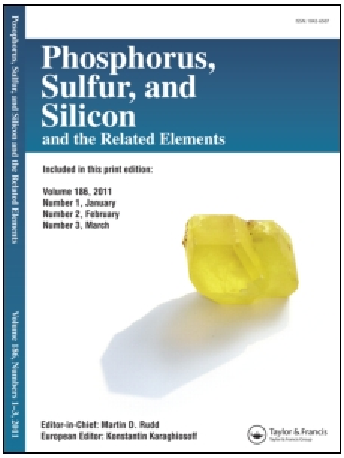
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Phosphorus Metal Double Bond Complexes: Functional and Chiral Species $Cp(L)(L')M{=}PR_2$ (M = Mo, W) and the Iron Derivative Cp (CO) Fe = $PMes_2$

Wolfgang Malisch[a]; Martin Märkl[a]; Sandro Amann[a]; Ulrich Hirth[a]; Martin Schmeußer[a]
[a] Institut fur Anorganische Chemie, Universitat Wurzburg, Wurzburg, FRG

To cite this Article Malisch, Wolfgang , Märkl, Martin , Amann, Sandro , Hirth, Ulrich and Schmeußer, Martin(1990) 'Phosphorus Metal Double Bond Complexes: Functional and Chiral Species $Cp(L)(L')M{=}PR_2$ (M = Mo, W) and the Iron Derivative Cp (CO) Fe = $PMes_2$', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 441 — 444

To link to this Article: DOI: 10.1080/10426509008038998

URL: http://dx.doi.org/10.1080/10426509008038998

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

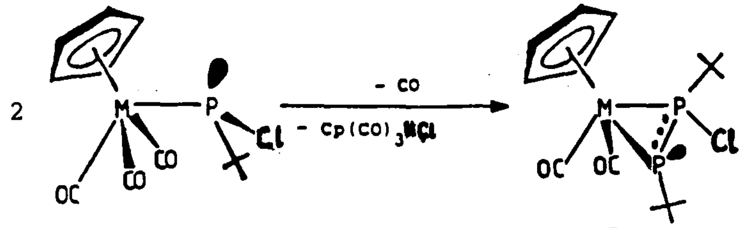
Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 441–444

PHOSPHORUS METAL DOUBLE BOND COMPLEXES: FUNCTIONAL AND CHIRAL SPECIES $Cp(L)(L')M{=}PR_2$ (M = Mo, W) AND THE IRON DERIVATIVE $Cp(CO)Fe{=}PMes_2$

WOLFGANG MALISCH, MARTIN MÄRKL, SANDRO AMANN, ULRICH HIRTH and MARTIN SCHMEUßER
Institut für Anorganische Chemie, Universität Würzburg,
Am Hubland, D-8700 Würzburg, FRG

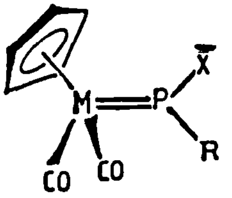
Abstract Novel M=P-complexes are discussed with respect to synthesis, structure and reactivity.

Complexes of the type $Cp(CO)_2M{=}PR_2$ (M = Cr, Mo, W) with a metal phosphorus double bond can be prepared either via decarbonylation of metallo-phosphanes $Cp(CO)_3M{-}PR_2$ or via dehydrochlorination of bifunctional complexes $Cp(CO)_2$-$(R_2PX)M{-}Y$ (X = Cl, H, ; Y = H, Cl) respectively.[1,2] These procedures are complementary and allow even the synthesis of functional metal phosphorus double bonded complexes $Cp(CO)_2M{=}P(X)R$ (**1**) (X = H, Cl; R = alkyl, aryl, dialkylamino, alkoxy) bearing a hydrogen or chlorine substituent at the sp^2-hybridized phosphorus. The metallo-chlorophosphanes $Cp(OC)_3M{-}P(Cl)R$ (**2**) necessary for the decarbonylation route are easily available from the reaction of diverse phosphanes $RPCl_2$ with the sodium metallates $Na[M(CO)_3Cp]$ (M = Mo, W). While metallo-chloro-dialkylaminophosphanes $Cp(OC)_3M{-}P(Cl)NR_2$ (R = Me, i-Pr) (**3**) with small ligands R preferentially decompose to the corresponding metalchloride $Cp(OC)_3MCl$, in the case of the metallo-tert.-butylchlorophosphanes **4** decarbonylation gives rise to the formation of the phosphametallacycles **5**, which involves the addition of a tert.-butylphosphinidene to the double bond complex $Cp(CO)_2M{=}P(t\text{-}Bu)X$ (M = Mo, W), formed as an intermediate (eq. 1). Only when R represents an extremely bulky ligand (2.2.6.6-tetramethylpiperidino-, 2.4-di(tert.-butyl)phenoxy) the metallo-chlorophosphane **2** smoothly decarbonylate to the corresponding double bonded species $Cp(OC)_2M{=}P(R)Cl$ (**6**a,b), which are isolated as crystalline solids.[2,3]

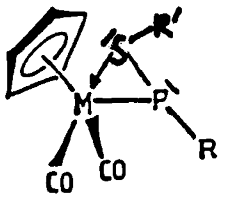


4 5 (1)

6a,b are highly reactive with respect to substitution of the chlorine atom against a vast series of nucleophiles $X^{\ominus}$ like $RO^{\ominus}$, $RS^{\ominus}$, $R_2N^{\ominus}$ to give the double bonded derivatives 7.



7

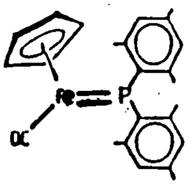


9

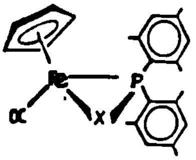
In contrast the decarbonylation of metallo-alkylthiophosphanes $Cp(OC)_3M-P(SR')R$ (R' = t-Bu, R = S-t-Bu; R' = i-Pr, t-Bu, R = t-Bu, N-i-Pr_2) (8) with less bulky groups R yields the three membered metallacycles 9, in which the alkylthio ligand bridges the M-P bond and the phosphorus is pyramidal. For the synthesis of P-H functional M=P complexes the dehydrohalogenation route is most efficient, starting with the bifunctional complexes $Cp(OC)_2[H_2(R)P]MCl$ (10). The double bonded species $Cp(OC)_2M=P(H)R$ (11) is obtained on treatment with DBU either as crystalline solid (R = 2.4.6-$(t\text{-}Bu)_3C_6H_3$) or as a short lived species (R = = t-Bu), stable in toluene at -60°C for 3 hours. However dehydrohalogenation of $Cp(CO)_2[H_2(Mes)P]MCl$ (12) directly yields the organometal substituted M=P-complexes $Cp(CO)_2M$-=P(Mes)-$M(CO)_2[P(Mes)H_2]ClCp$ (13) deriving from the interaction of primarily formed $Cp(CO)_2M=P(H)Mes$ with the starting material. This finding indicates high exchange activity of the phosphorus bound hydrogen of the M=P-compound 1, which can be used to introduce halogen, diverse transition metal fragments or organoelement groups at the sp^2-phosphorus, by means of $CHal_4$, transition metal and organoelement halides.

Chiral metal phosphorus double bond complexes $Cp(CO)(R_2PH)M{=}PR_2$ (14) ($R_2P = Ph_2P$, t-Bu(Ph)P) are obtained via dehydrohalogenation of $Cp(CO)(R_2PH)_2MCl$ (15) with $Me_3P{=}CH_2$. D-NMR studies prove, that the complexes exist in solution as a mixture of stereoisomers interconverting by rotation of the R_2P-fragment. 14 can be further deprotonated to the anionic diphosphametalla-alkyl species $[Cp(CO)(R_2P)_2M]^{\ominus}$ (16).

Dehydrohalogenation of $Cp(CO)(HMes_2P)Fe{-}Hal$ (17) gives access to 18, the first example of a species with an iron phosphorus double bond.

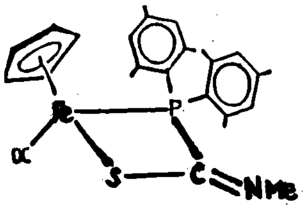


18

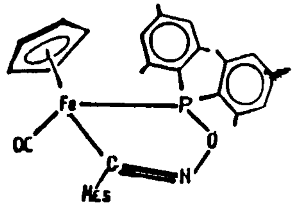


20

X = S, Se,
CH_2,
CHC(O)OEt



21



22

In comparison to the well-established M=P-complexes $Cp(CO)_2M{=}PR_2$ (M = Cr, Mo, W), 18 is characterized by the lower coordination number of its metal centre. This fact is reflected in a considerably increased reactivity of the M=P-bond, which opens up the possibility to generate sterically crowded ferrio-phosphanes $Cp(CO)(L)Fe{-}PMes_2$

(L = CO, R_3P, t-BuNC) (19) via reaction with CO, phosphanes or isonitriles respectively. Morever treatment of 18 with S_8, Se_8, $R(H)CN_2$ (R = H, CHC(O)OEt), MeNCS or MesCNO gives the novel three, four and five membered metallacycles 20-22 as the products of a [2+1]-, [2+2]- or [2+3]-cycloaddition.

REFERENCES

1. E.Groß, K.Jörg, K.Fiederling, A.Göttlein, W.Malisch, R.Boese, Angew. Chem. 96 (1984) 705; Angew. Chem., Int. Ed. Engl. 23 (1984) 738. - K.Jörg, W.Malisch, W.Reich, A.Meyer, U.Schubert, Angew. Chem. 98 (1986) 103; Angew. Chem., Int. Ed. Engl. 25 (1986) 92. - W.Malisch, K.Jörg, E.Groß, M.Schmeußer, A.Meyer, Phosphorus and Sulfur, 26 (1986) 25. - W.Malisch, K.Jörg, E.Groß, M.Schmeußer, R.Schemm, W.S.Sheldrick, ibid. 30 (1987) 205.
2. W.Malisch, S.Amann, E.Nodes, U.Hirth, M.Schmeußer, XIII. International Conference on Organometallic Chemistry, Torino (1938); Abstracts of Papers, p. 132. - W.Malisch M.Märkl, S.Amann, E.Nodes, U.Hirth, Eurochem Conference Psiblocs, Paris (1988), Abstracts of Papers, p. 3.
3. A.H.Cowley, D.Giolando, C.Nunn, M.Pakulski, D.Westmoreland, J. Chem. Soc., Dalton 1988, 2127.