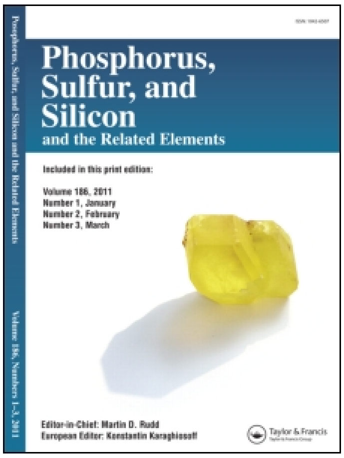

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# Phosphino and Phosphido Ligands in Molybdenocene (and Tungstenocene) Chemistry

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# PHOSPHINO AND PHOSPHIDO LIGANDS IN MOLYBDENOCENE (AND TUNGSTENOCENE) CHEMISTRY

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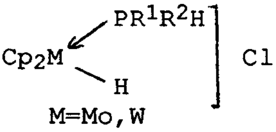
Abstract Reactions of metallophosphines bearing biscyclopentadienylhydridomolybdenum unit with MeI and metal carbonyls (Cr,Mo,W) and the chemical and spectroscopic properties of their products are presented. Some tungstenocene derivatives are included.

## INTRODUCTION

There is an increasing interest in transition-metal phosphido compounds as appropriate materials for stereochemical studies[1] and for synthesis of phosphido bridged bimetallic systems with potential catalytic activity.[2-4] Recently we prepared diphenylmetallophosphines (Mo,W) starting from the corresponding biscyclopentadienyl dihydrides and $PPh_2Cl$.[5-7] This method is applied now for syntheses of new metallophosphines with different substituents on phosphorus.

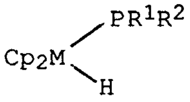
## RESULTS

Reactions of $Cp_2MH_2$ with chlorophosphines $PR^1R^2Cl$ ($R^1=R^2=$ Ph,Me,$NEt_2$; $R^1=$Ph, $R^2={}^iPr$,$NEt_2$) give metallophosphonium chlorides **1**. Deprotonation of **1** by NaOH leads to the neutral complexes **2** or **3**, depending on the nature of $R^1$ and $R^2$.



$[Cp_2M(PR^1R^2H)(H)]Cl$ **1**

M=Mo,W



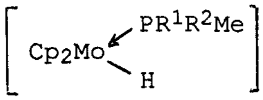
$Cp_2M(PR^1R^2)(H)$ **2**

$R^1$=Ph, $R^2$=Ph,${}^iPr$

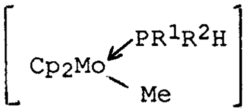
$Cp_2Mo\leftarrow PR^1R^2H$ **3**

$R^1=R^2$=Me,$NEt_2$
$R^1$=Ph,$R^2$=$NEt_2$

Reactions of MeI with **2** and **3** give phosphonium iodides **4** and **5**, respectively.

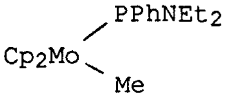


$[\mathrm{Cp_2Mo}(\leftarrow \mathrm{PR^1R^2Me})(\mathrm{H})]\,\mathrm{I}$ **4**



$[\mathrm{Cp_2Mo}(\leftarrow \mathrm{PR^1R^2H})(\mathrm{Me})]\,\mathrm{I}$ **5**

Action of KH on complexes **5** with aminophosphines leads to the neutral complexes **6** and **3**.



$\mathrm{Cp_2Mo(PPhNEt_2)(Me)}$ **6**

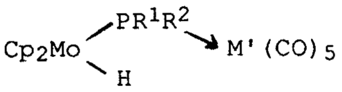
$\mathrm{Cp_2Mo \leftarrow P(NEt_2)_2H}$ **3**

Electronic structures of these complexes may be checked by $^{31}P$ and $^{1}H$ NMR spectroscopies. Data for the compounds with aminophosphines are given below (in acetone, $d^6$) as example.

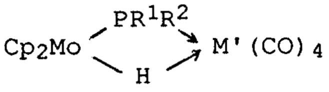
| | $\delta^{31}P$ | $^{1}J_{PH}$ | $\delta^{1}H(Cp)$ | $J_{PH}$ |
|---|---|---|---|---|
| $[\mathrm{Cp_2Mo^{IV}(H)(P(NEt_2)_2H]Cl}$ | 133.9 | 411 | 5.41 | 2.5 |
| $[\mathrm{Cp_2Mo^{IV}(Me)(P(NEt_2)_2H]Cl}$ | 133.4 | 414 | 5.29 | 2.4 |
| $\mathrm{Cp_2Mo^{II}\ P(NEt_2)_2H}$ | 160.3 | 350 | 3.92 | 5.7 |
| $[\mathrm{Cp_2Mo^{IV}(Me)(PPhNEt_2H)]Cl}$ | 105.0 | 400 | 5.43 | 2.6 |
| | | | 5.09 | 1.8 |
| $\mathrm{Cp_2Mo^{IV}(Me)(PPh(NEt_2))}$ | 102.3 | - | 4.69 | 1.4 |

$^{1}H$ chemical shift values are useful probes for electron buffering abilities of the Cp rings. The lowest fields are observed for cationic Mo(IV) complexes, followed by the neutral Mo(IV) complex and the neutral Mo(II) one. In this last product, the Cp protons resonate at the highest field observed to day in bent molybdenocenes. The $^{1}H$ resonances indicate that the positive charge in cationic complexes is localised rather on the $\mathrm{Cp_2Mo}$ fragment than on the phosphorus atom. The ligand behaves so as a normal phosphine bound to a metal. Higher $J_{PH(Cp)}$ coupling constant in Mo(II) complex than in all Mo(IV) complexes is due to a higher electron density on the rings. $^{31}P$ resonances in complexes with $\mathrm{P(NEt_2)_2H}$ give important informations on the nature of the Mo - P bonding. These resonances are little or not affected by changing the second $\sigma$ ligand on Mo(IV) (H vs.Me) but a deshielding by 27 ppm is observed in Mo(II) complex. This clearly indicates the presence of a rather strong metal to phosphorus π-back bonding. The smaller value of $^1J_{PH}$ in Mo(II) than in Mo(IV) compounds agrees with this description.

Complexes **2** and **3** ($R^1$=Ph, $R^2$=Ph,$^i$Pr, $R^1$=$R^2$=Me) react with M'$(CO)_5$THF (M'=Cr,Mo,W) giving phosphido bridged complexes **7** and **8**.

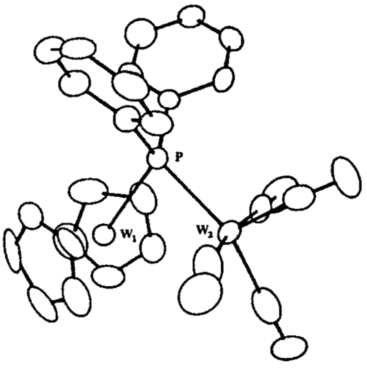


**7**



**8**

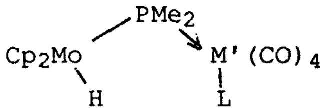
A deshielding of $^{31}P$ resonances of bridging phosphide by 90 to 120 ppm is observed in dibridged complexes **8**, with respect to the monobridged ones (**7**). Such a deshielding is a result of geometrical modifications of the bridging ligand and may be due to the presence of metal-metal interactions. X-ray structure analysis of one representative compound $Cp_2W(\mu\text{-}H,PPh_2)W(CO)_4$ confirms the above conclusion. The W-P-W angle of 81.6° is much more acute than in the monobridged $Cp_2Mo(H)(\mu\text{-}PPh_2)Mn(CO)_2Cp$[7] (124.5°) and the metal - metal separation of 3.271(1) Å shorter than in the Mo - Mn complex (4.391(1) Å).



An opening of the hydrido bridge in **8** ($R^1=R^2=Me$) was observed upon the action of different phosphines ($PPh_3$,$PPh_2H$, $PPh_2Me$,$PPhMe_2$,$PPh_2NEt_2$,$PMe_2Cl$), diphosphines (dppm,dppp), phosphite ($P(OMe)_3$) and metallophosphines ($Cp_2Mo(PMe_2H)$ **3**, $Cp_2Nb(PMe_2)(CO)$, and $Cp_2Ta(PMe_2)(CO)$). Di-, tri- and tetranuclear complexes with *cis* or *trans* geometries on metal M' are formed in these reactions.

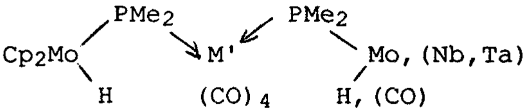
Dinuclear:

(phosphines, $P(OMe)_3$, dppm)



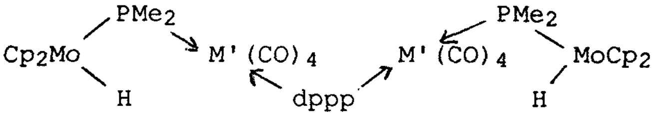
Trinuclear:

(metallophosphines)



Tetranuclear:

(dppp)



These studies are currently in progress.

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