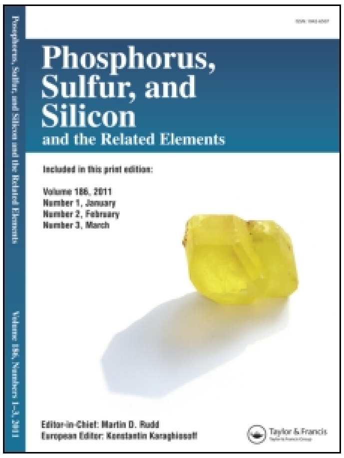

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New Bimetallics of Mo and W with Metallocene, Metal Carbonyl and Bridging PPh_2 or 'Cp'PPh_2 Units

VIRGINIE COMTE, OLIVIER BLACQUE, CLAUDE MOÏSE and MAREK M. KUBICKI

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques (UMR 5632) Université de Bourgogne, Dijon, France

Ring substituted (R=^{t}Bu, $SiMe_3$) metallocene dichlorides undergo a nucleophilic substitution on one of the two rings upon the action of $LiPPh_2M'(CO)_x$ salts with the formation of chloro-hydrido complexes $[C_5H_3(R)PPh_2M'(CO)_x](C_5H_4R)M(H)Cl$. Their UV irradiation leads to the chloro-bridged M(μ-Cl)M' separable diastereoisomers. Use of the *ansa*-metallocene dichlorides $[Me_2X(C_5H_4)_2MCl_2]$ (X=Si or C) allowed the access to the new bridging system [M(μ-PPh_2, μ-Cl)M'] (M=Mo, W ; M'=W).

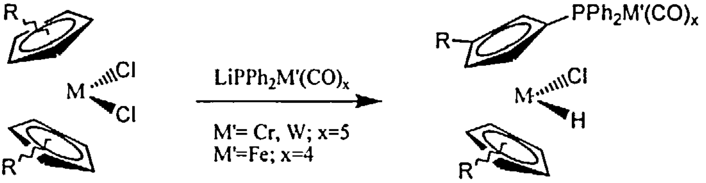
Keywords: bent metallocenes; metallophosphides; bimetallics; stereochemistry

INTRODUCTION

Dinuclear organometallics based on the bent metallocene connected to the M'L_n fragment through the "phosphorus" bridge (Cp_2M"P"M'L_n) may be formed by many ways. In particular, we explored the chemistry of phosphido (PR_2) bridged systems. The precursors for these bimetallics are the metallophosphines $Cp_2M(L)PR_2$ obtained by reactions of hydrides Cp_2MH_2 (M=Mo, W) [1], $Cp_2M(H)L$ (M=Nb, Ta) [2] or Cp_2MH_3 (M=Nb, Ta) [3] with chlorophosphines PR_2Cl. Alternative way consists of a metathesis reaction between the chloride Cp_2MCl_2 and the ionic phosphide (MPR_2) in the case of group 4 metallocenes [4,5]. Applied to the group 6 metallocene dichlorides, this last way leads to the not defined products. However, when a metallophosphide reagent $^-PPh_2M'(CO)_x$ is used, its nucleophilic attack on one of the two Cp rings occurs generating a chiral metal center and leading to the orthometallation in the case of Mo [6].

RESULTS

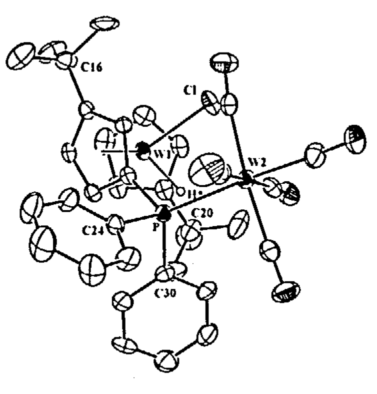
Ring substituted (^{t}Bu or SiMe$_3$) metallocene (M=Mo, W) dichlorides (**1**) react with metallophosphides giving, after the nucleophilic attack on one of the two "Cp" rings, the chloro-hydrido bimetallics (**2**).



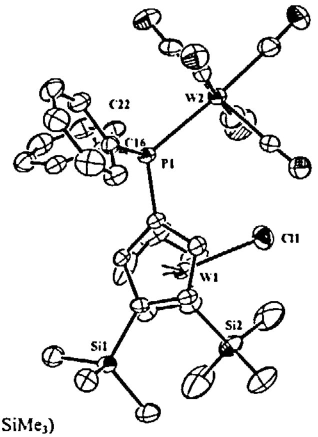
(1)
M=Mo, W; R= ^{t}Bu, SiMe$_3$

(2)

Two initially formed 1,3-disubstituted on one ring diastereoisomers with M=Mo epimerise over the metallic center (H *vs.* Cl inversion). A sole diastereoisomer SR/RS is isolated with M=W. The overall geometry of (**2**, ^{t}Bu, SiMe$_3$) depends on sterical requirements of substituants R.

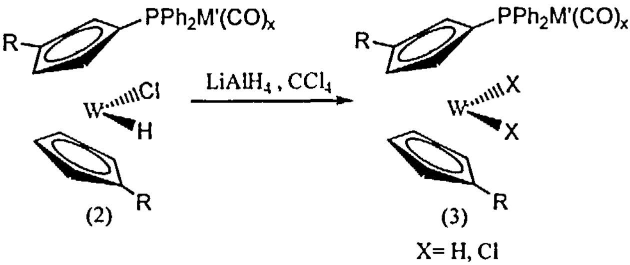


(2, ^{t}Bu)



(2, SiMe$_3$)

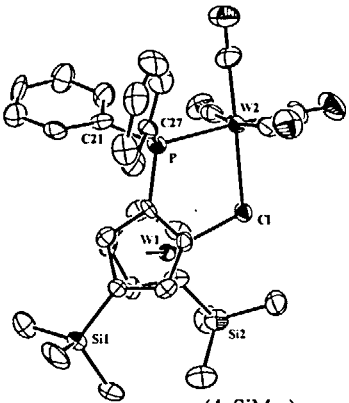
The orthometallation of the phenyl group from PPh_2 is not observed in our complexes. This is certainly due to the steric hindrances induced by the presence of bulky substituants on the rings. The chloro-hydrido complexes (**2**-W) are easily transformed to the corresponding bimetallic dihydrides or dichlorides (**3**).



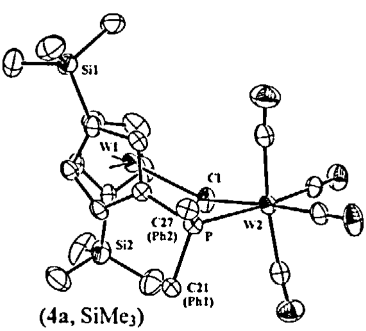
(2)

(3)
X= H, Cl

Reaction of (**1**, $SiMe_3$) (M=W) with $LiPPh_2M'(CO)_x$ gives some of the μ-Cl bridged complex (**4**). This compound has a SR/RS diastereoisomeric structure which confirms a regio- and diastereoselective nature of initial nucleophilic metallophosphide attack. However, the UV irradiation of (**2**-W) (M=W, SR/RS isomers) leads to two μ-Cl complexes SR/RS (minor, **4**) and SS/RR (major, **4a**).

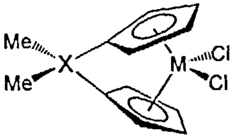


(**4**, $SiMe_3$)



(**4a**, $SiMe_3$)

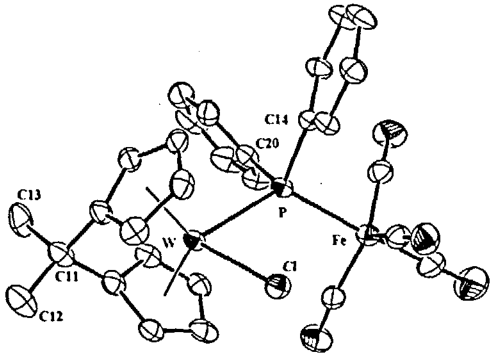
In order to make the metal center accessible for nucleophilic attack of $LiPPh_2M'(CO)_x$, we attempted the use of *ansa*-metallocenes (M=Mo, W).



X=Si, C

(5)

The metallophosphide attacks the ring when X=Si, while the metal is directly involved in the case of X=C. These observations agree with the steric constraints (Si *vs.* C) in *ansa*-metallocenes. The opening of the Cp'MCp' angle (ansa-C, up to 125°) allows the metal approach of metallophosphide as illustrated by the structure of the W-P-Fe system.



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