

Synthesis by the Arbuzov-like dealkylation reaction, characterization, and reactivity of phosphonate and amino-substituted phosphonate ruthenium complexes, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OR})_n(\text{NC}_4\text{H}_8)_{2-n}\}]$ ($n = 0\text{--}2$), and comparison with the iron analogues

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Abstract

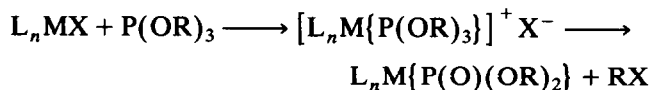
The reaction of $\text{Cp}(\text{CO})_2\text{RuCl}$ with a trivalent phosphorus compound (L) having OR group(s) and/or pyrrolidyl group(s) ($\text{L} = \text{P}(\text{OR})_n(\text{NC}_4\text{H}_8)_{3-n}$ ($\text{R} = \text{Me, Et}; n = 0\text{--}3$)) was examined in benzene at room temperature, revealing that Cl/L and CO/L exchange reactions take place simultaneously to give $[\text{Cp}(\text{CO})_2\text{RuL}]\text{Cl}$ and $\text{Cp}(\text{CO})\text{RuClL}$, respectively. When L is $\text{P}(\text{OR})_3$ or $\text{P}(\text{OR})_2(\text{NC}_4\text{H}_8)$, $[\text{Cp}(\text{CO})\text{RuL}_2]\text{Cl}$ is also formed. $[\text{Cp}(\text{CO})_2\text{RuL}]^+$ is isolated as a BF_4^- salt in good yield in the reaction of $\text{Cp}(\text{CO})_2\text{RuCl}$ with AgBF_4 and L when L is $\text{P}(\text{OR})_3$ or $\text{P}(\text{OR})_2(\text{NC}_4\text{H}_8)$, and is isolated as a Cl^- salt on treatment with L when L is $\text{P}(\text{OR})(\text{NC}_4\text{H}_8)_2$ or $\text{P}(\text{NC}_4\text{H}_8)_3$. Treatment of $[\text{Cp}(\text{CO})_2\text{RuL}]\text{BF}_4$ with Et_4NCl or refluxing a benzene solution of $[\text{Cp}(\text{CO})_2\text{RuL}]\text{Cl}$ undergoes the Arbuzov-like dealkylation reaction to give the corresponding phosphonate ruthenium complex, $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OR})_n(\text{NC}_4\text{H}_8)_{2-n}\}$ ($n = 0\text{--}2$), whereas $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{NC}_4\text{H}_8)_3\}]\text{Cl}$ shows no reaction. The comparison of spectroscopic data of $[\text{Cp}(\text{CO})_2\text{ML}]^+$ and $\text{Cp}(\text{CO})_2\text{M}\{\text{P}(\text{O})(\text{OR})_n(\text{NC}_4\text{H}_8)_{2-n}\}$ ($\text{M} = \text{Fe, Ru}$) reveals that $\text{M}^{\delta+}\text{-P}^{\delta-}$ polarization is greater for Ru than Fe. $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{NC}_4\text{H}_8)_2\}$ shows an $\text{NC}_4\text{H}_8/\text{OR}$ exchange reaction in ROH at 65°C for 5 h to give $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OR})(\text{NC}_4\text{H}_8)\}$, whereas the corresponding iron complex shows no reaction. The exchange reaction of the Ru complex proceeds faster in EtOH than in MeOH, which is rationalized in terms of a strong hydrogen bond between the phosphoryl oxygen in the Ru phosphonate complex and an alcohol hydrogen.

Key words: Ruthenium; Phosphonate; Phosphite; Amino substitution

1. Introduction

Arbuzov-like dealkylation reactions of trialkyl phosphites with transition-metal complexes have been employed to prepare transition-metal phosphonate complexes [1]. The reaction mechanisms have also been studied, and most of these rearrangements have been found to proceed by an ionic mechanism, where the halide in L_nMX is replaced by a phosphite molecule to give the cationic complex $[\text{L}_n\text{M}\{\text{P}(\text{OR})_3\}]^+$, which is then subjected to nucleophilic attack by the released

halide ion at the α -carbon of the coordinated phosphite [1a].



Although many phosphonate complexes of a variety of transition metals have been prepared, there are few studies on direct comparison of preparative facility, spectroscopic data, and reactivity with organic substrates, among transition-metal phosphonate complexes having the same ligands and configuration but having different transition metals of the same group. Some attempts have been reported between the complexes of Cr and Mo [2], Fe and Ru [3], Rh and Ir [4,5], Ni and Pd [6], Pd and Pt [7,8], but these phosphonate

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complexes have not been prepared by the Arbuzov-like dealkylation reaction.

We have been studying piano-stool iron complexes containing a phosphonate ligand [9]. Here we report the synthesis of piano-stool ruthenium complexes formulated as $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})\text{XY}\}$ (Cp stands for $\eta^5\text{-C}_5\text{H}_5$), by the Arbuzov-like dealkylation reactions, and we also compare the ruthenium complexes with the corresponding iron complexes with respect to preparative facility, spectroscopic data and reactivity with alcohols, and discuss the nature of the bond between a transition metal and a phosphonate phosphorus.

2. Results and discussion

In order to compare the Arbuzov-like dealkylation reaction of ruthenium complexes with that of iron complexes previously reported [9d], we examined reactions of $\text{Cp}(\text{CO})_2\text{RuCl}$ with a trivalent phosphorus compound containing alkoxy group(s) (OR) and/or pyrrolidyl group(s) (NC_4H_8), *i.e.* $\text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$, $\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)$, $\text{P}(\text{OEt})_2(\text{NC}_4\text{H}_8)$, $\text{P}(\text{OMe})(\text{NC}_4\text{H}_8)_2$, $\text{P}(\text{OEt})(\text{NC}_4\text{H}_8)_2$ and $\text{P}(\text{NC}_4\text{H}_8)_3$.

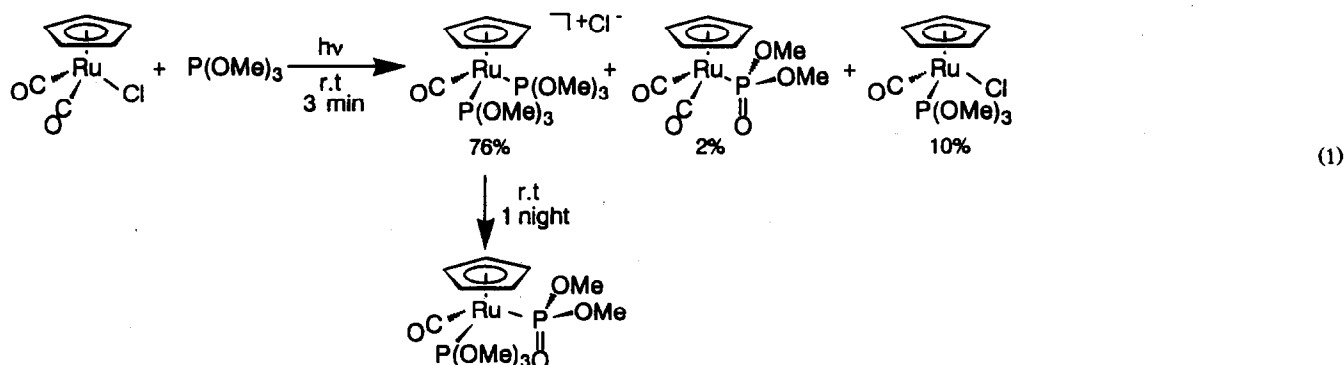
2.1. Reaction of $\text{Cp}(\text{CO})_2\text{RuCl}$ with $\text{P}(\text{OR})_n(\text{NC}_4\text{H}_8)_{3-n}$ ($R = \text{Me}, \text{Et}; n = 0-3$)

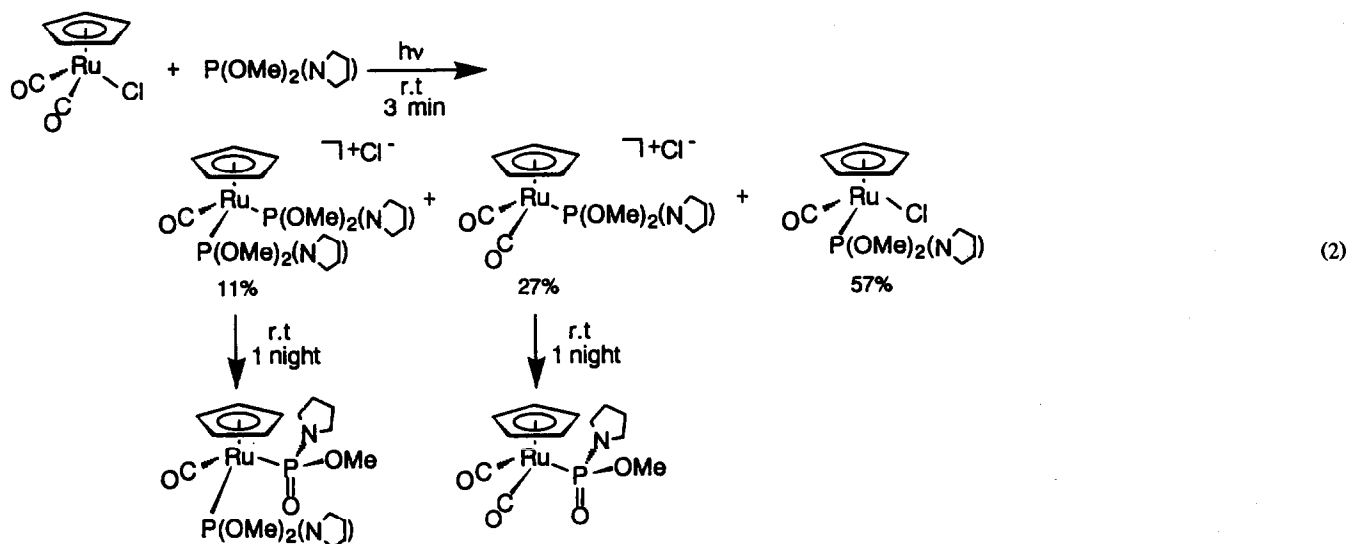
Treatment of $\text{Cp}(\text{CO})_2\text{RuCl}$ with $\text{P}(\text{OMe})_3$ in benzene at room temperature showed no reaction. However, when the solution was exposed to the sunlight or a strong fluorescent light only for a few minutes, precipitations of $[\text{Cp}(\text{CO})\text{Ru}\{\text{P}(\text{OMe})_3\}_2]\text{Cl}$ were formed in 76% yield. The supernatant contained two kinds of electrically neutral Ru complexes, $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OMe})_2\}$ (2% yield) and $\text{Cp}(\text{CO})\text{RuCl}\{\text{P}(\text{OMe})_3\}$ (10% yield), in addition to the starting complex $\text{Cp}(\text{CO})_2\text{RuCl}$. Stirring the suspension at room temperature for one night gave a homogeneous solution containing

$\text{Cp}(\text{CO})\text{Ru}\{\text{P}(\text{OMe})_3\}\{\text{P}(\text{O})(\text{OMe})_2\}$, $\text{Cp}(\text{CO})\text{RuCl}\{\text{P}(\text{OMe})_3\}$, $\text{Cp}(\text{CO})_2\text{RuCl}$, and a small amount of $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OMe})_2\}$ (eqn. (1)). The reaction of $\text{Cp}(\text{CO})_2\text{FeCl}$ with $\text{P}(\text{OMe})_3$ has been reported to form $\text{Cp}(\text{CO})\text{Fe}\{\text{P}(\text{OMe})_3\}\{\text{P}(\text{O})(\text{OMe})_2\}$, $\text{Cp}(\text{CO})\text{FeCl}\{\text{P}(\text{OMe})_3\}$, and $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})(\text{OMe})_2\}$ [10]. These products correspond to those of our Ru case, but the distribution is different; in the Fe case, $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})(\text{OMe})_2\}$ is a major product and $\text{Cp}(\text{CO})\text{Fe}\{\text{P}(\text{OMe})_3\}\{\text{P}(\text{O})(\text{OMe})_2\}$ and $\text{Cp}(\text{CO})\text{FeCl}\{\text{P}(\text{OMe})_3\}$ are minor products. Since $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OMe})_2\}$ is produced in good yield by the Arbuzov-like dealkylation reaction of $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OMe})_3\}]\text{BF}_4$ with Et_4NCl (*vide infra*), the low yield of $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OMe})_2\}$ comes from the low yield of $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OMe})_3\}]\text{Cl}$, which may be attributed to the high activation energy for the displacement of Cl in $\text{Cp}(\text{CO})_2\text{RuCl}$ by $\text{P}(\text{OMe})_3$, compared with the iron analogue.

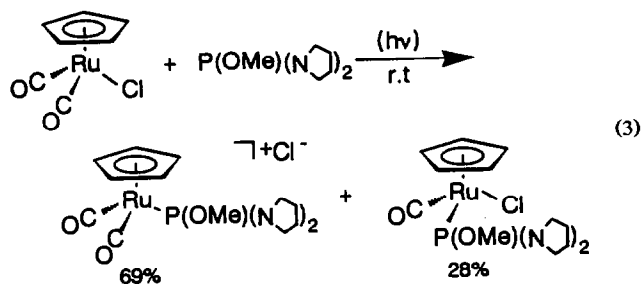
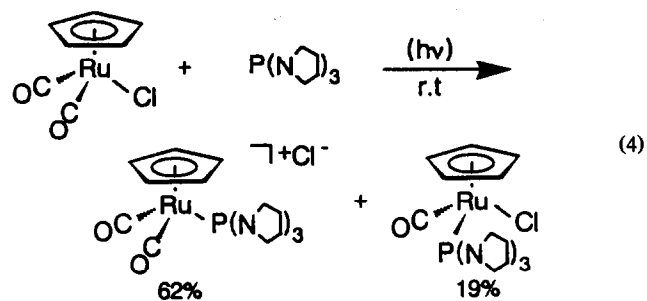
The reaction of $\text{Cp}(\text{CO})_2\text{RuCl}$ with $\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)$ also required sunlight or strong fluorescent light irradiation for a few minutes, to give precipitations of $[\text{Cp}(\text{CO})\text{Ru}\{\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)\}_2]\text{Cl}$ (11% yield) and $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)\}]\text{Cl}$ (27% yield). The supernatant contained $\text{Cp}(\text{CO})\text{RuCl}\{\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)\}$ (57% yield). The starting complex $\text{Cp}(\text{CO})_2\text{RuCl}$ was also observed. Stirring the suspension at room temperature for one night yielded a homogeneous solution containing $\text{Cp}(\text{CO})\text{Ru}\{\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)\}\{\text{P}(\text{O})(\text{OMe})(\text{NC}_4\text{H}_8)\}$, $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OMe})(\text{NC}_4\text{H}_8)\}$, and $\text{Cp}(\text{CO})\text{RuCl}\{\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)\}$, in addition to the starting complex $\text{Cp}(\text{CO})_2\text{RuCl}$ (eqn. (2)).

The reaction of $\text{Cp}(\text{CO})_2\text{RuCl}$ with $\text{P}(\text{OMe})(\text{NC}_4\text{H}_8)_2$ proceeded without light, but the irradiation for a few minutes accelerated the reaction. The precipitates consisted of $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OMe})(\text{NC}_4\text{H}_8)_2\}]\text{Cl}$ (69% yield) and the supernatant contained $\text{Cp}(\text{CO})\text{RuCl}\{\text{P}(\text{OMe})(\text{NC}_4\text{H}_8)_2\}$ (28% yield) (eqn. (3)). No further

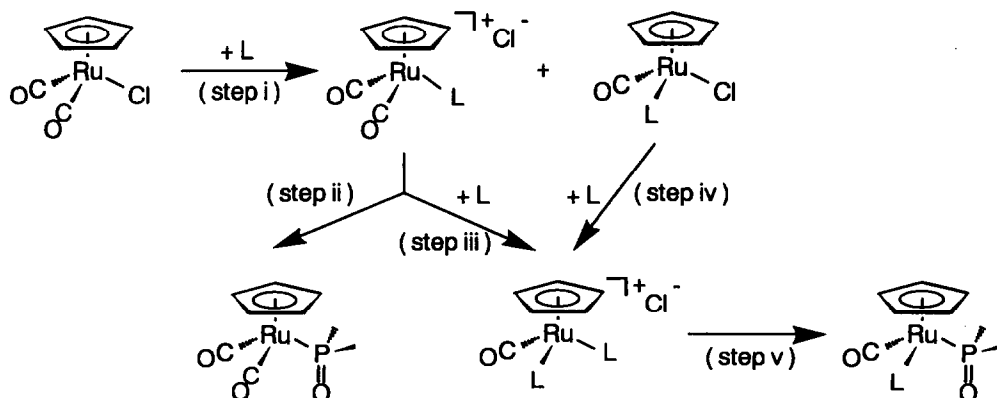




reaction was observed by stirring the suspension at room temperature. A similar reaction was observed on treatment of $\text{Cp}(\text{CO})_2\text{RuCl}$ with $\text{P}(\text{NC}_4\text{H}_8)_3$ (eqn. (4)).



The results mentioned above can be understood systematically as shown in Scheme 1. In the reaction of



Scheme 1.

$\text{Cp}(\text{CO})_2\text{RuCl}$ with L (i.e. $\text{P}(\text{OR})_n(\text{NC}_4\text{H}_8)_{3-n}$), Cl/L exchange and CO/L exchange reactions take place simultaneously to give $[\text{Cp}(\text{CO})_2\text{RuL}]\text{Cl}$ and $\text{Cp}(\text{CO})\text{RuClL}$, respectively (step (i)), irrespective of the kind of L (in other words, irrespective of the number of n in $\text{P}(\text{OR})_n(\text{NC}_4\text{H}_8)_{3-n}$).

When L is $\text{P}(\text{OR})_3$, since $[\text{Cp}(\text{CO})_2\text{RuL}]\text{Cl}$ is very reactive, the successive Arbuzov-like dealkylation reaction proceeds rapidly to give $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OR})_2\}$ (step (ii)). When L has more than one amino substituent, $[\text{Cp}(\text{CO})_2\text{RuL}]\text{Cl}$ can be isolated. The isolation of the cationic complex as a chloride salt has also been observed in the iron analogues [9d]. The complex corresponds to the intermediate of the Arbuzov-like dealkylation reaction to form $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OR})_n(\text{NC}_4\text{H}_8)_{2-n}\}$. The stabilization of these cationic complexes by introduction of amino group(s) on the coordinating phosphorus may come from the π -donation from the amino nitrogen(s) to the phosphorus atom, which decreases the electrophilicity of the alkoxy α -carbon(s) and then causes the resistance to dealkylation by Cl^- .

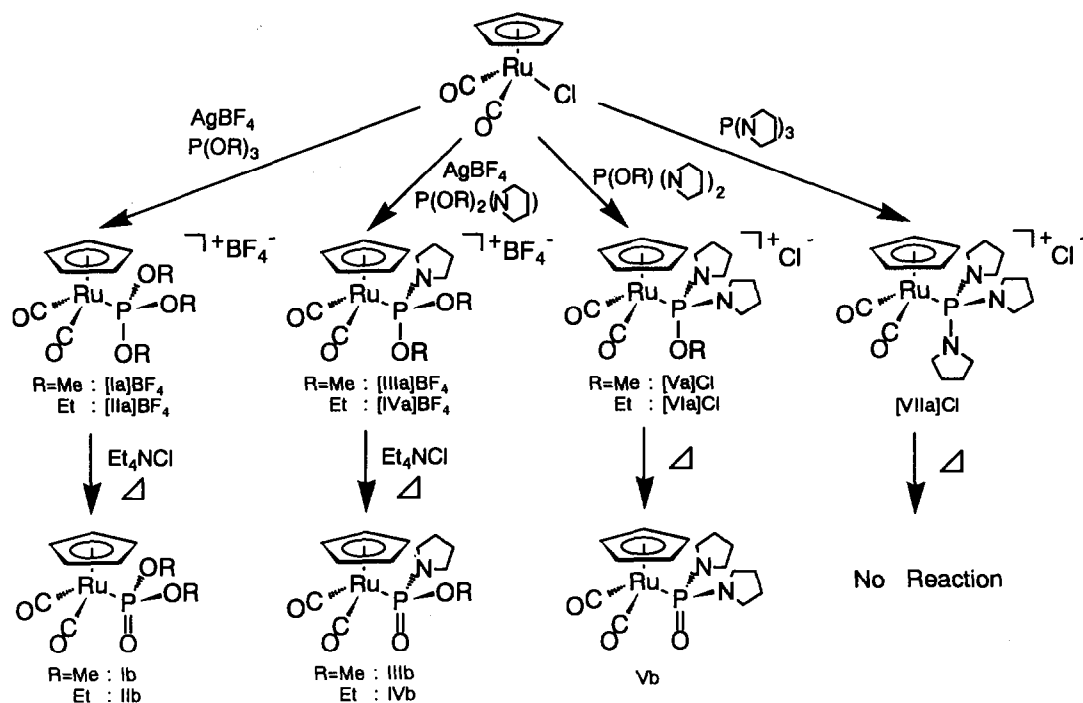
When L is $\text{P}(\text{OR})_3$ or $\text{P}(\text{OR})_2(\text{NC}_4\text{H}_8)$, $\text{Cp}(\text{CO})\text{RuClL}$ reacts with another L to give $[\text{Cp}(\text{CO})\text{RuL}_2]\text{Cl}$ (step (iv)). $[\text{Cp}(\text{CO})\text{RuL}_2]\text{Cl}$ may also be formed from $[\text{Cp}(\text{CO})_2\text{RuL}]\text{Cl}$ and L (step (iii)). $[\text{Cp}(\text{CO})\text{RuL}_2]\text{Cl}$ shows the Arbuzov-like dealkylation reaction by stirring in benzene at room temperature for one night to

give $\text{Cp}(\text{CO})\text{RuL}\{\text{P}(\text{O})(\text{OR})_n(\text{NC}_4\text{H}_8)_{2-n}\}$ ($n = 1, 2$) (step (v)). Since it has been shown that the CO ligand in $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})(\text{OEt})_2\}$ and in $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})(\text{Ph})_2\}$ is not displaced by a phosphine or phosphite [9d, 9f], $\text{Cp}(\text{CO})\text{RuL}\{\text{P}(\text{O})(\text{OR})_n(\text{NC}_4\text{H}_8)_{2-n}\}$ may not be prepared by the displacement of CO in $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{OR})_n(\text{NC}_4\text{H}_8)_{2-n}\}$ by L.

When L is $\text{P}(\text{OR})(\text{NC}_4\text{H}_8)_2$ or $\text{P}(\text{NC}_4\text{H}_8)_3$, $[\text{Cp}(\text{CO})\text{RuL}_2]\text{Cl}$ is not formed either from $[\text{Cp}(\text{CO})_2\text{RuL}]\text{Cl}$ or from $\text{Cp}(\text{CO})\text{RuClL}$. The reason may be due to the steric repulsion. A phosphorus compound (L) becomes bulkier with increasing the number of pyrrolidyl groups, and the threshold of constituting $[\text{Cp}(\text{CO})\text{RuL}_2]^+$ may lie between $\text{P}(\text{OR})_2(\text{NC}_4\text{H}_8)$ and $\text{P}(\text{OR})(\text{NC}_4\text{H}_8)_2$. This explanation can be applied to the reaction of $\text{Cp}(\text{CO})_2\text{FeCl}$ with $\text{P}(\text{OPh})_3$, where the products are $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OPh})_3\}]\text{Cl}$ and $\text{Cp}(\text{CO})\text{FeCl}\{\text{P}(\text{OPh})_3\}$, but not $[\text{Cp}(\text{CO})\text{Fe}\{\text{P}(\text{OPh})_3\}_2]\text{Cl}$ [10b].

2.2. Formation of $\text{Cp}(\text{CO})_2\{\text{P}(\text{O})(\text{OR})_n(\text{NC}_4\text{H}_8)_{2-n}\}$ ($R = \text{Me}, \text{Et}; n = 0-2$)

The reaction sequences are summarized in Scheme 2. When L is $\text{P}(\text{OR})_3$ or $\text{P}(\text{OR})_2(\text{NC}_4\text{H}_8)$, the reaction of $\text{Cp}(\text{CO})_2\text{RuCl}$ with L did not give considerable amounts of the phosphonate complexes. Thus, the abstraction of Cl in $\text{Cp}(\text{CO})_2\text{RuCl}$ by AgBF_4 was employed for preparation of $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OR})_3\}]^+$ and $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OR})_2(\text{NC}_4\text{H}_8)\}]^+$, and cationic com-



Scheme 2.

plexes **Ia–IVa** could be isolated as BF_4^- salts in good yield. These cationic complexes were then treated with 1.5–2.5 equiv of Et_4NCl in refluxing benzene for 1–3 h to give the corresponding phosphonate complexes **Ib–IVb** in 75–98% yields. When L is $\text{P}(\text{OR})(\text{NC}_4\text{H}_8)_2$,

$[\text{Cp}(\text{CO})_2\text{RuL}]\text{Cl}$ could be isolated in good yield. Therefore, the benzene solution was refluxed to give the corresponding phosphonate complex.

The results mentioned above suggest that the cationic ruthenium complexes containing $\text{P}(\text{OR})_n(\text{NC}_4\text{H}_8)^-$

TABLE 1. Spectroscopic data

Complex	IR, ν (CO) (cm^{-1}) ^a	¹ H NMR (δ (ppm)) ^b	³¹ P NMR (δ (ppm)) ^a
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{OMe})_3)]\text{BF}_4$ Ia BF ₄	2081 2034	3.88 (d, $J = 12.2$ Hz, 9H, CH ₃) 5.94 (s, 5H, C ₅ H ₅)	136.8 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{OEt})_3)]\text{BF}_4$ IIa BF ₄	2079 2032	1.39 (t, $J = 7.0$ Hz, 9H, CH ₃) 4.15 (m, 6H, CH ₂) 5.83 (d, $J = 0.7$ Hz, 5H, C ₅ H ₅)	128.8 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8))] \text{BF}_4$ IIIa BF ₄	2073 2025	1.98 (m, 4H, CH ₂ CH ₂ CH ₂ CH ₂) 3.27 (m, 4H, CH ₂ CH ₂ CH ₂ CH ₂) 3.71 (d, $J = 11.3$ Hz, 6H, CH ₃) 5.79 (s, 5H, C ₅ H ₅)	134.9 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{OEt})_2(\text{NC}_4\text{H}_8))] \text{BF}_4$ IVa BF ₄	2073 2025	1.38 (t, $J = 6.8$ Hz, 6H, CH ₃) 1.96 (m, 4H, CH ₂ CH ₂ CH ₂ CH ₂) 3.23 (m, 4H, CH ₂ CH ₂ CH ₂ CH ₂) 4.02 (m, 4H, OCH ₂ CH ₃) 5.75 (d, $J = 0.7$ Hz, 5H, C ₅ H ₅)	127.8 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{OMe})(\text{NC}_4\text{H}_8)_2)] \text{Cl}$ Va Cl	2063 2014	1.98 (m, 8H, CH ₂ CH ₂ CH ₂ CH ₂) 3.19 (m, 8H, CH ₂ CH ₂ CH ₂ CH ₂) 3.67 (d, $J = 12.7$ Hz, 3H, CH ₃) 5.95 (s, 5H, C ₅ H ₅)	120.0 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{OEt})(\text{NC}_4\text{H}_8)_2)] \text{Cl}$ VIa Cl	2064 2014	1.33 (t, $J = 6.8$ Hz, 3H, OCH ₂ CH ₃) 1.96 (m, 8H, CH ₂ CH ₂ CH ₂ CH ₂) 3.18 (m, 8H, CH ₂ CH ₂ CH ₂ CH ₂) 3.97 (m, 2H, OCH ₂ CH ₃) 5.95 (d, $J = 0.7$ Hz, 5H, C ₅ H ₅)	117.1 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{NC}_4\text{H}_8)_3)] \text{Cl}$ VIIa Cl	2060 2009	1.95 (m, 12H, CH ₂ CH ₂ CH ₂ CH ₂) 3.08 (m, 12H, CH ₂ CH ₂ CH ₂ CH ₂) 5.91 (s, 5H, C ₅ H ₅)	95.7 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{O})(\text{OMe})_2)]$ Ib	2052 1997	3.67 (d, $J = 11.8$ Hz, 6H, CH ₃) 5.54 (s, 5H, C ₅ H ₅)	85.6 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{O})(\text{OEt})_2)]$ IIb	2050 1995	1.28 (t, $J = 7.2$ Hz, 6H, CH ₃) 4.02 (m, 4H, CH ₂) 5.49 (d, $J = 0.8$ Hz, 5H, C ₅ H ₅)	81.3 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{O})(\text{OMe})(\text{NC}_4\text{H}_8))] \text{Cl}$ IIIb	2044 1987	1.84 (m, 4H, CH ₂ CH ₂ CH ₂ CH ₂) 3.15 (m, 4H, CH ₂ CH ₂ CH ₂ CH ₂) 3.55 (d, $J = 11.8$ Hz, 3H, CH ₃) 5.56 (d, $J = 0.8$ Hz, 5H, C ₅ H ₅)	81.9 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{O})(\text{OEt})(\text{NC}_4\text{H}_8))] \text{Cl}$ IVb	2043 1987	1.25 (t, $J = 7.3$ Hz, 3H, CH ₃) 1.83 (m, 4H, CH ₂ CH ₂ CH ₂ CH ₂) 3.18 (m, 4H, CH ₂ CH ₂ CH ₂ CH ₂) 4.07 (m, 2H, OCH ₂) 5.51 (d, $J = 0.7$ Hz, 5H, C ₅ H ₅)	80.0 (s)
$[\text{Cp}(\text{CO})_2\text{Ru}(\text{P}(\text{O})(\text{NC}_4\text{H}_8)_2)] \text{Cl}$ Vb	2033 1976	1.82 (m, 8H, CH ₂ CH ₂ CH ₂ CH ₂) 3.17 (m, 8H, CH ₂ CH ₂ CH ₂ CH ₂) 5.54 (d, $J = 0.8$ Hz, 5H, C ₅ H ₅)	69.9 (s)

^a In CH₂Cl₂. ^b In CDCl₃.

$\text{H}_8)_{3-n}$ ($n = 1-3$) correspond to the intermediate in the ionic mechanism of the Arbuzov-like dealkylation reaction of $\text{Cp}(\text{CO})_2\text{RuCl}$ with $\text{P}(\text{OR})_n(\text{NC}_4\text{H}_8)_{3-n}$.

Compound **VIIa** showed no reaction when its benzene solution was refluxed, as expected from the fact that the phosphorus ligand has no OR group.

2.3. Spectroscopic data

Table 1 summarizes the IR ($\nu(\text{CO})$), ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR data for the ruthenium complexes isolated in the present study. A comparison of these data shows the following tendency. On going from a parent cationic complex to the corresponding Arbuzov-like dealkylation product, (i) concerning the two $\nu(\text{CO})$ bands in the IR spectra, low frequency shifts by 29–31 cm^{-1} for the higher frequency band and by 37–38 cm^{-1} for the lower frequency band were observed, (ii) concerning the resonance due to Cp protons in the ^1H NMR spectra, a high field shift by 0.23–0.45 ppm was observed, and (iii) in the ^{31}P NMR spectra, a high field shift by 43–53 ppm was observed. These shifts are consistent with the general trend observed between cationic and neutral complexes.

Next, let us see how these spectroscopic data change with changing the number of pyrrolidyl groups on the phosphorus. For cationic ruthenium phosphite complexes, both the $\nu(\text{CO})$ values and the chemical shift value in the ^{31}P NMR spectra decreases (**Ia** > **IIIa** > **Va** > **VIIa**, **IIa** > **IVa** > **VIa** > **VIIa**) with increasing the number of pyrrolidyl groups on the phosphorus. These data appear to indicate that the electron on N is donated to P through a $p\pi-d\pi$ interaction and then the electron density flows into the ruthenium atom, and the degree of the sequential interaction increases with the number of amino groups on the P atom. This tendency can also be seen for neutral ruthenium phosphonate complexes (**Ib** → **IIIb** → **Vb**, **IIb** → **IVb** → **Vb**).

Changing an OR group from OMe to OEt between the related complexes also causes a low frequency shift of $\nu(\text{CO})$ values and a high field shift in ^{31}P NMR spectra, which is consistent with the fact that an OEt group is a more electron donating group than an OMe group.

2.4. Comparison of ruthenium complexes with iron complexes

A comparison of IR, ^1H NMR and ^{31}P NMR data between iron and ruthenium complexes has been attempted in order to obtain some information about the nature of Fe–P and Ru–P bonds in $[\text{Cp}(\text{CO})_2\text{M}\{\text{P}(\text{OMe})_n(\text{NC}_4\text{H}_8)_{3-n}\}]\text{Cl}$ ($n = 1, 2$) and $\text{Cp}(\text{CO})_2\text{M}\{\text{P}(\text{O})(\text{OR})_n(\text{NC}_4\text{H}_8)_{2-n}\}$ ($n = 0, 1$). The spectroscopic data are listed in Table 2 together with those for $\text{Cp}(\text{CO})_2\text{M}(\text{CH}_3)$ and $\text{Cp}(\text{CO})_2\text{MH}$ [11]. For every complex $\nu(\text{CO})$ bands are observed at higher frequencies, the resonance due to Cp protons is observed at a lower field, and the resonance in ^{31}P NMR is observed at a higher field for Ru complexes than for the corresponding Fe complexes.

It can be speculated from the electronegativity that a bond between a transition metal (M) and a phosphorus atom is polarized as $\text{M}^{\delta+}-\text{P}^{\delta-}$. The tendency mentioned above indicates that $\text{Ru}^{\delta+}-\text{P}^{\delta-}$ polarization is greater than $\text{Fe}^{\delta+}-\text{P}^{\delta-}$ polarization regardless of M–P(phosphite) or M–P(phosphonate) bonds. However, it should be noted that the resonance due to CH_3 for $\text{Cp}(\text{CO})_2\text{M}(\text{CH}_3)$ or H for $\text{Cp}(\text{CO})_2\text{MH}$ in the ^1H NMR spectra is observed at a lower field for Ru than for Fe complexes. Therefore, the greater $\text{M}^{\delta+}-\text{P}^{\delta-}$ polarization for Ru than for Fe may come from the greater back-donation for Ru than for Fe.

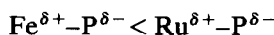


Table 2. Comparison of spectroscopic data for Fe and Ru complexes

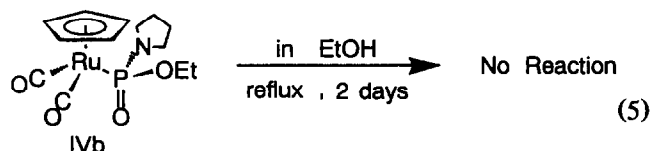
Complex	M	IR, $\nu(\text{CO})$ (cm^{-1}) ^a		^1H NMR (Cp, $\delta(\text{ppm})$) ^b		^{31}P NMR (δ ppm) ^a
$[\text{Cp}(\text{CO})_2\text{M}\{\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)\}]\text{Cl}$	Fe ^c	2062	2017	5.57		157.2
	Ru ^{d,e}	2073	2025	5.79		134.9
$[\text{Cp}(\text{CO})_2\text{M}\{\text{P}(\text{OMe})(\text{NC}_4\text{H}_8)_2\}]\text{Cl}$	Fe ^c	2051	2005	5.13		140.4
	Ru ^d	2063	2014	5.95		120.0
$\text{Cp}(\text{CO})_2\text{M}\{\text{P}(\text{O})(\text{OMe})(\text{NC}_4\text{H}_8)\}$	Fe ^c	2032	1981	4.93		101.3
	Ru ^d	2044	1987	5.56		81.9
$\text{Cp}(\text{CO})_2\text{M}\{\text{P}(\text{O})(\text{NC}_4\text{H}_8)_2\}$	Fe ^c	2020	1967	5.00		87.4
	Ru ^d	2033	1976	5.54		69.9
$\text{Cp}(\text{CO})_2\text{M}(\text{CH}_3)$	Fe ^f	2016	1925 ^g	4.70	0.11 (CH_3) ^h	
	Ru ^f	2028	1960 ^g	5.24	0.29 (CH_3) ^h	
$\text{Cp}(\text{CO})_2\text{MH}$	Fe ^f	2014	1960 ^g	4.74	–11.91 (H) ⁱ	
	Ru ^f	2025	1966 ^g	5.16	–10.92 (H) ⁱ	

^a In CH_2Cl_2 . ^b In CDCl_3 . ^c Ref. 9d. ^d This work. ^e This complex was isolated as a BF_4^- salt. ^f Ref. 11. ^g In CS_2 . ^h In CCl_4 . ⁱ In C_6H_{12} .

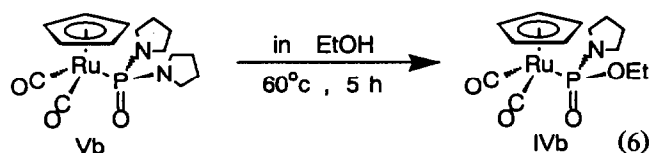
2.5. Reactivity of the phosphonate complexes with alcohols

It is known that amino-substituted phosphines and phosphine oxides, which are free from coordination to a transition metal, readily react with alcohols, where an amino/alkoxy exchange reaction takes place [12]. Phosphonate iron complex, $[\text{Cp}(\text{CO})_2\text{Fe}(\text{P}(\text{O})(\text{NEt}_2)_2)]$, has also been reported to undergo the exchange reaction [9d]. The reason for the exchange is that these compounds are protonated at the N atom which makes the amine a good leaving group. Thus, we attempted the reaction of phosphonate ruthenium complexes with alcohols.

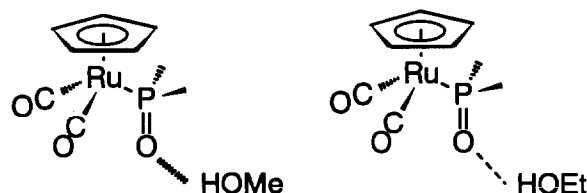
Monoamino-substituted phosphonate Ru complex, **IVb**, was dissolved in EtOH and stirred for several days, but no reaction was observed. Next, refluxing the EtOH solution for 2 days was attempted, but the starting complex remained unreacted (eqn. (5)).



In contrast, diamino-substituted phosphonate Ru complex, **Vb**, showed an $\text{NC}_4\text{H}_8/\text{OEt}$ exchange reaction to give **IVb** when the complex was heated in EtOH at 60°C for 5 h (eqn. (6)). Interestingly, the exchange reaction did not take place in MeOH in the same reaction conditions mentioned above. (The reaction proceeded in MeOH on heating at 65°C for 5 h to give **IIIb**.) Since the acidity is greater for MeOH than EtOH (the $\text{p}K_a$ values are 16 and 18 for MeOH and EtOH, respectively [13]), the above seems to be incompatible with the fact that the P–N bond is cleaved by the protonation at the N atom.



In order to overcome the apparent discrepancy, we suggest a strong hydrogen bond between a phosphoryl oxygen in a phosphonate complex and an alcohol hydrogen. The existence of the hydrogen bond is supported by the solvent dependence of the ^{31}P NMR chemical shift. Table 3 shows the ^{31}P NMR chemical shifts of phosphonate complexes (**Ib**, **IIIb** and **Vb**) and cationic phosphite complex (**[Va]Cl**) of ruthenium in CH_2Cl_2 , MeOH and EtOH. With the phosphonate complexes, a large low field shift (about 10 ppm) irrespective of the number of amino groups on the phosphorus is observed on going from CH_2Cl_2 to EtOH. And a low field shift by about 2 ppm is also observed when the solvent is changed from EtOH to more acidic MeOH. In contrast, **[Va]Cl** with amino groups and without a phosphoryl group shows no considerable solvent dependence. These data indicate that an alcohol makes a strong hydrogen bond to a phosphoryl oxygen rather than to an amino group, and the hydrogen bond is stronger for more acidic MeOH than for EtOH as shown below. Some clear examples exhibiting a hydrogen bond between an oxygen atom in an alkoxide ligand on a transition metal and an alcohol have recently been reported [14–16].



Here, let us consider why diamino-substituted phosphonate Ru complex undergoes an amino/alkoxy exchange reaction faster in EtOH than in more acidic MeOH. In an alcohol, most amino-substituted phosphonate molecules make the hydrogen bond through the phosphoryl oxygen. The strong hydrogen bond makes the electron density on the phosphorus decrease, which induces more π -donation from an amino group to the phosphorus atom. Therefore, the basicity of the amino group decreases, resulting in low amino/alkoxy exchange reactivity.

TABLE 3. Chemical shifts in ^{31}P NMR of ruthenium complexes

Solvent	Ib	IIIb	Vb	[Va]Cl
CH_2Cl_2	85.6	81.9	69.9	120.0
EtOH	95.2	92.1	79.4	121.4
MeOH	97.5	94.3	81.5	121.3

It might be interesting to compare the amino/alkoxy exchange reaction between iron and ruthenium complexes. $\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{O})(\text{NC}_4\text{H}_8)_2\}$ (**Vb**) and the iron analogue $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})(\text{NC}_4\text{H}_8)_2\}$ were dissolved in EtOH or MeOH individually. The reaction mixtures were heated at 65°C for 5 h, then the products were examined. In the case of the Ru complex, an amino/alkoxy exchange reaction took place completely both in EtOH and in MeOH to give **IVb** and **IIIb**, respectively. In the case of the Fe complex, the exchange reaction was not observed and the starting complex remained unreacted in EtOH and in MeOH. (When EtOH was used, a trace amount of the exchange product, $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})(\text{OEt})(\text{NC}_4\text{H}_8)\}$, was detected.) These results can be understood from the greater $M^{\delta+}-P^{\delta-}$ polarization for Ru than for Fe. That is, the Ru complex has greater electron density on the phosphorus than the corresponding Fe complex, causing less π -donation from an amino group to the P atom. Thus, the basicity of the amino group is greater for Ru than for Fe complexes, which leads to the greater amino/alkoxy exchange reactivity.

3. Experimental details

3.1. General remarks

All reactions were carried out under an atmosphere of dry nitrogen by use of Schlenk tube techniques. All solvents used were purified by distillation: benzene and hexane were distilled from sodium metal, CH_2Cl_2 was distilled from P_2O_5 , and MeOH and EtOH were distilled from $\text{Mg}(\text{OMe})_2$ and $\text{Mg}(\text{OEt})_2$, respectively. $\text{Cp}(\text{CO})_2\text{RuCl}$ was synthesized by published procedures [17]. $\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)$ and $\text{P}(\text{OEt})_2(\text{NC}_4\text{H}_8)$ were prepared in the reaction of $\text{PCl}_2(\text{NC}_4\text{H}_8)$ [18] with MeOH and EtOH, respectively, in a manner similar to that for $\text{P}(\text{OMe})_2(\text{NMe}_2)$ [19]. $\text{P}(\text{OMe})(\text{NC}_4\text{H}_8)_2$ and $\text{P}(\text{OEt})(\text{NC}_4\text{H}_8)_2$ were synthesized in the reaction of $\text{PCl}(\text{NC}_4\text{H}_8)_2$ with MeOH and EtOH, respectively, in a manner similar to that for $\text{P}(\text{OMe})(\text{NEt}_2)_2$ [20]. $\text{P}(\text{NC}_4\text{H}_8)_3$ was prepared from PCl_3 and pyrrolidine in a manner similar to that for $\text{P}(\text{NMe}_2)_3$ [21].

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. JEOL PMX-60 and EX-400 instruments were used to obtain ^1H and ^{31}P NMR spectra. ^1H NMR data were referenced to $(\text{CH}_3)_4\text{Si}$, and ^{31}P NMR data referenced to 85% H_3PO_4 .

3.2. $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OMe})_3\}]\text{BF}_4$ (**[Ia]** BF_4)

To a solution of $\text{Cp}(\text{CO})_2\text{RuCl}$ (828 mg, 3.21 mmol) in benzene (20 ml) was added $\text{P}(\text{OMe})_3$ (558 mg, 0.53 ml, 4.49 mmol) and AgBF_4 (840 mg, 4.31 mmol). The

reaction mixture was stirred for 1 h at room temperature to give a brown powder, which was isolated by filtration. Soluble materials were extracted twice from the brown powder with 10 ml of CH_2Cl_2 , then the solvent was removed under reduced pressure. The residue was dissolved in a small amount of acetone, loaded on an alumina column, and then eluted with acetone. Only one pale yellow band was eluted with a brown band remaining on the top of the column. The band eluted was collected and the solvent was removed under reduced pressure. The residue was washed with benzene (15 ml \times 2), benzene/hexane (1/1) (15 ml \times 2), and hexane (20 ml \times 2), then dried *in vacuo* to give **[Ia]** BF_4 as a white crystalline powder. Yield 1039 mg (2.40 mmol, 75%). Anal. Found: C, 28.06; H, 3.31. $\text{C}_{10}\text{H}_{14}\text{BF}_4\text{O}_5\text{PRu}$ calc.: C, 27.73; H, 3.26%.

3.3. $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OEt})_3\}]\text{BF}_4$ (**[IIa]** BF_4)

Complex **[IIa]** BF_4 was prepared from $\text{Cp}(\text{CO})_2\text{RuCl}$ and $\text{P}(\text{OEt})_3$ in the same manner as that for **[Ia]** BF_4 . Yield 90%. Anal. Found: C, 33.09; H, 4.12. $\text{C}_{13}\text{H}_{20}\text{BF}_4\text{O}_5\text{PRu}$ calc.: C, 32.86; H, 4.24%.

3.4. $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)\}]\text{BF}_4$ (**[IIIa]** BF_4)

Complex **[IIIa]** BF_4 was prepared from $\text{Cp}(\text{CO})_2\text{RuCl}$ and $\text{P}(\text{OMe})_2(\text{NC}_4\text{H}_8)$ in the same manner as that for **[Ia]** BF_4 except that CH_2Cl_2 /acetone (1/1) was used as an eluent. Yield 33%. Anal. Found: C, 33.25; H, 3.96; N, 2.94. $\text{C}_{13}\text{H}_{19}\text{BF}_4\text{NO}_4\text{PRu}$ calc.: C, 33.07; H, 4.06; N, 2.97%.

3.5. $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OEt})_2(\text{NC}_4\text{H}_8)\}]\text{BF}_4$ (**[IVa]** BF_4)

Complex **[IVa]** BF_4 was prepared from $\text{Cp}(\text{CO})_2\text{RuCl}$ and $\text{P}(\text{OEt})_2(\text{NC}_4\text{H}_8)$ in the same manner as that for **[Ia]** BF_4 . Yield 72%. Anal. Found: C, 35.90; H, 4.56; N, 3.34. $\text{C}_{15}\text{H}_{23}\text{BF}_4\text{NO}_4\text{PRu}$ calc.: C, 36.02; H, 4.63; N, 2.80%.

3.6. $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OMe})(\text{NC}_4\text{H}_8)_2\}]\text{Cl}$ (**[Va]** Cl)

$\text{P}(\text{OMe})(\text{NC}_4\text{H}_8)_2$ (828 mg, 0.92 ml, 4.09 mmol) was added to a solution of $\text{Cp}(\text{CO})_2\text{RuCl}$ (878 mg, 3.41 mmol) in benzene (45 ml). The homogeneous solution was stirred overnight at room temperature to give a white powder, which was filtered, washed with benzene (35 ml \times 2), benzene/hexane (1/1) (15 ml \times 2), and hexane (35 ml \times 2), and dried *in vacuo*. Yield 1075 mg (2.34 mmol, 69%). Anal. Found: C, 41.68; H, 5.37; N, 6.08. $\text{C}_{16}\text{H}_{24}\text{ClN}_2\text{O}_3\text{PRu}$ calc.: C, 41.79; H, 5.26; N, 6.09%.

3.7. $[\text{Cp}(\text{CO})_2\text{Ru}\{\text{P}(\text{OEt})(\text{NC}_4\text{H}_8)_2\}]\text{Cl}$ (**[VIa]** Cl)

Complex **[VIa]** Cl was prepared from $\text{Cp}(\text{CO})_2\text{RuCl}$ and $\text{P}(\text{OEt})(\text{NC}_4\text{H}_8)_2$ in the same manner as that for

[Va]Cl. Yield 61%. Anal. Found: C, 42.76; H, 5.41; N, 5.59. C₁₇H₂₆ClN₂O₃PRu calc.: C, 43.08; H, 5.53; N, 5.91%.

3.8. [Cp(CO)₂Ru{P(NC₄H₈)₃}]Cl ([VIIa]Cl)

Complex [VIIa]Cl was prepared from Cp(CO)₂RuCl and P(NC₄H₈)₃ in the same manner as that for [Va]Cl. Yield 62%. Anal. Found: C, 45.67; H, 6.04; N, 8.24. C₁₉H₂₉ClN₃O₂PRu calc.: C, 45.74; H, 5.86; N, 8.42%.

3.9. [Cp(CO)₂Ru{P(O)(OMe)₂}] (Ib)

Et₄NCl (58 mg, 0.35 mmol) was added to a suspension of [Ia]BF₄ (105 mg, 0.24 mmol) in benzene (10 ml). After 3 h refluxing, the mixture was filtered to remove the insoluble materials such as Et₄NBF₄ and unreacted Et₄NCl. The volatile solvent was removed from the filtrate under reduced pressure. The resultant residue was dissolved in a small amount of acetone, loaded on a silica gel column, and eluted with acetone, and then EtOH. The colorless band eluted with EtOH was collected, and the solvent was removed under reduced pressure to give **Ib** as a white crystalline powder (63 mg, 0.19 mmol, 79%). Anal. Found: C, 32.29; H, 3.22. C₉H₁₁O₅PRu calc.: C, 32.63; H, 3.35%.

3.10. [Cp(CO)₂Ru{P(O)(OEt)₂}] (IIb)

Et₄NCl (650 mg, 3.92 mmol) was added to a suspension of [IIa]BF₄ (1028 mg, 2.16 mmol) in benzene (50 ml). After 1.5 h refluxing, the mixture was filtered, and the solvent was removed from the filtrate under reduced pressure. The resultant residue was loaded on a silica gel column and eluted with acetone, and then with EtOH. The band eluted with EtOH was collected, and the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ (7 ml) and then hexane (50 ml) was added to the solution. The gradual removal of the solvents under reduced pressure gave **IIb** as a white powder (719 mg, 2.00 mmol, 93%). Anal. Found: C, 36.28; H, 4.28. C₁₁H₁₅O₅PRu calc.: C, 36.77; H, 4.21%.

3.11. [Cp(CO)₂Ru{P(O)(OMe)(NC₄H₈)}] (IIIb)

Et₄NCl (200 mg, 1.21 mmol) was added to a suspension of [IIIa]BF₄ (231 mg, 0.49 mmol) in benzene (40 ml). After 1 h refluxing, the mixture was filtered to remove the insoluble materials. The solvent was removed from the filtrate under reduced pressure. The resultant residue was dissolved in CH₂Cl₂ (25 ml) and then hexane (25 ml) was added to the solution. The gradual removal of the solvent under reduced pressure gave **IIIb** as a white powder (178 mg, 0.48 mmol, 98%). Anal. Found: C, 38.50; H, 4.36; N, 3.73. C₁₂H₁₆NO₄PRu calc.: C, 38.92; H, 4.36; N, 3.78%.

3.12. [Cp(CO)₂Ru{P(O)(OEt)(NC₄H₈)}] (IVb)

Complex **IVb** was prepared from [IVa]BF₄ and Et₄NCl in the same manner as that for **IIb**. Yield 75%. Anal. Found: C, 40.71; H, 4.88; N, 3.48. C₁₃H₁₈NO₄PRu calc.: C, 40.63; H, 4.72; N, 3.64%.

3.13. [Cp(CO)₂Ru{P(O)(NC₄H₈)₂}] (Vb)

A suspension of [Va]Cl (786 mg, 1.71 mmol) in benzene (35 ml) was refluxed until it became homogeneous. It took about 30 min. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography and **Vb** was obtained as a white powder (660 mg, 1.61 mmol, 94%) in the same manner as that for **IIb**. Anal. Found: C, 44.44; H, 5.34; N, 6.36. C₁₅H₂₁N₂O₃PRu calc.: C, 44.01; H, 5.17; N, 6.84%.

Complex **Vb** was also obtained from [VIa]Cl. The procedure was similar to that mentioned above, except refluxing for 5 h. The yield was 60%.

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