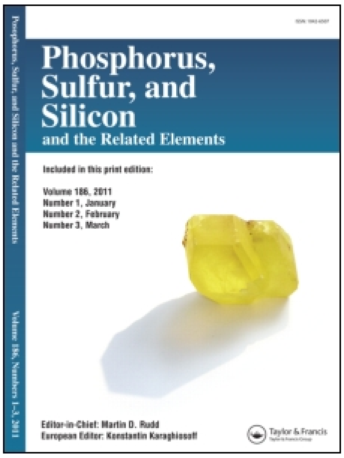

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Novel Aspects in Metal Phosphorus Double Bond Chemistry: Simple Access to P-Arylated, P-Alkylated and Chiral Derivatives and their Conversion to Three Membered Metallacycles

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NOVEL ASPECTS IN METAL PHOSPHORUS DOUBLE BOND CHEMISTRY: SIMPLE ACCESS TO P-ARYLATED , P-ALKYLATED AND CHIRAL DERIVATIVES AND THEIR CONVERSION TO THREE MEMBERED METALLACYCLES.

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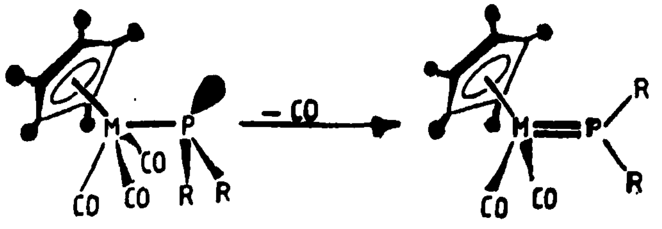
Complexes $Cp(CO)_2M{=}PR_2$ (M = Cr, Mo, W) with a metal phosphorus double bond can be prepared either via decarbonylation of the metallo-phosphanes $Cp(CO)_3M{-}PR_2$ or dehydrochlorination of the bifunctional complexes $Cp(CO)_2(R_2PX)M{-}Y$ (X = Cl, H, NMe_2; Y = H, Cl) respectively. These procedures are complementary and allow the introduction of diverse substituents at the phosphorus (R = alkyl, aryl, alkoxy, dialkylamino) as well as the synthesis of species $Cp(CO)(Me_3P)M{=}PR_2$ with a chiral metal centre. The high reactivity of the M=P-complexes offers easy access to diverse three membered metalla- and dimetallacycles.

A great deal of interest has focussed in the very last time on complexes featuring a double bond between phosphorus and a transition metal due to their high reactivity, which opens up novel synthetic pathways[1]. Moreover the electronic relationship to carbene complexes implies attractive stereochemical aspects.

For the generation of species with the general formula $Cp(CO)_2M{=}PR_2$ (M = Mo, W) two efficient synthetic procedures have been elaborated, starting from the corresponding metallo-phosphanes $Cp(CO)_3M{-}PR_2$[1c,e,2,3] (a) or the bifunctional complexes $Cp(CO)_2(R_2PX)M{-}Y$ (X = Cl, H, NMe_2; Y = H, Cl) (b)[1a,b]. (a) makes use of the fact, that the metallo-phosphanes 1a-g due to the pronounced Lewis basicity of the phosphorus and exchange activity of one CO ligand show a high tendency to undergo an intramolecular CO-substitution process according to equ. (1) involving the pyramidal phosphorus. The result is the formation of the metal phosphorus double bonded species 2a-g, exhibiting decreasing thermal stability in the series 2d,e; 2a-c, 2f,g.

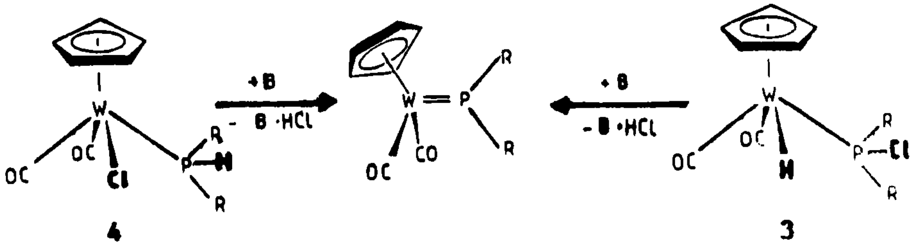


(1)

1a-g

	2a	b	c	d	e	f	g
M	Cr	Mo	W	Mo	W	Mo	W
R_2P	$P{-}OCMe_2{-}CMe_2{-}O$			$PMes_2$		PPh_2	
●—	H	H	H	H	H	Me	Me

Route (b) represents a new approach to M=P-complexes and applies for the first time a 1.2-elimination reaction to a main group element transition metal unit. It provides an extreme extension of the class of phosphorus transition metal double bonded compounds, since base promoted dehydrochlorination can be realized from the R_2PCl-substituted metalhydrides 3 as well as from the R_2PH-substituted metalchlorides 4[1a,b].



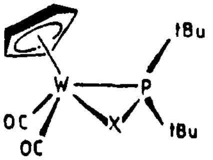
	5a	b	c	d	e	f	2c
R_2P	Me_2P	iPr_2P	tBu_2P	Ph_2P	P(Me)Ph	P(tBu)Ph	$\overline{POCMe_2CMe_2O}$

(2)

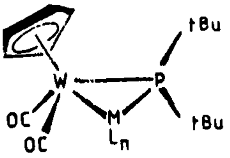
Moreover (2) can be successfully used for the synthesis of the species $Cp(CO)(Me_3P)M{=}PR_2$ bearing a chiral transition metal centre, which are accessible via CO/Me_3P exchange only in the case of the mesityl derivatives 2d,e. In special cases Me_2NH elimination from aminophosphane-substituted metalhydrides $Cp(CO)_2(Me_2N{-}PR_2)M{-}H$ opens up an additional possibility to get M=P-complexes[1a].

The conformation of the metal phosphorus double bonded complexes in solution follows from the temperature dependent ^1H-n.m.r. spectra of 2d,e,5c showing two resonances for the tert. butyl groups or the ortho-methyl groups respectively at low temperature. This clearly indicates a perpendicular orientation of the R_2P-plane with respect to the cyclopentadienyl ring and the $M(CO)_2$-plane, which is also found in the solid state and substantiates the importance of π-bonding resulting from a $dxz(W) \rightarrow p(P)\pi$ orbital overlap. The existence of a metal phosphorus double bond involving a trigonal planar, sp^2-hybridized phosphorus atom is proved by the short W-P-bond distance (218 - 228 pm) and the unusual high coupling constant J(WP) (550 - 850 Hz).

5c is characterized by a high reactivity of its double bond towards alcohols and water yielding the phosphine substituted metalhydrides $Cp(CO)_2[(RO)tBu_2]WH$ (R=H, Me, Et) (6a-c). The reaction of 5c with sulfur, selenium, diazomethane, $(MeP)_5$, Me_2PCl, $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$ results in the formation of the three membered metalla- and dimetallacycles 7a-e, 8a,b.



	7a	b	c	d	e
X	S	Se	CH_2	MeP	Me_2P^+



	8a	b
ML_n	$Fe(CO)_4$	$Ru(CO)_4$

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