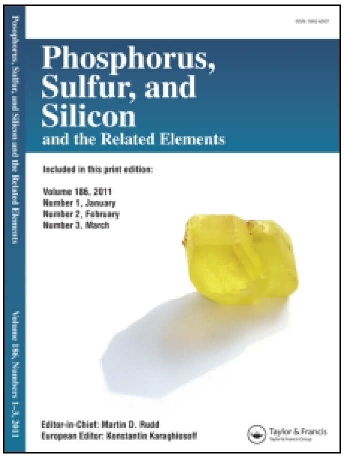


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Oligomerization Of σ^L, λ^1-Phosphaalkynes at Transition Metal Templates

P. Binger[a]; S. Barth[a]; B. Biedenbach[a]; J. Haas[a]; A. T. Herrmann[a]; R. Milczarek[a]; R. Schneider[a]
[a] Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, F.R.G.

To cite this Article Binger, P. , Barth, S. , Biedenbach, B. , Haas, J. , Herrmann, A. T. , Milczarek, R. and Schneider, R.(1993) 'Oligomerization Of σ^L, λ^1-Phosphaalkynes at Transition Metal Templates', Phosphorus, Sulfur, and Silicon and the Related Elements, 77: 1, 1 — 4

To link to this Article: DOI: 10.1080/10426509308045604

URL: http://dx.doi.org/10.1080/10426509308045604

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, pp. 1–4
Reprints available directly from the publisher
Photocopying permitted by license only

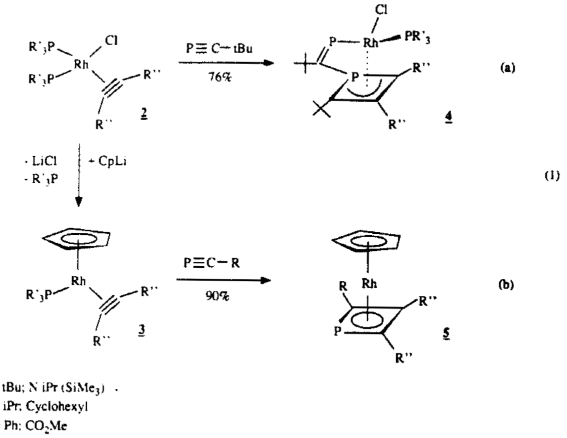
OLIGOMERIZATION OF σ^1,λ^1-PHOSPHAALKYNES AT TRANSITION METAL TEMPLATES

P. BINGER*, STEFAN BARTH, BRUNO BIEDENBACH, JOSEF HAAS,
ALBERT T. HERRMANN, ROMAN MILCZAREK, RONALD SCHNEIDER
Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr, F.R.G.

Abstract Some cooligomerization between phosphaalkynes and alkynes in the coordination sphere of a transition metal are reported.

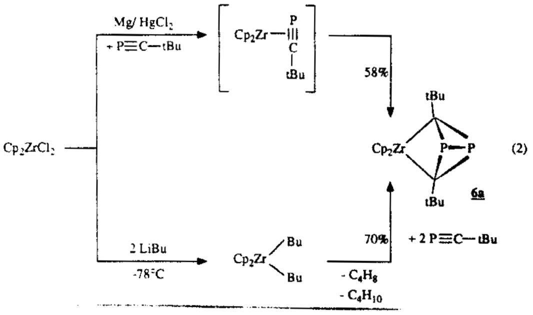
Whereas cyclodimerization of phosphaalkynes 1 leading to η^4-1,3-diphosphacyclobutadiene complexes of cobalt, rhodium or iron are now well known[1], comparable cyclocodimerization between a phosphaalkyne and an alkyne to give η^4-monophosphacyclobutadiene metal complexes are rare.[2]

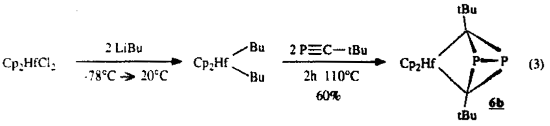
We now found that this goal can be readily achieved when η^5-cyclopentadienyl-(tri-sec.-alkylphosphane)-η^2-alkyne rhodium complexes[3] 2 are used as starting materials (Eq. 1 b).[4] On the other hand, from η^2-alkyne-bis(tri-sec.-alkylphosphane)rhodiumchloride 2 and 1 the primarily formed monophosphacyclobutadiene rhodium complex reacts with a second phosphaalkyne, presumably by insertion into the P-Rh σ-bond of the η^1,η^3-monophosphacyclobutadiene form to give the new rhodium complex 4[4] (Eq. 1 a). Over all, in this reaction a cotrimerization between two phosphaalkynes and one alkyne has been achieved for the first time. Cyclodimerization of phosphaalkynes as well as cyclocodimerization with alkynes can also be carried out in the coordination sphere of metallocene(II) derivatives of Zr and Hf, but the structures of the resulting new complexes are completely different from those obtained with Co or RH as central metal.

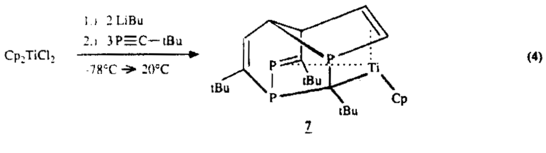


R = tBu; N iPr(SiMe$_3$)
R' = iPr; Cyclohexyl
R'' = Ph; CO$_2$Me

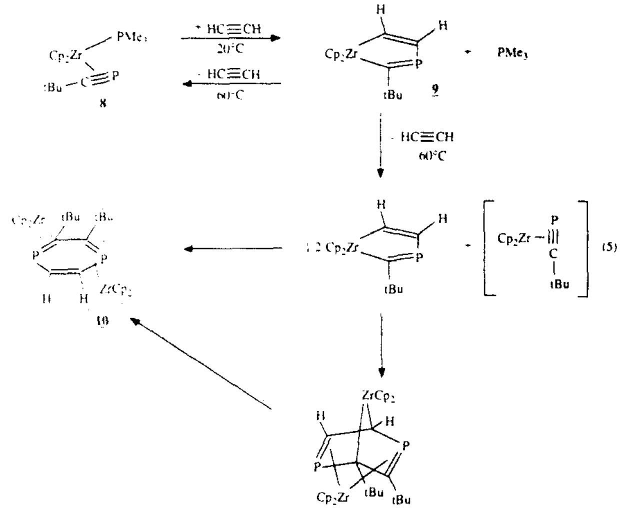
The one pot cyclodimerization of phosphaalkynes starting with zirconocendichloride and hafnocendichloride gives the corresponding 1,3-diphosphabicyclo[1.1.0]butandiyl metallocenes 6 a,b in good yield^5 (Eq. 2 and 3). The analogous reaction sequence starting with titanocene dichloride is much more complicated and incooperation of the cyclopentadiene group into the new formed oligomere is observed leading to the titanium complex 7 (Eq. 4).







Contrary to these findings, codimerization between a phosphaalkyne and an alkyne is best accomplished starting with a preformed phosphaalkyne metallocene complex, e. g. 8.[6] As an example, the codimerization of acetylene with tert-butyl phosphaacetylene affords complex 9 (Eq. 4). In an analogous manner, mono- and disubstituted alkynes react to give 1-phospha-3-metallacyclopentadiene derivatives of type 9. All these 1-phospha-3-metallacyclopentadienes are thermally much less stable than the corresponding metallacyclopentadiene derivatives; e. g. in complex 9 the new formed P-C bond is broken by heating to 60°C. In the presence of trimethylphosphane the educts 8 and acetylene are regained; in the absence of trimethylphosphane the coordinative unsaturated phosphaalkyne complex undergoes a [4+2]cycloaddition to complex 9. After rearrangement the unknown 1,4-diphosphabenzene derivative 10 can be isolated which is stabilized by η^2-complexation of the two P=C double bonds to two zirconocene units. Other 1-phospha-3-zirconacyclopentadienes decompose into the educts even at 0°C, especially those bearing phenyl groups at the C=C double bond.



1,3-diphosphabicyclo[1.1.0]butanediyl zirconocene 6 a and hafnocene 6 b are excellent starting materials for the synthesis of new phosphorous heterocycles. The products are often not predictable because after splitting of the M-C bond unusual rearrangements or cycloadditions are observed. One prominent example is the high yield synthesis of tetraphosphacubane from complex 6 a and hexachlorethane.[5]

REFERENCES

1. Reviews: J.F. Nixon, Chem. Rev., 88, 1327 (1988).- J.F. Nixon, Endeavour, 15, 49 (1991).- M. Regitz, P. Binger, Angew. Chem., 100, 1541 (1988); Angew. Chem. Int. Ed. Engl., 27, 1484 (1988).- P. Binger, in Multiple Bonds and Low Coordination in Phosphorous Chemistry, eds. M. Regitz and O.J. Scherer (G. Thieme Verlag, Stuttgart, 1990), pp. 90.
2. P. Binger, R. Milczarek, R. Mynott, M. Regitz, J. Organomet. Chem., 323, C35 (1987).
3. H. Werner, J. Wolf, U. Schubert, K. Ackermann, J. Organomet. Chem., 317, 327 (1986).
4. P. Binger, J. Haas, A.T. Herrmann, F. Langhauser, C. Krüger, Angew. Chem., 103, 316 (1991); Angew. Chem. Int. Ed. Engl., 30, 310 (1991).
5. P. Binger, B. Biedenbach, C. Krüger, M. Regitz, Angew. Chem., 99, 798 (1987); Angew. Chem. Int. Ed. Engl., 26, 764 (1987).- T. Weddling, B. Geissler, R. Schneider, S. Barth, P. Binger, M. Regitz, Angew. Chem., 104 761 (1992).
6. P. Binger, B. Biedenbach, A.T. Herrmann, F. Langhauser, P. Betz, R. Goddard, C. Krüger, Chem. Ber., 123, 1617 (1990).