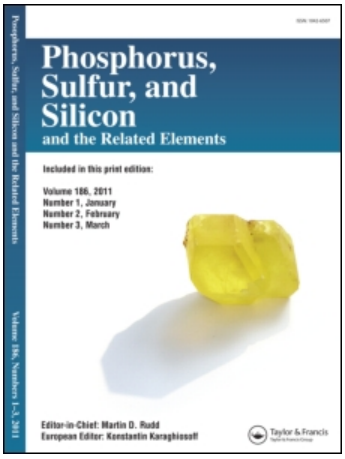


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Complexes with a Metal Phosphorus Triple Bond

Manfred Scheer; Peter Kramkowski; Michael Schiffer; Jan Müller

To cite this Article Scheer, Manfred , Kramkowski, Peter , Schiffer, Michael and Müller, Jan(1999) 'Complexes with a Metal Phosphorus Triple Bond', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 717 — 720
To link to this Article: DOI: 10.1080/10426509908546345
URL: http://dx.doi.org/10.1080/10426509908546345

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 717-720
Reprints available directly from the publisher
Photocopying permitted by license only

Complexes with a Metal Phosphorus Triple Bond

MANFRED SCHEER, PETER KRAMKOWSKI, MICHAEL SCHIFFER and JAN MÜLLER

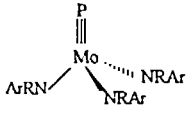
Institute of Inorganic Chemistry, University of Karlsruhe, D-76128 Karlsruhe, Germany

Herein we report the synthesis of different phosphido-complexes and -intermediates with W≡E-triple bond. These compounds reveal different reactivity patterns. Details of reactivity as well as spectroscopic and theoretical aspects will be discussed in detail.

Keywords: phosphido ligands; alkoxide complexes; metal-phosphorus-multiple bond

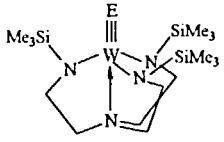
INTRODUCTION

Complexes with terminal pnicogenido ligands (except nitrogen) are a new class of compounds[1] the first examples being phosphido(P^{3-}) ligands which were first isolated and structurally characterized in 1995 by Cummins and Schrock in form of the complexes of type **A**[2] and **B**[3], respectively. These complexes reveal „end-on" reactivity. Our synthetic goal however, has been directed towards the alkoxide substituted complexes of type **C**, showing a high „side-on" reactivity.



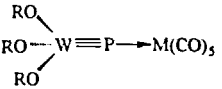
R = $C(CD_3)_2CH_3$
Ar = $3,5\text{-}C_6H_3Me_2$

A



1: E = P
2: E = As

B



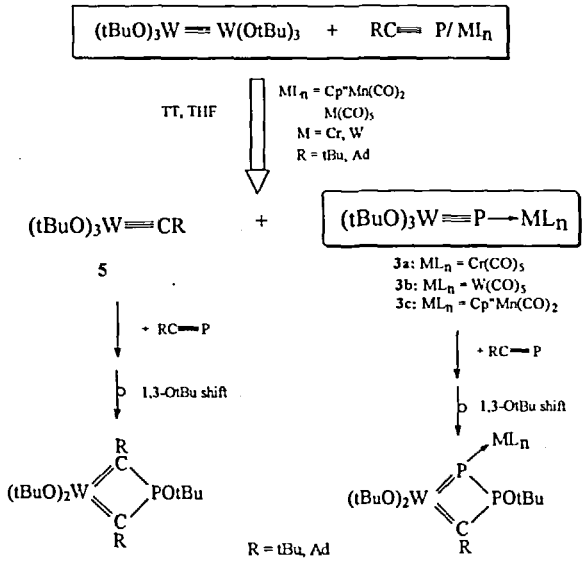
3: R = *t*Bu; M = Cr (a), W (b)
4: R = Ar; M = Cr (a), W (b)
Ar = $2,6\text{-}Me_2C_6H_3$

C

RESULTS AND DISCUSSION

Using our concept of the three-component-reaction[4] to stabilize reactive intermediates the reaction of $W_2(OtBu)_6$ with R'C≡P (R' = *t*Bu, Ad) was carried out in the presence of Lewis acidic carbonyl complexes and resulted in the formation of the alkylidyne complexes **5** and the phosphido complexes **3**[5]. However, a subsequent reaction with additional R'C≡P followed by 1,3-migration of the alkoxy ligand to form compounds with four-membered rings, cannot be completely prevented. Due to the decomposition

of the products a separation of the reaction mixture by column chromatography failed. The enrichment of **3a** in solution was achieved by fractional crystallization. The ^{31}P NMR chemical shifts at δ = 595.4, (**3a**) 544.6 (**3b**) and 614.0 (**3c**), the large $^{1}J(^{183}W,^{31}P)$ coupling constants of 536 Hz (**3a**), 554 Hz (**3b**) and 566 Hz (**3c**), and the appearance of a second coupling in the case of the $[W(CO)_5]$-substituted product **3b** of J = 163 Hz together with the ratio of the signal integrals prove the existence of **3**.

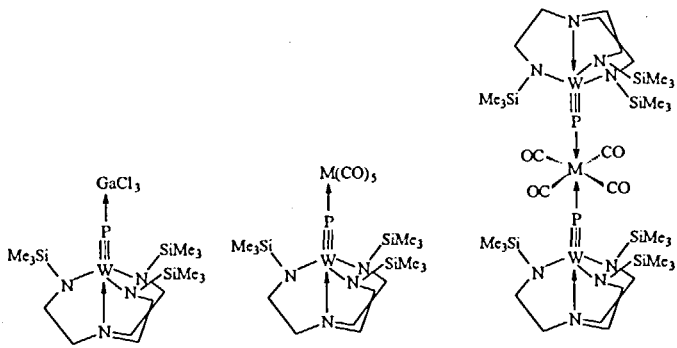


When Schrock reported the NMR-data of **1**[3], the $^{183}W,^{31}P$ coupling constant of 138 Hz contradicted to the coupling constants observed for our carbonyl stabilized phosphido species **3a-c**[5]. To shed light into this problem, we decided to synthesize **1**, using $Li[P(SiMe_3)_2]$ and then achieve complexation with $[W(CO)_5(thf)]$. The break through for the high yield synthesis and structural characterisation of the type **C** complexes **3** and **4** occurs when MesC≡P (Mes = 2,4,6-$Me_3C_5H_2$) is used in the reaction with $W_2(OR)_6$ and $[M(CO)_5(thf)]$.

By PESHO analysis[6] we searched for the triple bonding characteristics of **1** consisting of one d_σ-p_σ bond and two d_π-p_π bonds. Only a small contribution of the 6s W and the 3s orbital of P for the d_σ-p_σ bond is found. Coordination of **1** to a simple σ acceptor (e.g. BH_3, calculated) leads to a small shortening of the W≡P bond due to the increase of the 3s orbital participation of the phosphido ligand. With an approximately constant π-bonding contribution, the phosphorus-3s orbital contribution to a W-P bond

increases whilst at the same time the phosphorus-3p σ-contribution decreases. Therefore, the corresponding Fermi contact term results in an increase of the $^{183}W,^{31}P$ coupling constant upon linear coordination of the phosphido ligand complex to a σ acceptor, which is both, expected and experimentally observed. Moreover the phosphido complex **1** is expected to have σ-donor and π-acceptor abilities and can be characterized by similar, but less pronounced, ligating properties as CO.

In fact the formation of linear complexes with σ acceptors such as $GaCl_3$[7] is possible, shown in the synthesis of complex **6**. Furthermore, **1** reacts with $[M(CO)_5(thf)]$ (M = Cr, W) to form first complexes **7** although a second substitution in the *trans*-position is preferred leading to the $M(CO)_4$ complexes **8**[6]. The driving force for the *trans* substitution was found to be the formation of $M(CO)_6$[6].



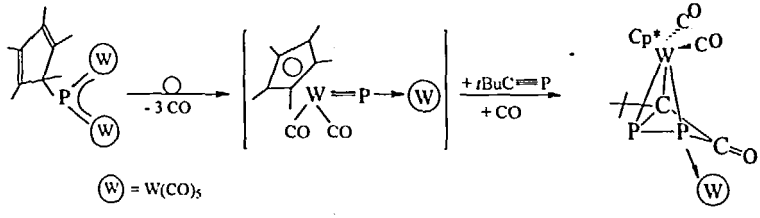
6 **7**: M = W (**a**), Cr (**b**) **8**: M = W (**a**), Cr (**b**)

From experimental data the coordination of the σ acceptor $GaCl_3$ or the σ-acceptor/π-donor $M(CO)_n$ (M = Cr, W; n = 4, 5) results in a high field shift of the ^{31}P-NMR resonances and an increase of the $^{183}W,^{31}P$ coupling constants to about 400-750 Hz. This increase in coupling constants is much stronger for σ acceptors (> 700 Hz). For the latter complexes, the M≡E bond length remains more or less the same as predicted by the theoretical studies[6]. However, a σ-acceptor/π-donor group such as $M(CO)_n$ increases the triple bond distance due to the occupation of antibonding orbitals at the pnictinido atom.

Furthermore, the use of $[E(SiMe_3)_2]^-$ (E = As, Sb, Bi) should open the possibility to synthesize complexes containing the heavier homologues of phosphorus. In the case of E = As, the arsenido complex $[(N_3N)W{\equiv}As]$ **2** is obtained. However, no E≡W bond formation could be achieved for the heavier congeners so far. It is interesting to note

that the calculated W≡Sb distance in the compound $[(N_3N)W{\equiv}Sb]$ is 2.514 Å[6]. Attempts using less bulky organic substituents on the tren ligands result in the formation of the first neutral, paramagnetic heterocumulens of the type $[(N_3N)W{=}Sb{=}W(N_3N)]$ ($N_3N = N(CH_2CH_2NNp)_3$)[8].

Additionally, a novel approach to highly reactive phosphido complex intermediates of the type $[L_nM{\equiv}P{\rightarrow}M'(CO)_5]$ (M' = Cr, W) is achieved by a migration of a σ-bounded Cp* at the P atom in the phosphinidene complex $[Cp^*P\{W(CO)_5\}_2]$ to give η^5-coordination at a transition metal. The intermediate stabilises itself by dimerisation to yield $[\{Cp^*(CO)_2W\}_2((\mu,\eta^2\text{-}P_2)\{W(CO)_5\})]$[9]. If this thermolysis reaction is carried out in the presence of *t*BuC≡P, a novel *cyclo*-diphosphabutenon ligated complex is formed.



Acknowledgments

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

[1] Review: M. Scheer, *Coord. Chem. Rev.*, **163**, 271 (1997).
[2] C. E. Laplaza, W. M. Davis and C. C. Cummins, *Angew. Chem. Int. Ed. Engl.*, **34**, 2042 (1995).
[3] R. R. Schrock, N. C. Zanetti and W. N. Davis, *Angew. Chem. Int. Ed. Engl.*, **34**, 2044 (1995).
[4] M. Scheer, K. Schuster and U. Becker, *Phosphorus, Sulfur, and Silicon*, **109–110**, 141 (1996).
[5] M. Scheer, K. Schuster, T. A. Budzichowski, M. H. Chisholm and W. E. Streib, *J. Chem. Soc. Chem. Commun.*, **1995**, 1671.
[6] M. Scheer, J. Müller and M. Häser, *Angew. Chem. Int. Ed. Engl.*, **35**, 2492 (1996).
[7] M. Scheer, J. Muller, G. Baum, M. Häser, *J. Chem. Soc. Chem. Commun.*, **1998**, 1051.
[8] M. Scheer, J. Müller, M. Häser, *Angew. Chem.*, submitted.
[9] M. Scheer, E. Leiner, P. Kramkowski, M. Schiffer, G. Baum, *Chem. Eur. J.*, accepted.