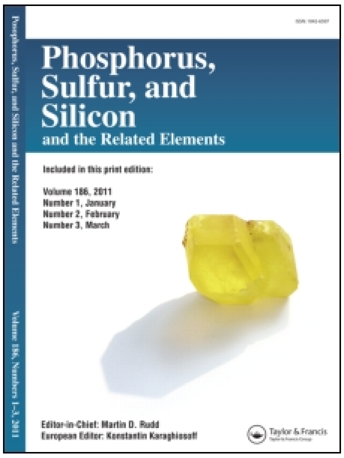

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Complexes with a Metal-Phosphorus Triple Bond as Versatile Building Blocks in Coordination and Organometallic Chemistry

Manfred Scheer[a]; Michael Schiffer[a]; Eva Leiner[a]; Brian P. Johnson[a]; Corinna Haindl[a]; Shubhangi Umbarkar[a]
[a] Institute of Inorganic Chemistry, University of Karlsruhe, Karlsruhe, Germany

To cite this Article Scheer, Manfred , Schiffer, Michael , Leiner, Eva , Johnson, Brian P. , Haindl, Corinna and Umbarkar, Shubhangi(2002) 'Complexes with a Metal-Phosphorus Triple Bond as Versatile Building Blocks in Coordination and Organometallic Chemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1617 — 1620

To link to this Article: DOI: 10.1080/10426500212300

URL: http://dx.doi.org/10.1080/10426500212300

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1617–1620

1042-6507/02 \$12.00 + .00
DOI: 10.1080/10426500290092767

COMPLEXES WITH A METAL–PHOSPHORUS TRIPLE BOND AS VERSATILE BUILDING BLOCKS IN COORDINATION AND ORGANOMETALLIC CHEMISTRY

Manfred Scheer, Michael Schiffer, Eva Leiner, Brian P. Johnson, Corinna Haindl, and Shubhangi Umbarkar
Institute of Inorganic Chemistry, University of Karlsruhe, Karlsruhe, Germany

(Received August 3, 2001; accepted December 25, 2001)

Trapping reactions of the phosphido complex intermediate $[Cp^*(CO)_2W{\equiv}P{\rightarrow}W(CO)_5]$*, generated by thermolysis of* $[Cp^*P\{W(CO)_5\}_2]$ ***1****, occur via [2 + 2] cycloaddition reactions with* P_4*, phosphaalkynes, alkynes, and* $[CpMo(CO)_2]_2$*, respectively. However, with nitriles, insertion reactions into the P—C σ bond of* ***1*** *are observed already at room temperature to give novel P-containing heterocycles. Furthermore, irradiation of* ***1*** *gives the tetrahedral complex* $[Cp^*(CO)_6W_2\}(\mu\text{-}H)(\mu,\eta^2\text{-}P_2)\{W(CO)_5\}_2]$*, which indicates that besides the formation of the triple-bond intermediate* $[Cp^*(CO)_2W{\equiv}P{\rightarrow}W(CO)_5]$ *a second Cp* elimination intermediate of the type* $[P\{W(CO)_5\}_2]$ *occurs.*

Keywords: Cyloadditions; insertion reactions; multiple bonds; P ligands

Recently we have developed a direct synthetic approach to complexes of the type $[L_nM{\equiv}P{\rightarrow}M(CO)_5]$[1] as highly reactive intermediates. The principle of their generation is based on the migration of a σ-bound Cp* at the phosphorus atom of the phosphinidene complex **1** to give an η^5-coordination mode at the transition metal in the formed intermediate **A**. In the absence of any reactive substrate, the intermediate stabilizes itself by dimerization to yield complex **2** (Figure 1).[2]

The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for comprehensive financial support.

Address correspondence to Manfred Scheer, Institute of Inorganic Chemistry, University of Karlsruhe, Karlsruhe D-76128, Germany.

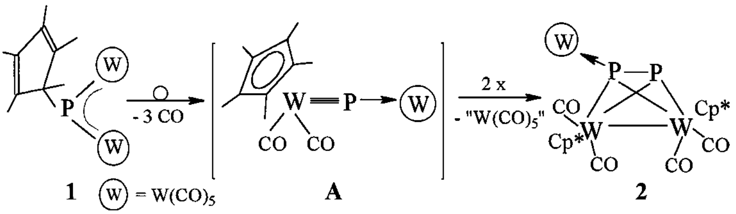

FIGURE 1

RESULTS AND DISCUSSION

The trapping reaction chemistry of the highly reactive triple bond intermediate **A** is mainly characterized by [2 + 2] cycloaddition reactions. Thus, thermolysis of the phosphinidene complex $[Cp^*P\{W(CO)_5\}_2]$ **1** in the presence of P_4 phosphorus yields the cyclo-P_3-containing complex $[Cp^*(CO)_2W(\eta^3\text{-}P_3)]$ **3**, where P_4 acts as a source of "P_2" moieties. In the reaction with *t*-BuC≡P a novel *cyclo*-diphosphabutenone ligated complex **4** is obtained (Eq. 2 in Figure 2). Here the cycloaddition reaction occurs with participation of one molecule CO. The thermolysis reactions of **1** in the presence of PhC≡CPh lead to complex **5** (Eq. 3),[3] while use of $[CpMo(CO)_2]_2$ as a trapping reagent leads to the tetrahedral cluster **6** (Eq. 4) as the major reaction products. In the case of the reaction with alkynes, after [2 + 2] cycloaddition, the resulting four-membered ring

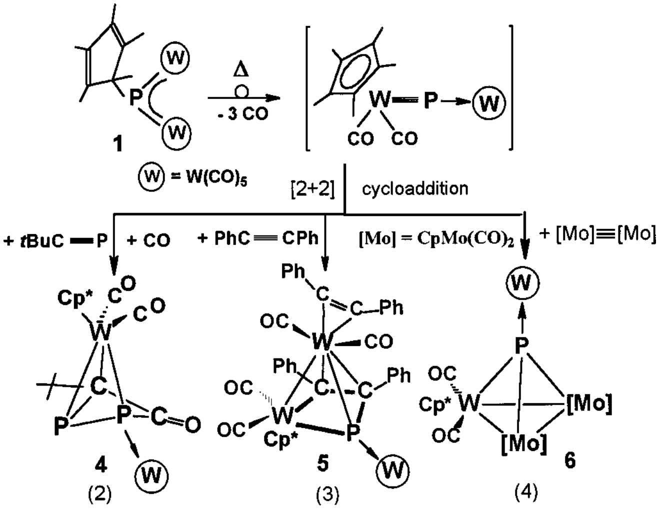

FIGURE 2

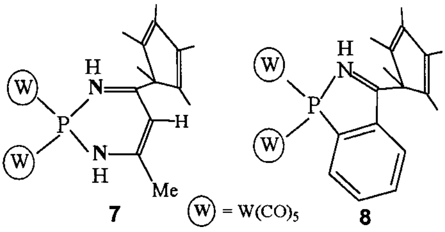

FIGURE 3

derivative needs for stabilization an external tungsten carbonyl group as capping complex fragment to form **5**.[3]

For transition-metal complexes containing metal–metal multiple bonds like $[CpMo(CO)_2]_2$, metal–phosphorus and metal–metal bond formation occurs upon cycloaddition to give the tetrahedral cluster **6**.

Additionally, reactions of $[Cp^*P\{W(CO)_5\}_2]$ with nitriles, such as MeCN and PhCN, occur already at ambient temperature. As products, the novel derivatives 1,2-dihydro-1,3,2-diazaphosphinine **7** and benzo-1*H*-1,2-azaphosphole **8** were obtained (Figure 3), which indicate the unusual insertion reaction of nitriles into the P—C σ bond of the phosphinidene complex and additionally CH-activation reactions even under mild conditions.[4]

Furthermore, irradiation of the phosphinidene complex **1** in the absence of any other substrate gives the tetrahedral complex $[Cp^*(CO)_6W_2\}(\mu\text{-}H)(\mu,\eta^2\text{-}P_2)\{W(CO)_5\}_2]$ **9**. The product shows the occurrence of the triple-bond intermediate **A** as well as another intermediate **B**, resulting from a Cp* elimination process (Figure 4). Intermediates **A** and **B** undergo a dimerization reaction to form the tetrahedral cluster **9**.[5]

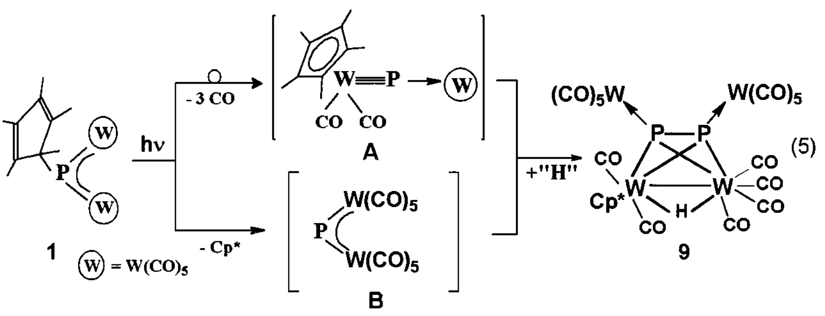

FIGURE 4

REFERENCES

[1] For reviews compare: M. Scheer, *Angew. Chem. Int. Ed. Engl.*, **34,** 1997 (1995); *Coord. Chem. Rev.*, **163,** 271 (1997).

[2] M. Scheer, E. Leiner, P. Kramkowski, M. Schiffer, and G. Baum, *Chem. Eur. J.*, **4,** 1917 (1998).

[3] M. Schiffer and M. Scheer, *Chem. Eur. J.*, **7,** 1855 (2001).

[4] M. Schiffer and M. Scheer, *Angew. Chem.*, **113,** 3520 (2001).

[5] M. Schiffer, E. Leiner, and M. Scheer, *Eur. J. Inorg. Chem.*, 1661 (2001).