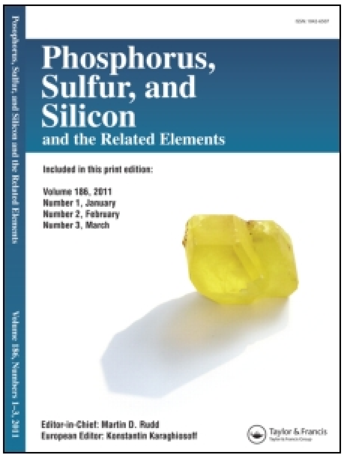

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Leiner, Eva and Scheer, Manfred(2001) 'Cp* - Migration - an Approach to Novel Group 13 Element Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 165 — 168

To link to this Article: DOI: 10.1080/10426500108546616

URL: http://dx.doi.org/10.1080/10426500108546616

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 165-168
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Cp^*- Migration – an Approach to Novel Group 13 Element Complexes

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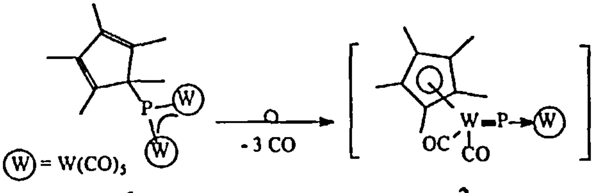
The reaction of Cp^*GaCl_2 with $Na_2W_2(CO)_{10}$ yield $[Cp^*GaW(CO)_5]$, whereas the reactions with $KCo(CO)_4$ lead to the ionic complexes $[\{Co_2(CO)_6(\mu\text{-}CO)\}_2(\mu_4\text{-}Ga)]^-$ and $[\{Co_2(CO)_6(\mu\text{-}CO)\}(\mu\text{-}Ga(Cl)\{Co(CO)_4\}]$. In contrast, Cp^*_2GaCl reacts with $KCo(CO)_4$ to give $[Co_2(CO)_6(\mu\text{-}GaCp^*)_2]^-$. With $K[(CO)_2CpFe]$ the complex $[\{CpFe(CO)\}_2(\mu\text{-}CO)(\mu GaCp^*)]$ is formed. The results show, that both starting materials offer an alternative synthetic route to subvalent Ga(I) compounds via reductive dehalogenation.

Keywords: carbonyl complexes; cobalt; iron; redox chemistry; gallium

INTRODUCTION

Previously we have shown, that a new strategy to generate phosphido ligand complexes, as highly reactive intermediates, is the thermolysis of the phosphinidene complex $Cp^*P[W(CO)_5]_2$ (1) [1]. The intermediate $[Cp^*(CO)_2W{\equiv}P{\rightarrow}W(CO)_5]$ (2) is formed via Cp^*-migration from the σ-bound phosphorus atom of the phosphinidene complex to a tungsten atom in a η^5-coordination mode.

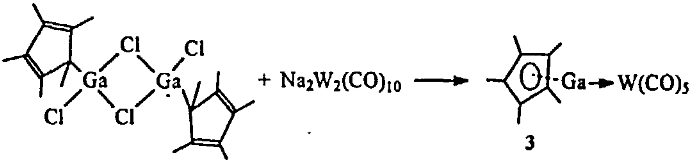


1 **2**

To extend this principle to group 13 element complexes, we were interested to synthesise complexes of the general formula $Cp^{*}Ga(ML_n)_2$. Thus, we use $Cp^{*}{}_2GaCl$ and $Cp^{*}GaCl_2$ as starting materials.

RESULTS AND DISCUSSION

The reaction of $Cp^{*}GaCl_2$ dimer ($Cp^{*} = \eta^1\text{-}C_5Me_5$) with $Na_2W_2(CO)_{10}$ in *n*-hexane at low temperatures leads to complex **3**, which can be described as a derivative of the tungsten carbonyl complex $W(CO)_6$ in which one of the CO unites is replaced by a Cp*Ga ligand ($Cp^{*} = \eta^5\text{-}C_5Me_5$).



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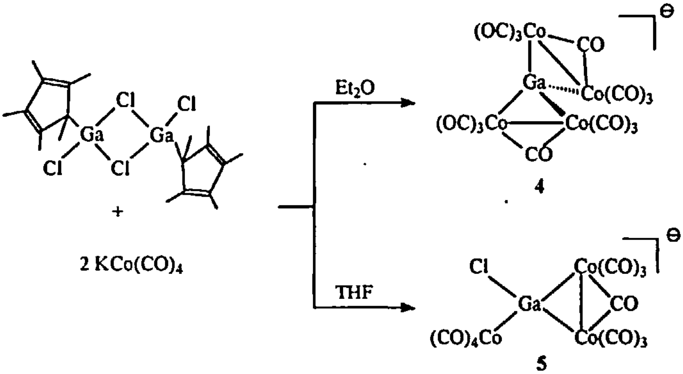
The reaction can be considered as reductive dehalogenation of the Ga(III) complex $Cp^{*}GaCl_2$ to give complex **3** with Ga in the formal oxidation state +1. Similar reactions are known for Al and B compounds and also for Ga compounds with bulky organic substituents [2,3]. Fischer et al. reported the synthesis of $[Cp^{*}AlFe(CO)_4]$ ($Cp^{*} = \eta^5\text{-}C_5Me_5$) by the reaction of $Cp^{*}AlCl_2$ with $Na_2Fe(CO)_4$ [4]. Jutzi et al.

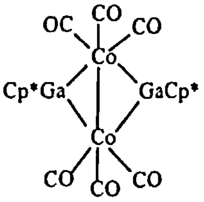
synthesised the Cr analogue of **3** via the direct reaction of Cp*Ga with $Cr(CO)_5(C_8H_{14})$ [2].

Furthermore, Cp^*GaCl_2 was treated with two equivalents of $KCo(CO)_4$ in Et_2O as well as in THF solution, which yielded the ionic products **4** and **5**, respectively. In both the Ga atom is coordinated in a tetrahedral coordination mode. In complex **4** the Ga atom is surrounded by four metal atoms, represents an unusual coordination mode in Ga chemistry [3].



The fact that both products do not contain any Cp* ligands indicates, that under these reaction conditions the Cp* elimination is favored in contrast to alkalimetal halogenide elimination reactions.

Due to these observations we employ Cp^*_2GaCl as starting material to obtain derivatives of the general type $Cp^*Ga(ML_n)_2$. Consequently, the reaction of Cp^*_2GaCl with $KCo(CO)_4$ leads to complex **6**, as a derivative of the Cp*Ga(I) ligand. The complex can be regarded as a derivative of $Co_2(CO)_8$, where the bridging CO ligands are substituted by Cp*Ga. The same product was obtained by Jutzi et al. by the direct reaction of Cp*Ga with $Co_2(CO)_8$ [2].



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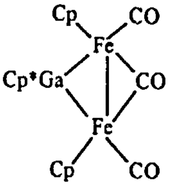

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The analogous reaction of $Cp^*{}_2GaCl$ with $K[CpFe(CO)_2]$ leads to complex 7 in which two Fe atoms are bridged by Cp*Ga and CO ligands, respectively.

In summary, reactions starting from $Cp^*{}_2GaCl$ offer a suitable route for the preparation of novel subvalent Ga compounds without the use of isolated Cp*Ga.

Acknowledgments

We thank the *Deutsche Forschungsgemeinschaft* for comprehensive financial support. E. Leiner is grateful to the *Fonds der Chemischen Industrie* for a Ph.D. fellowship.

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