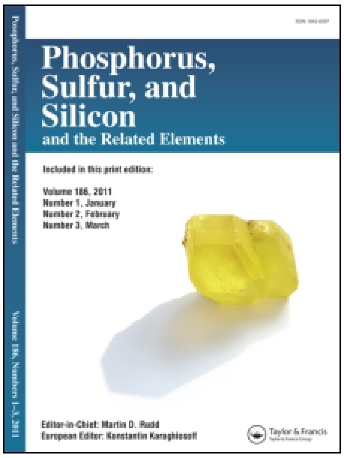

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From Metallo-Phosphines To Complexes With A Metal—Phosphorus Double Bond

Wolfgang Malisch[a]; Klaus Jörg[a]; Elisabeth Gross[a]; Martin Schmeusser[a]; Angelika Meyer[a]
[a] Institut für Anorganische Chemie der Universität Würzburg Am Hubland, Würzburg, GFR

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FROM METALLO-PHOSPHINES TO COMPLEXES WITH A METAL—PHOSPHORUS DOUBLE BOND

WOLFGANG MALISCH, KLAUS JÖRG, ELISABETH GROSS,
MARTIN SCHMEUSSER and ANGELIKA MEYER

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland,
8700 Würzburg, GFR.

The synthesis and reactivity of diverse metallo-phosphines $L_nM—PR_2$ ($L_nM{=}C_5R'_5(CO)_2Fe(Ru)$, $C_5R'_5(CO)_3Mo(W)$, $R'{=}H, Me$) is discussed. The generation of the metal—phosphorus double-bonded complexes $C_5H_5(CO)_2M{=}PR_2$ ($M{=}Mo, W$) via several routes is presented and the structure both in the solid state and in solution described in detail. Examples for the outstanding usefulness of M=P complexes as building blocks in the synthesis of metallacycles, dimetallacycles and clusters are given.

Metallo-phosphines $L_nM—PR_2$ (**1**) are now available by diverse routes. The most productive one is the nucleophilic metallation process, which has to be run in most of the cases heterogeneously in benzene or cyclohexane.[1]

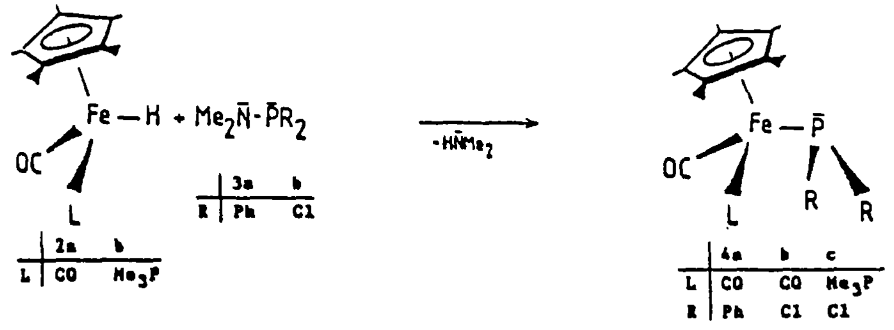
$$Na[ML_n] + R_2PCl \rightarrow L_nM - PR_2 + NaCl \qquad (1)$$

$L_nM{=}C_5R'_5(CO)_2Fe(Ru)$, $C_5R'_5(CO)_3Mo(W)$, $R'{=}H, Me$

$R_2P{=}Me_2P, Ph_2P, Cl_2P, \overline{OCMe_2 - CMe_2 - OP}$

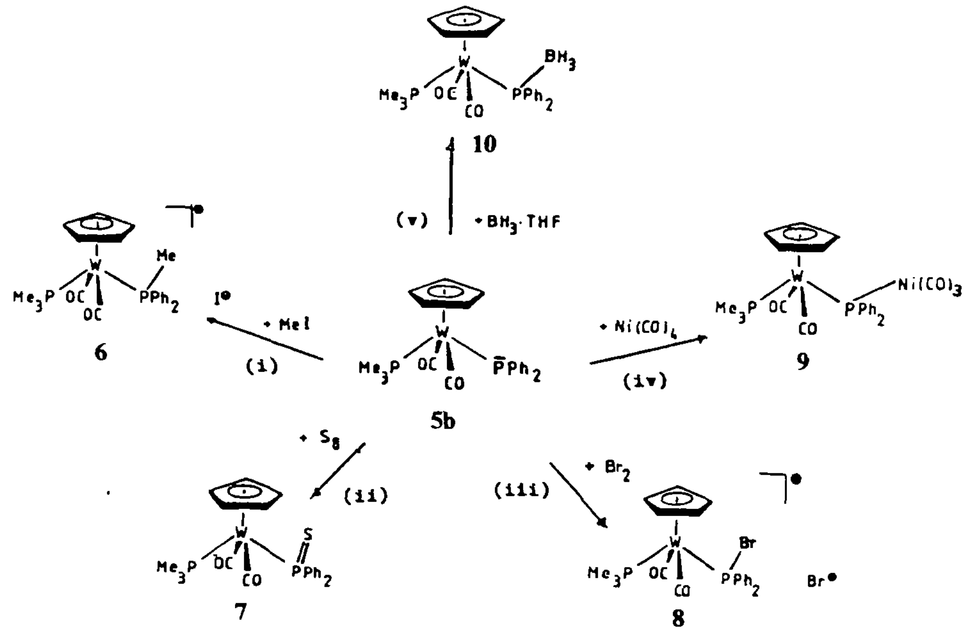
1

As a more special procedure the cleavage of the P—N-bond in the aminophosphines **3a, b** by the iron hydrides **2a, b** has been worked out, which allows even the introduction of the extremely electron-rich organoiron group $C_5Me_5(CO)(Me_3P)Fe$ at a trivalent phosphorus atom.[2]



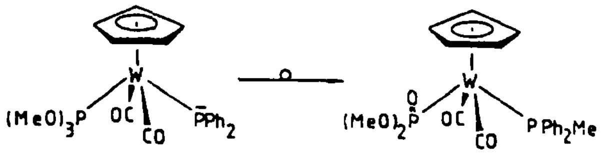
(2)

Among the reactivities of Mo- and W-derivatives, the pronounced CO-exchange activity towards Me_3P is remarkable, yielding the metallo-phosphines $Cp(CO)_2(Me_3P)M—PPh_2$ (M = Mo (**5a**), W (**5b**)) with the phosphine and phosphido donor mutually trans. Moreover, the metallo-phosphines are characterized by a high Lewis basicity, which is demonstrated by the easy alkylation of **5b** with MeI (i), oxidation with elemental sulfur (ii) or molecular bromine (iii), addition of the $Ni(CO)_3$ fragment (iv) or BH_3 (v) to give the tetravalent phosphorus compounds **6–10** illustrated below.[1,3]



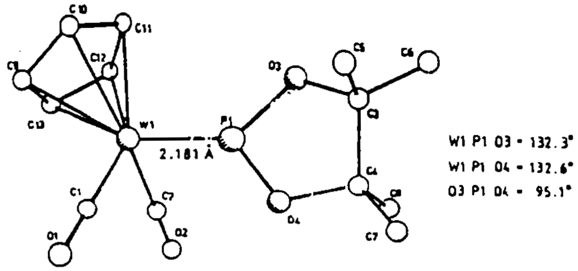
SCHEME 1

An extraordinarily impressive proof for this property is given by the ready isomerization of the phosphite-substituted metallo-phosphane **11** via alkyl migration to give the metal-phosphonate complex **12**.[4]



11 **12** (3)

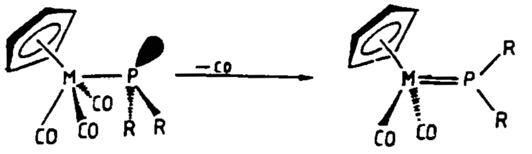
Lewis basicity and CO-exchange activity are responsible for the high tendency of metallo-phosphines to undergo an intramolecular CO-substitution process involving the trivalent phosphorus atom and the transition metal next to it.[5] The result is the formation of the metal—phosphorus double-bonded species **13a-e** with a trigonal planar, sp^2-hybridized phosphorus atom (Figure 1), which is indicated by the sum of



3

FIGURE 1

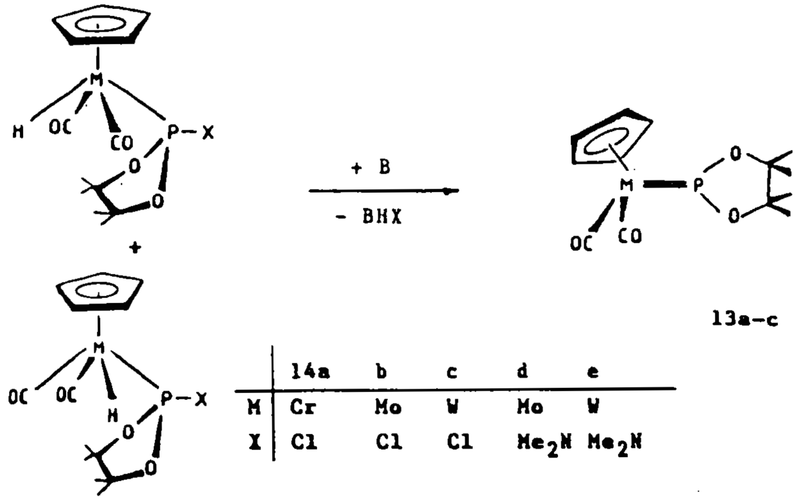
angles of 360° at the phosphorus and the unusually high coupling constant J(PW) for the tungsten derivatives, which is 847 Hz (**13c**) or 575 Hz (**13e**), respectively.



(4)

	13a	b	c	d	e
M	Cr	Mo	W	Mo	W
R_2P	$P{-}OCMe_2{-}CMe_2{-}O$			$PMes_2$	

An extreme extension of this attractive class of main group element transition-metal double-bonded compounds is given by the HCl- or Me_2N-elimination from the cis/trans metal-hydride complexes **14a–e** bearing a functionalized phosphorus ligand, according to eq. (5). This process can take place even at −40°C with the assistance of the strong base $Me_3P = CH_2$.[6]



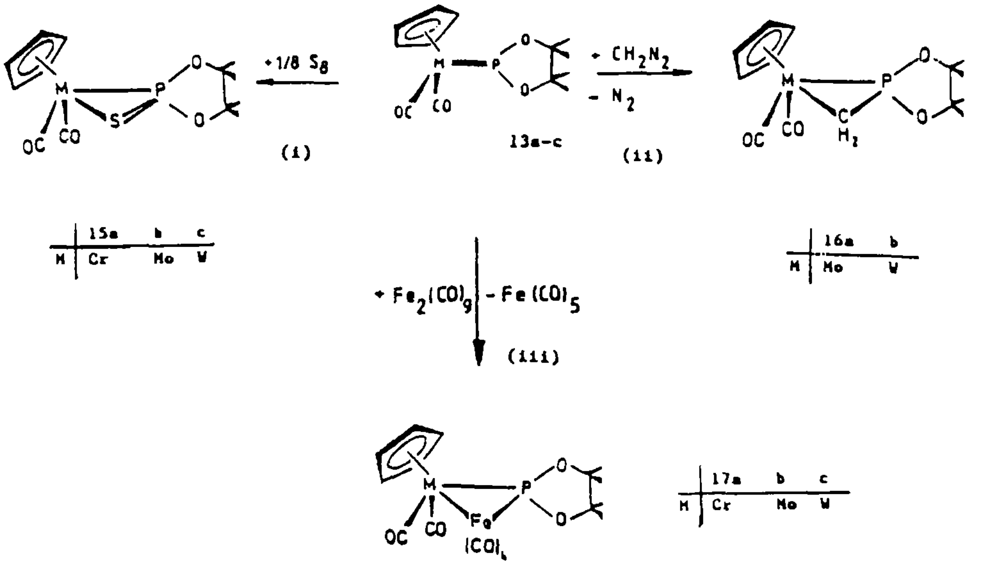
(5)

13a–c

	14a	b	c	d	e
M	Cr	Mo	W	Mo	W
X	Cl	Cl	Cl	Me_2N	Me_2N

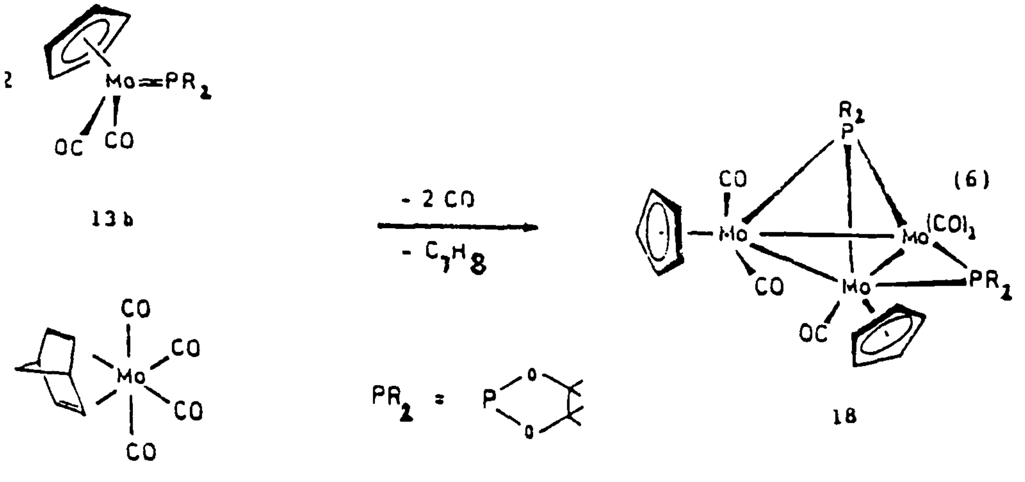
Substantial information concerning the conformation of the metal—phosphorus double-bonded complexes in solutions is obtained from temperature-dependent ^{1}H-NMR spectra of the mesityl derivatives **13d**, and **e**, which show two resonances for the orthomethyl groups and for the β hydrogens of the aryl substituent at low temperature. This clearly indicates a perpendicular orientation of the Mes_2P-plane with respect to the cyclopentadienyl ring and the $M(CO)_2$ plane. This finding is identical with the situation in the solid state (Figure 1) and indicates the importance of π-bonding resulting from a dxz(W) → p(P) orbital overlap. At room temperature only one signal is found owing to rapid rotation of the Mes_2P-fragment. The $\Delta G^\ddagger$ value for this process is estimated to be 12.8 kcal/mol.

The metal—phosphorus double-bonded complexes **13a–c** are characterized by an unusually high reactivity of the double bond towards elemental sulfur (i), diazomethane (ii) and $Fe_2(CO)_9$ (iii) resulting in the formation of the spirocyclic species **15–17** bearing a three-membered metalla- or dimetallacycle (Scheme 2).



SCHEME 2

Moreover, the double-bonded complexes can be used as an efficient building block in cluster synthesis. An outstanding example is illustrated in eq. (6), where the Mo—P double-bonded complex **13b** reacts with $C_7H_8Mo(CO)_4$ in the molar ratio of 2 : 1 with elimination of the bisolefin and carbon monoxide to generate the cluster **18** having a Mo_3P-core and both doubly and triply bridging dioxaphospholane units.[7]



REFERENCES

1. W. Malisch, R. Maisch, J. Colquhoun and W. McFarlane, *J. Organomet. Chem.*, **220**, C1 (1981); W. Angerer, W. S. Sheldrick and W. Malisch, *Chem. Ber.*, **118**, 1261 (1985).
2. W. Angerer and W. Malisch, unpublished result.
3. R. Maisch, E. Ott, W. Buchner, W. Malisch, W. S. Sheldrick and W. McFarlane, *J. Organomet. Chem.*, **286**, C31 (1985).
4. R. Maisch and W. Malisch, unpublished results.
5. For other examples of this route, see L. D. Hutchins, N. E. Deusler and R. T. Paine, *Organometallics*, **3** 399 (1984); A. H. Cowley, N. C. Norman and S. Quashie, *J. Am. Chem. Soc.*, **106**, 5007 (1984); E. Niecke, D. Gudat, W. Malisch, U. Hofmockel, A. H. Cowley, A. M. Arif, S. Quashie, B. Krebs and M. Dartmann, *Angew. Chem.*, submitted for publication.
6. E. Groß, K. Jörg, K. Fiederling, A. Göttlein, W. Malisch and R. Böse, *Angew. Chem. Int. Ed. Engl.*, **23**, 738 (1984).
7. W. Malisch, E. Groß, K. Jörg, M. Schmeußer and M. L. Ziegler, *Angew. Chem.*, submitted for publication.