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Ulrich Hofmockel^a; Wolfgang Malisch^a

^a Institut für Anorganische Chemie der Universität Würzburg, Würzburg, FRG

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Metal Phosphorus Double-bonded Complexes with Alkyl and Aryl Substituted Phosphorus

Ulrich Hofmockel und **Wolfgang Malisch** *

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg, FRG

The phosphane substituted complexes $\text{Cp}(\text{CO})_2[\text{R}(\text{Ph})\text{PH}]\text{M}-\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{Me}, \text{t.Bu}$) (**2a-d**) are obtained via exchange of one CO ligand versus $\text{R}(\text{Ph})\text{PH}$ in the metalchlorides $\text{Cp}(\text{CO})_3\text{M}-\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$) (**1a, b**).

While dehydrohalogenation of $\text{Cp}(\text{CO})_2[\text{t.Bu}(\text{Ph})\text{PH}]\text{W}-\text{Cl}$ (**2d**) with diazabicyclo-undecene(5.4.0) yields $\text{Cp}(\text{CO})_2\text{W}=\text{P}(\text{t.Bu})\text{Ph}$ (**3d**) as a violett-blue crystalline solid, which is stable at room temperature, the analogous reaction of $\text{Cp}(\text{CO})_2[\text{Me}(\text{Ph})\text{PH}]\text{M}-\text{Cl}$ (**2a, c**) results in the formation of the dinuclear hydrido-phosphido-bridged¹ species $(\mu-\text{H})(\mu-\text{MePhP})[\text{M}(\text{CO})_2\text{Cp}]_2$ (**4a, b**). The intermediate formation of $\text{Cp}(\text{CO})_2\text{M}=\text{P}(\text{Me})\text{Ph}$ ($\text{M} = \text{Mo}, \text{W}$) (**3a, c**) was proved by trapping experiments, e.g. sulfur addition, which gives the three membered metallacycles $\text{Cp}(\text{CO})_2\text{M}-\text{P}(\text{S})\text{MePh}$ (**5a, c**).

Information concerning the reactivity of $\text{Cp}(\text{CO})_2\text{W}=\text{P}(\text{t.Bu})\text{Ph}$ towards divers small molecules (CO , CO_2 , SO_2) will be given.