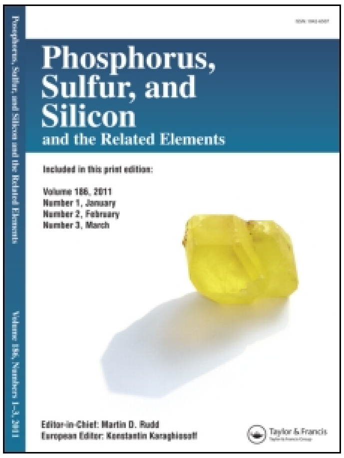

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NOVEL COMPOUNDS FORMED FROM REACTIONS OF $[(\eta^5\text{-}Me_5C_5)MCl_2]_2$ (M = Ru, Rh) WITH VINYLDIPHENYLPHOSPHINE AND ALLYLDIPHENYLPHOSPHINE

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Abstract The complexes $[(\eta^5\text{-}Me_5C_5)Ru(R_3P)_2(NCCH_3)]^+$ PF_6^-, where R_3P is vinyldiphenylphosphine and allyldiphenylphosphine, readily dissociate CH_3CN to form η^3-phosphaallyl and η^3-homophosphaallyl complexes (**1** and **2**) respectively. While **1** is conformationally rigid in solution, **2** undergoes inversion by a dissociative process in solution. The analogous complex $[(\eta^5\text{-}Me_5C_5)Rh(Ph_2PCHCH_2)_2Cl]^+$ PF_6^- undergoes a novel Michael type addition of the methyl CH bonds across the vinyl functionalities of the coordinated phosphine to produce chelating 1,2- and 1,3-*bis*(diphenylphosphinopropyl) trimethylcyclopentadienides (**3** and **4**) respectively. In contrast, with $Ph_2PCH_2CHCH_2$ the classical phosphine complex $[(\eta^5\text{-}Me_5C_5)Rh(Ph_2PCH_2CHCH_2)_2Cl]^+$ PF_6^- (**5**) is formed. These new complexes have been characterized by a variety of NMR techniques and by single crystal X-ray crystallography.

Key Words phosphaallyl, NMR spectroscopy, X-ray crystallography, CH Michael additions.

We previously reported[1] that $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCHCH_2)_2(CH_3CN)]^+$ PF_6^- reversibly dissociates CH_3CN to form the η^3-phosphaallyl complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-}Ph_2PCHCH_2)(\eta^3\text{-}Ph_2PCHCH_2)]^+$ PF_6^- and showed that the η^1-to-η^3 conversion is endothermic and entropy driven. Since $\eta^5\text{-}Me_5C_5^-$ is a better donor than $C_5H_5^-$, the metal in complexes of the former should be more electron rich than in complexes of the latter. An electron rich metal center would be expected to facilitate the η^1-to-η^3 conversion. Accordingly, the $\eta^5\text{-}Me_5C_5$

phosphaallyl complex was synthesized in high yield *via* reaction 1. That the η^3-phosphaallyl complex was formed in this

$$[(\eta^5\text{-Me}_5C_5)RuCl_2]_2 \xrightarrow[\substack{\text{i. Zn}\\ \text{ii. 2Ph}_2\text{PCHCH}_2\\ \text{iii. NH}_4\text{PF}_6}]{CH_3CN} [(\eta^5\text{-Me}_5C_5)Ru(\eta^1\text{-Ph}_2PCHCH_2)(\eta^3Ph_2PCHCH_2)]PF_6 \quad \text{(1) (60\%)} \qquad (1)$$

reaction rather than $[(\eta^5\text{-Me}_5C_5)Ru(Ph_2PCHCH_2)_2(CH_3CN)]^+ PF_6^-$ was established by $^{31}P\{^1H\}$ NMR spectroscopy and X-ray crystallography (Figure 1).

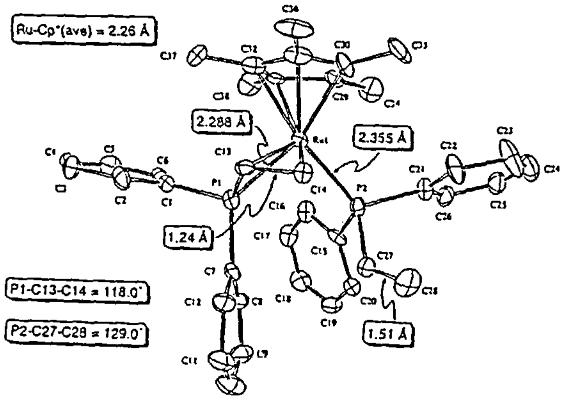
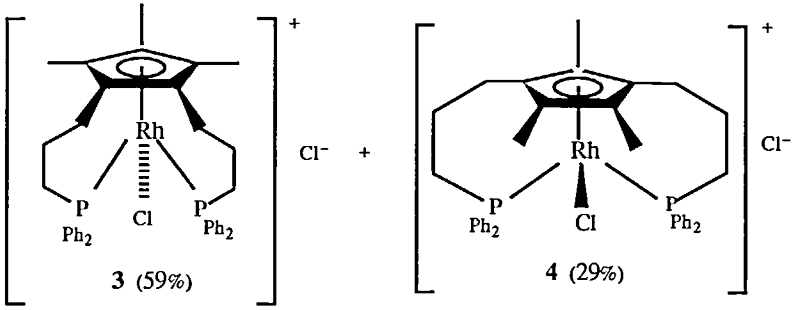


Figure 1. Structure of the cation of 1

The $^{31}P\{^1H\}$ NMR spectrum exhibited three resonances: δ - 145.0 (septet, $^1J(PF)$ = 7 12.7 Hz, PF_6^-), 12.9 (d, $^2J(PP)$ = 48.7 Hz, η^3 - Ph_2PCHCH_2), 43.3. (d, $^2J(PP)$ = 48.7 Hz, η^1 - Ph_2PCHCH_2) rather than the two expected for the CH_3CN adduct. Thus, the η^1-to-η^3 conversion is spontaneous even in CH_3CN solution. X-ray crystallography and ^1H NOE difference spectroscopy established that the phosphaallyl moiety adopts the *exo-* configuration in both the solid and solution states. Reaction **1** with $Ph_2PCH_2CHCH_2$ in place of Ph_2PCHCH_2 produced the η^3-homophosphaallyl analog $[(\eta^5\text{-Me}_5C_5)Ru(\eta^1\text{-Ph}_2PCH_2CHCH_2)(\eta^3\text{-}Ph_2PCH_2CHCH_2)]^+ PF_6^-$ (2) in high yield. Compound (2) is dynamic in solution as shown by variable temperature $^{31}P\{^1H\}$ NMR spectroscopy.

Analogous reactions of $[(\eta^5\text{-Me}_5C_5)RhCl_2]_2$ with Ph_2PCHCH_2 proceed quite unexpectedly[2] (reaction 2).

$$[(\eta^5\text{-Me}_5C_5)RhCl_2]_2 + 2\,Ph_2PCHCH_2 \xrightarrow[\Delta]{C_6H_6} \qquad (2)$$



The structures of the two novel products of reaction 2 are shown in Figure 2.

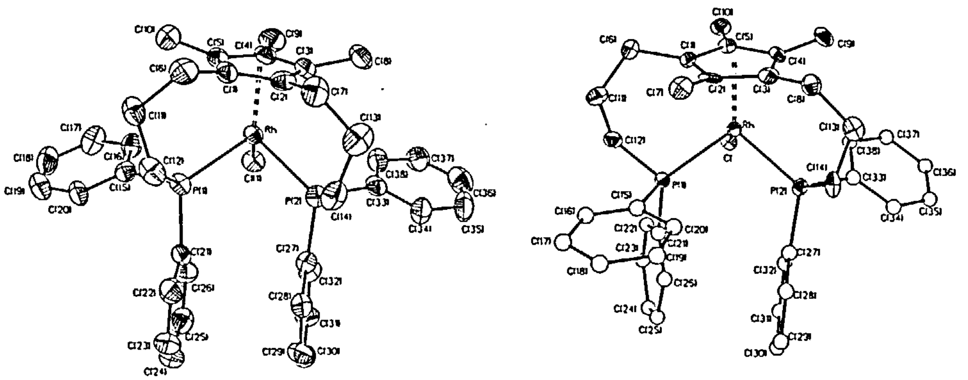


Figure 2. Structures of the cations of 3 (left) and 4 (right).

In contrast, reaction of $[(\eta^5\text{-Me}_5\text{C}_5)\text{RhCl}_2]_2$ with $\text{Ph}_2\text{PCH}_2\text{CHCH}_2$ and NaPF_6 gave the ligand substitution product $[(\eta^5\text{-Me}_5\text{C}_5)\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CHCH}_2)_2\text{Cl}]^+\ \text{PF}_6^-$ (5, Figure 3).

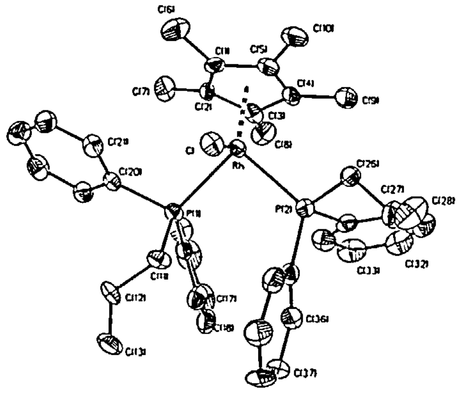


Figure 3. Structure of the cation of 5.

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