molecular orbitals of $[Fe(\eta\text{-}C_5H_5)(CO)_2(CH_2{=}CH_2)]^+$ suggested that the iron cation induces a considerable positive charge on the ethylene ligand [12]. The disagreement between this suggestion and the present observation could be attributed to an electron donating contribution by the phosphine ligand instead of the withdrawing carbonyl ligand, and/or the difference between the electronic structure of iron(II) and ruthenium(II).

The stabilities of o-methyl and o-chlorostyrene complexes were considerably less than those of m- and p-substituted styrene complexes. This may be due to steric hindrance between an $ortho$ substituent of styrenes and one of the tolyl groups of the dtpe. Details of the structural analysis of these complexes that support such hindrance are now under investigation by NMR spectroscopy and will be reported elsewhere.

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