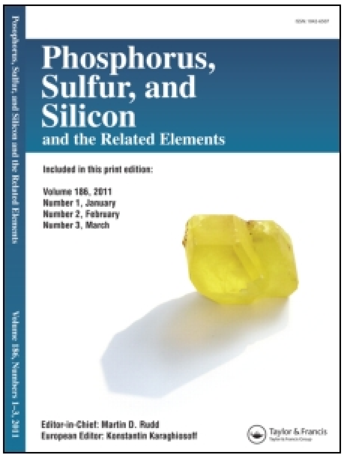

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Reactivity Study of the P_2 Ligand Complex $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$

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The complex $[\{CpCr(CO)_2\}_2(\mu\text{-}\eta^2\text{-}P_2)]$ has shown highly contrasting reactivity behavior towards ECl_3 (E = P, As, Sb) and $LiBEt_3H$. The reaction with ECl_3 has yielded the first example of *cyclo*-P_2E ligand complexes, $[Cp(CO)_2Cr(\eta^3\text{-}P_2E)]$. On the other hand, the reaction with $LiBEt_3H$ led to P-P bond cleavage and formation of novel PH_2 containing complexes $[Cp_2(CO)_4Cr_2(\mu\text{-}PH_2)(\mu\text{-}H)]$, and $[Cp_2(CO)_4Cr_2(\mu\text{-}PH_2)_2]$ and the complex $[(\{CpCr(CO)_2\}_2(\mu\text{-}PH))\{(CpCr)_2(\mu,\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}P_5)\}]$. The reaction of $[Cp_2(CO)_4Cr_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ with $[AuCl(PPh_3)]$ led to the formation of high nuclearity cluster $[\{CpCr(CO)_2\}_6(\mu_4\text{-}P)_3(\mu_4\text{-}Au)_3]$, which is the first example of a planar Au/P cluster.

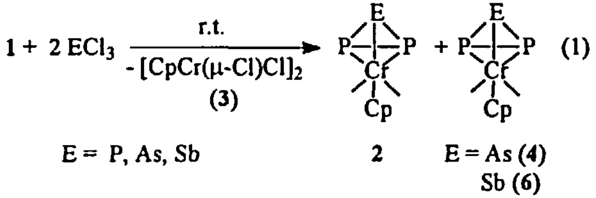
Keywords: phosphorous; chromium; gold; cluster; cyclopentadiene

INTRODUCTION

The last few decades have witnessed a surge in the area of co-ordination chemistry of naked Group 15 elements [1]. Although a large number of different coordination polyhedra have been discovered, in general, reactivity studies have lacked behind the discovery of new types of structures. In this context we are interested in exploring the reactivities of metal complexes containing Group 15 elements. The tetrahedral complex $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (**1**) [2] has been the focus of our attention, as a potential starting material.

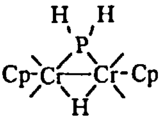
RESULTS AND DISCUSSION

Considering the successful use of PCl_5 as chlorinating agent in the past [3], chlorination of P–P bond in **1** was attempted using PCl_5. However, from this reaction $[Cp(CO)_2Cr(\eta^3\text{-}P_3)]$ (**2**) was isolated by formal removal of one $[CpCr(CO)_2]$ unit from **1**, as confirmed by isolation of the paramagnetic compound $[CpCr(\mu\text{-}Cl)]_2$ (**3**). Surprisingly, the use of PCl_3 shows the same reaction pattern. Treatment of **1** with $AsCl_3$ yielded compounds **2** and **3**, along with the mixed P/As analogue of **2**, $[Cp(CO)_2Cr(\eta^3\text{-}P_2As)]$ (**4**) (Eq. 1) [4].



Compounds **2** and **4** could not be separated by column or thin layer chromatography. Co-crystals of **2** and **4** were obtained, and these were subjected to single crystal X-ray analysis. A brown solid was also obtained and its mass spectrum shows it to be a mixture of the triple decker sandwich complexes $[(CpCr)_2(\eta^5\text{-}P_xAs_{5-x})]$ ($x = 1\text{-}5$) (**5**). When **1** was treated with $SbCl_3$ the antimony analogue of **4**, $[Cp(CO)_2Cr(\eta^3\text{-}P_2Sb)]$ (**6**) was obtained.

The reaction of **1** with 2 equiv of $LiBEt_3H$ at –78 °C resulted in the isolation of the new phosphanido complexes **7**, **8** and **9** [5].



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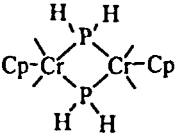

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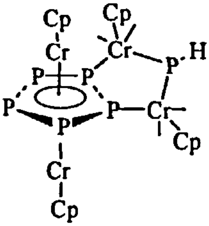

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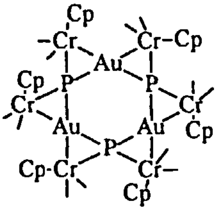
These compounds were characterized by X-ray diffraction analysis. The EPR spectrum of the paramagnetic ($S' = ½$) compound **9** is interpreted with a rhombic-symmetric spin Hamiltonian. A noticeable hyperfine interaction with two ^{31}P nuclei is observed. Structure of **9** shows a triple decker sandwich with a distorted cyclo-P_5 middle deck. The P–P distances in the P_5 middle deck suggest a distortion of the P_5 ring in an allylic P_3 and P_2 subunit.

Compound **7** is found to be a good starting material for cluster growth reaction. Reaction of **1** with KH in THF at room temperature, followed by addition of $AuCl(PPh_3)$, yielded a high nuclearity cluster, $[\{CpCr(CO)_2\}_6(\mu_4\text{-}P)_3(\mu_4\text{-}Au)_3]$ (**10**) which is the first example of a planar Au/P cluster. Structure of **10** shows the Au_3P_3 ring to be planar and all the $[Cp(CO)_2Cr]$ groups are above and below the plane.



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Acknowledgments

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