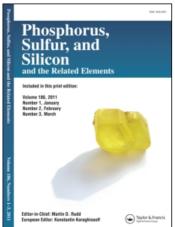
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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Barthel-Rosa, Luis P. , Nelson, John H. , Catalano, Vincent J. and Fischer, Jean(1996) 'Novel Compounds Formed from Reactions of $[(\epsilon^5\text{-Me}_5C_5)\text{Mcl}_2]_2$ (M = Ru, Rh) with Vinyldiphenylphosphine and Allyldiphenylphosphine', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 169 — 172

To link to this Article: DOI: 10.1080/10426509608545117 URL: http://dx.doi.org/10.1080/10426509608545117

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NOVEL COMPOUNDS FORMED FROM REACTIONS OF 1(n5- $Me_5C_5)MCl_2l_2$ (M = Ru, Rh) WITH VINYLDIPHENYLPHOSPHINE AND ALLYLDIPHENYLPHOSPHINE

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The complexes $[(\eta^5-\text{Me}_5\text{C}_5)\text{Ru}(\text{R}_3\text{P})_2(\text{NCCH}_3)]^+\text{PF}_6^-$, where R₃P is Abstract vinyldiphenylphosphine and allyldiphenylphosphine, readily dissociate CH3CN 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 $[(\eta^{5})]$ Me₅C₅)Rh(Ph₂PCHCH₂)₂Cl]⁺ PF₆⁻ 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 Ph₂PCH₂CHCH₂ the classical phosphine complex [(η⁵-Me₅C₅)Rh(Ph₂PCH₂CHCH₂)₂Cl]⁺ PF₆⁻ (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 reported¹ that [(η⁵-C₅H₅)Ru(Ph₂PCHCH₂)₂(CH₃CN)]⁺ PF₆⁻ reversibly dissociates CH₃CN to form the η^3 -phosphaallyl complex [(η^5 - C_5H_5)Ru(η' -Ph₂PCHCH₂) (η^3 -Ph₂PCHCH₂)]+ PF₆⁻ and showed that the η^1 -to- η^3 conversion is endothermic and entropy driven. Since η^5 -Me₅C₅⁻ is a better donor than C₅H₅, 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 η^5 -Me₅C₅

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

$$\begin{array}{c} [(\eta^5\text{-Me}_5C_5)\text{RuCl}_2]_2 \xrightarrow{\text{CH}_3\text{CN}} [(\eta^5\text{-Me}_5C_5)\text{Ru}(\eta^1\text{-Ph}_2\text{PCHCH}_2)(\eta^3\text{Ph}_2\text{PCHCH}_2)]\text{PF}_6 \\ \text{i. } Zn \\ \text{ii. } 2\text{Ph}_2\text{PCHCH}_2 \\ \text{iii. } \text{NH}_4\text{PF}_6 \end{array} \tag{1}$$

reaction rather than $[(\eta^5-Me_5C_5)Ru(Ph_2PCHCH_2)_2(CH_3CN)]^+ PF_6^-$ was established by $^{31}P\{^{1}H\}$ NMR spectroscopy and X-ray crystallography (Figure 1).

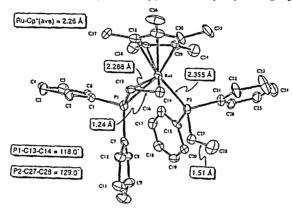
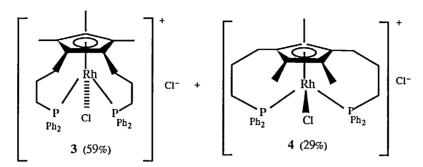


Figure 1. Structure of the cation of 1

The ${}^{31}P\{{}^{1}H\}$ NMR spectrum exhibited three resonances: δ - 145.0 (septet, ${}^{1}J(PF)$ = 7 12.7 Hz, PF_6^-), 12.9 (d, ${}^{2}J(PP)$ = 48.7 Hz, η^3 - Ph_2PCHCH_2), 43.3. (d, ${}^{2}J(PP)$ = 48.7 Hz, η^1 - Ph_2PCHCH_2) rather than the two expected for the CH₃CN adduct. Thus, the η^1 -to- η^3 conversion is spontaneous even in CH₃CN solution. X-ray crystallography and ${}^{1}H$ 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 $[(\eta^5-Me_5C_5)Ru(\eta^1-Ph_2PCH_2CHCH_2)]$ (η^3 - $Ph_2PCH_2CHCH_2)]^+$ PF_6^- (2) in high yield. Compound (2) is dynamic in solution as shown by variable temperature ${}^{31}P\{{}^{1}H\}$ NMR spectroscopy.

Analogous reactions of $[(\eta^5-Me_5C_5)RhCl_2]_2$ with Ph_2PCHCH_2 proceed quite unexpectedly² (reaction 2).

$$[(\eta^{5}-Me_{5}C_{5})RhCl_{2}]_{2} + 2Ph_{2}PCHCH_{2} \xrightarrow{C_{6}H_{6}}$$
(2)



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

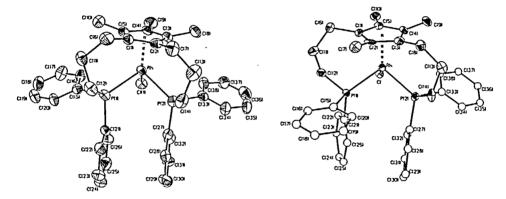


Figure 2. Structures of the cations of 3 (left) and 4 (right). In contrast, reaction of $[(\eta^5-Me_5C_5)RhCl_2]_2$ with $Ph_2PCH_2CHCH_2$ and $NaPF_6$ gave the ligand substitution product $[(\eta^5-Me_5C_5)Rh(Ph_2PCH_2CHCH_2)_2Cl]^+$ PF_6^- (5, Figure 3).

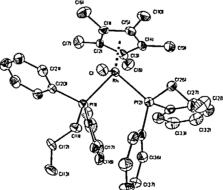


Figure 3. Structure of the cation of 5.

ACKNOWLEDGEMENTS We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support and Johnson Matthey, Aesar/Alfa for their generous loan of RuCl₃•3H₂O and RhCl₃•3H₂O.

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