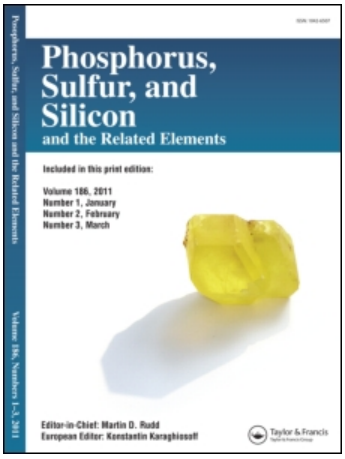

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PHOSPHENIUM COMPLEXES OF THE CHROMIUM AND IRON GROUP: NOVEL CYCLOADDITION REACTIONS AND THE CHEMISTRY OF PH-FUNCTIONAL AND CHIRAL DERIVATIVES[1]

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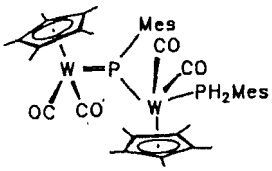
Abstract Synthesis of the highly reactive phosphenium complexes $C_5R_5(CO)_2M\text{-}P(H)R'$ (R = H, Me; R' = t-Bu, Mes, s-Mes) (**2a - d**) is described. The mesityl derivative shows spontaneous dimerization to give the dinuclear species $C_5R_5(CO)_2W{=}P(Mes)\text{-}W(CO)(PH_2Mes)C_5R_5$ (**6a, b**), a new type of phosphinidene complex. An alternative access to these species involves deprotonation and decarbonylation of the bis(metallo)phosphonium salts $\{[Cp(CO)_2W]_2P(Mes)H\}BF_4$ (**9a, b**). Cycloaddition reaction of the phosphenium complexes $Cp(CO)(HPh_2P)M{=}PPh_2$ (Mo, W) (**16a, b**) and $Cp(CO)Fe{=}PMes_2$ (**18a, b**) respectively with isothiocyanates yields novel fourmembered phosphametallacycles $L_nM\text{-}PR_2\text{-}C(NR')\text{-}S$ (R' = Et, t-Bu) (**17a, b, 18a, b**).

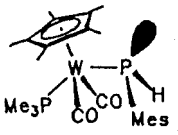
INTRODUCTION

Phosphenium complexes of the type $Cp(CO)_2M{=}PR_2$ (M = Cr, Mo, W; R = alkyl, aryl) show a versatile chemistry due to the high reactivity of M=P double bond.[2] It can be further raised by by using a less bulky phosphorus ligand R, e.g. hydrogen or by reducing the coordination number at the metal centre on going from the d^4 metals of the chromium group to the d^6 metals of the iron group.
As a profitable route to the complexes $Cp(CO)_2M{=}P(H)R$ (R =

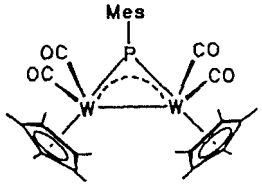
t-Bu, s-Mes) (**2a, b**) or $Cp(CO)M{=}PMes_2$ (M = Fe, Ru) (**4a, b**) respectively the dehydrohalogenation of the corresponding bifunctional phosphane complexes $Cp(CO)_2(Cl)MP(H_2)R$ (**1a, b**) and $Cp(CO)(Cl)MP(H)Mes_2$ (**3a , b**) has been found.
However treatment of $C_5R_5(CO)_2[Mes(H)_2P]WCl$ (R = H, Me) (**5a, b**) with a base surprisingly yields the dinuclear metal complexes **6a, b**, which represent a new type of phosphinidene complex. In **6a, b** for the first time stabilization of a phosphinidene unit is achieved by a 15 and a 17 electron metal fragment.[3] The originally expected mesitylphosphenium complex $C_5R_5(CO)_2W{=}P(H)Mes$ (**2c, d**) cannot be detected even spectroscopically but formation is proved by trapping experiments with Me_3P to furnish the metallo-phosphanes **7a, b.**



6a,b



7a, b



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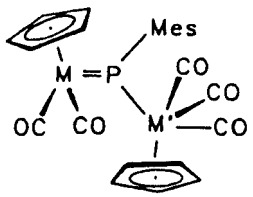
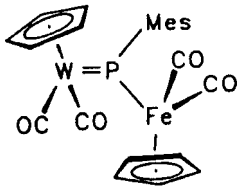
Due to this finding **6a,b** must be formed via dimerization of the mesitylphosphenium complexes **2c, d** involving the addition of a P-H function to the W-P double bond, a hitherto unknown kind of M-P bond formation. While **6a** is thermally extremely stable, the C_5Me_5 analogue **6b** reacts above -40°C to form the "closed" phosphinidene complex **8** by elimination of $MesPH_2$.

A different approach to the new type of phosphinidene complexes involves quarternization of the secondary metallo-phosphanes $Cp(CO)_3M{-}P(H)Mes$ (M = Mo, W) (**9a, b**) by a means of the organometallic Lewis acids $[Cp(CO)_3M]BF_4$ (M= Mo, W) followed by deprotonation and decarbonylation of the

bis(metallo)phosphonium salts $\{[Cp(CO)_3M]_2P(H)Mes\}BF_4$ (**10a, b**) to give **11a-c**. This route can in addition be used to generate heterodinuclear phosphinidene complexes like **12** by performing the quarternization reaction with $[Cp(CO)_3Fe]BF_4$.



11	a	b	c
M	Mo	Mo	W
M'	Mo	W	W



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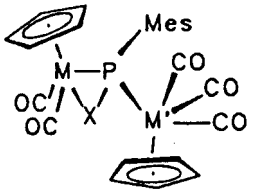
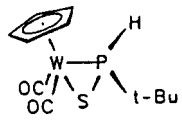


13	a	b	c	a	b	c
M	Mo	Mo	W	Mo	Mo	W
M'	Mo	W	W	Mo	W	W
X	S	S	S	Se	Se	Se

The phosphinidene complexes described in this paper contain a M=P double bond, which due to its pronounced reactivity offers good access to phosphametallacycles. Proof is given by the reaction with sulfur and selenium resulting in the formation of **13a-e**. This compounds contain a thioxo- or selenoxophosphane as a bridging ligand, which exerts stabilization via a η^2-coordination of the P=S(Se) unit and a σ-coordination of the phosphorus.

The sulfur addition product **14** obtained in the case of $Cp(CO)_2W{=}P(H)(t\text{-}Bu)$ (**2a**) can be metallated with n-BuLi at the phosphorus. Alkylation with MeI yields the phophametallacycle **15**, which is isomeric to **14**.



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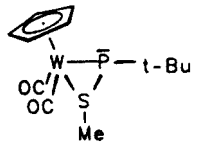

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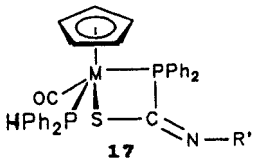

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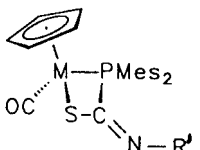

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Diastereoselective cycloaddition reactions are observed for the chiral phosphenium complexes $Cp(CO)(HPh_2P)M{=}PPh_2$ (M = Mo, W) (**16 a, b**) with diverse isothiocyanates. The novel phosphametallacycles **17 a, b** (R´ = t-Bu) obtained show a P-P coupling characteristic for pseudo square pyramidal complexes with trans positioned phosphorus ligands. Analogous experiments can be performed with the highly reactive phosphenium complexes of the iron group $Cp(CO)M{=}PMes_2$ (M = Fe, Ru) (**4a, b**) leading to the formation of the metallacycles **18 a, b** (R´ = Et) in excellent yield.

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