

Chemistry of phosphorus-carbon double bonds in the coordination sphere of transition metals

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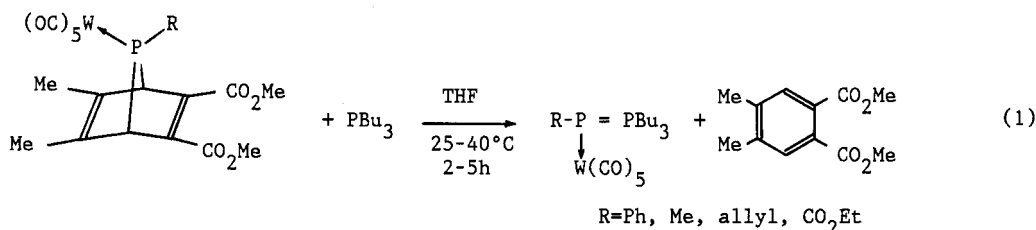
Abstract - The synthesis of two series of "phospha-Wittig" reagents is described. Both phosphoranylidenephosphine complexes $[R_3P=PR]M$ and phosphorylphosphide complexes $[(RO)_2P(O)-PR]M$ react with aldehydes and ketones to give the corresponding complexed phosphaaalkenes $[RP=CR^1R^2]M$. The complexing group serves to stabilize the P=C double bond and to mask the phosphorus lone pair. With these species, it is possible to develop new reactions of the P=C double bond. Epoxidation with *meta*-chloroperbenzoic acid affords oxaphosphirane complexes. Electron-poor phosphaaalkene complexes undergo [2+2] cycloadditions with electron-rich alkenes and alkynes. The synthesis of a series of new η^4 -complexes of 1- and 2-phosphadiene is also described.

INTRODUCTION

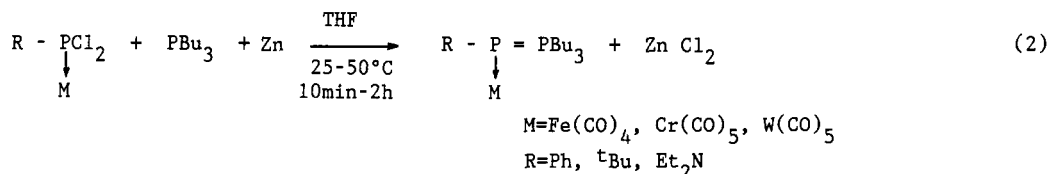
Since their discovery by Becker in 1976 (ref.1), phosphaaalkenes have been the subject of considerable study. Their electronic structure is characterized by an apolar π HOMO and a high-lying lone pair orbital (ref.2). Thus, their chemistry combines the typical reactivities of alkenes and phosphines. In order to fully exploit the synthetic potential of the P=C double bond, it was thus necessary to use a technique allowing the masking of the lone pair at phosphorus while keeping a high-lying and apolar π -system. The obvious solution was to complex the phosphorus lone pair by an electron-rich, low-valent metallic centre. Thus, we have performed a systematic study of the chemistry of the P=C double bond in some representative phosphaaalkene complexes with zerovalent metals.

THE PHOSPHA-WITTIG SYNTHESIS

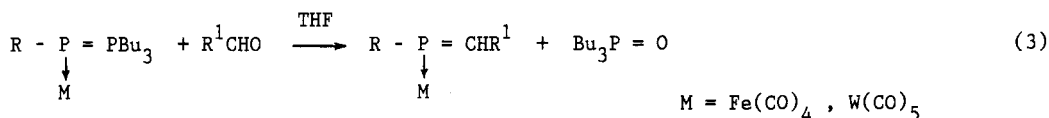
Phosphaaalkene complexes can obviously be obtained via the reaction of stable phosphaaalkenes with transition metal derivatives. However, the use of free phosphaaalkenes implies severe limitations on the choice of the substituents, as steric protection is needed in order to provide kinetic stability to the π -system. It seemed more logical to directly synthesize the P=C double bond in the coordination sphere of a transition metal in order to take advantage of the stabilizing effect of the metal and to remove some of the limitations on the choice of the phosphaaalkene substituents. We decided to investigate a possible transposition of the well-known Wittig-Horner synthesis of alkenes. The initial problem was to get a ready access to phosphoranylidenephosphine and to secondary phosphorylphosphine complexes. A few phosphoranylidenephosphines are known (ref.3) but all are stabilized either by bulky or electron-withdrawing substituents and are unreactive toward carbonyl compounds. Phosphoranylidenephosphine complexes with "ordinary" substituents were first obtained through the reaction of tributylphosphine with 7-phosphanorbornadiene complexes (ref.4) (eq.1)



Subsequently, they were obtained via a much simpler technique starting from dichlorophosphine complexes (ref.5) (eq.2)

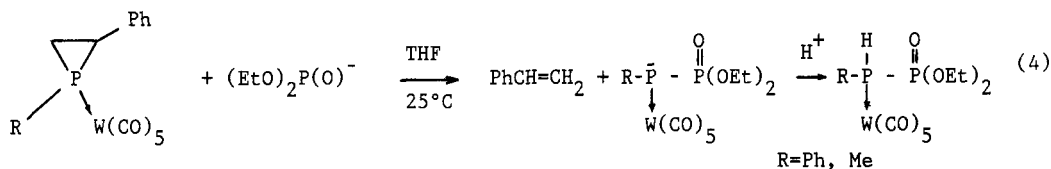


The complexes are characterized by a huge ¹J(P...P) coupling ca 400 Hz and a long zwitterionic phosphorus-phosphorus bond ca 2.15 Å. Except when stabilized by a conjugating substituent (CO₂Et or Et₂N), they are able to react with aldehydes at room temperature (eq.3)

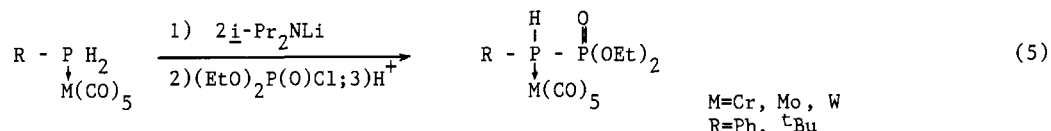


With ketones, the reaction only takes place upon heating and the phosphoranylidene phosphine complexes decompose.

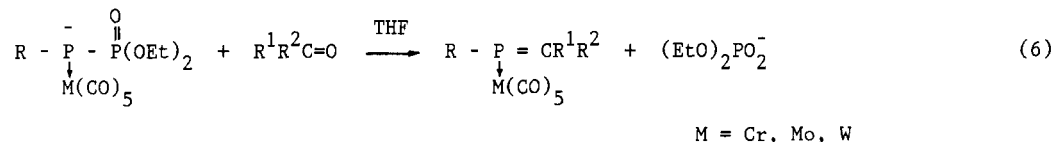
A more efficient synthesis of phosphalkene complexes resulted from the transposition of the Wittig-Horner synthesis of alkenes. Free secondary phosphoryl phosphines are normally unstable but we were able to obtain them as stable complexes via the reaction of (RO)₂P(O) with phosphirane complexes (ref.6) (eq.4)



Subsequently, we found a much simpler route starting from primary phosphine complexes (ref.7) (eq.5)



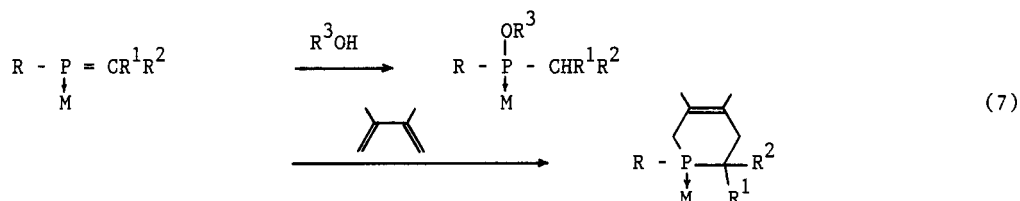
These secondary phosphoryl phosphine complexes are characterized by a small ¹J(P..P) coupling (<100 Hz). The acidic proton at phosphorus is easily removed by butyllithium at -70°C or DABCO at room temperature in THF. The corresponding anions display a huge ¹J(P...P) coupling ca 400 Hz suggesting some double bond character for the P-P bond as is the case in phosphoranylidene phosphine complexes. These anions proved to be quite reactive toward both aldehydes and ketones (ref.7,8) (eq.6)



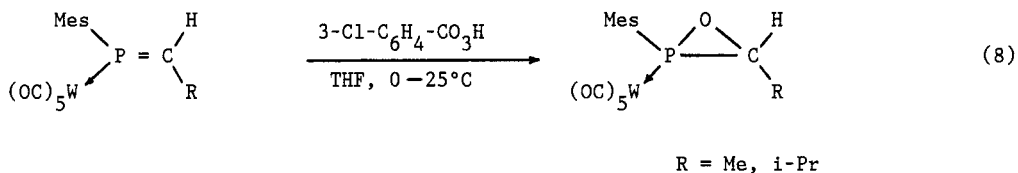
Having in hand these two versions of the "phospha-Wittig" synthesis, we started a thorough investigation of the chemistry of phosphalkene complexes.

THE CHEMISTRY OF THE P=C DOUBLE BOND IN PHOSPHAALKENE COMPLEXES

The most stable phosphalkene complexes are obtained when using Cr, Mo, W pentacarbonyls as the complexing groups. As a general rule, they are significantly more stable than the corresponding free species. The trisubstituted derivatives can be characterized by spectroscopy even though their isolation in the pure state is difficult with small substituents. The disubstituted derivatives obtained from aldehydes are reasonably stable only if bulky substituents are used. In any case, all these complexes can be easily trapped with alcohols or reactive dienes (eq.7)

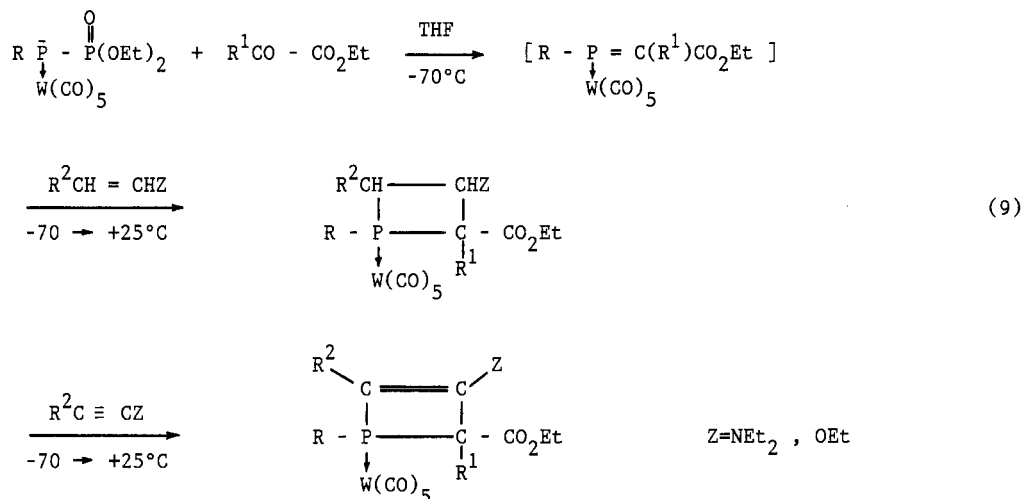


More original chemistry was also performed with these complexes. It is well known that the oxidation of phosphalkenes initially takes place at phosphorus with subsequent cleavage of the P=C double bond (ref.9). On the contrary, with phosphalkene complexes, a clean epoxidation of the P=C double bond can be performed (ref.10) (eq.8)

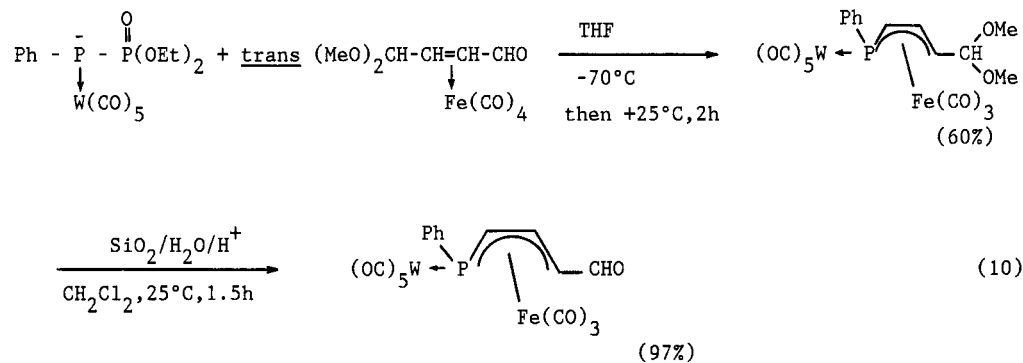


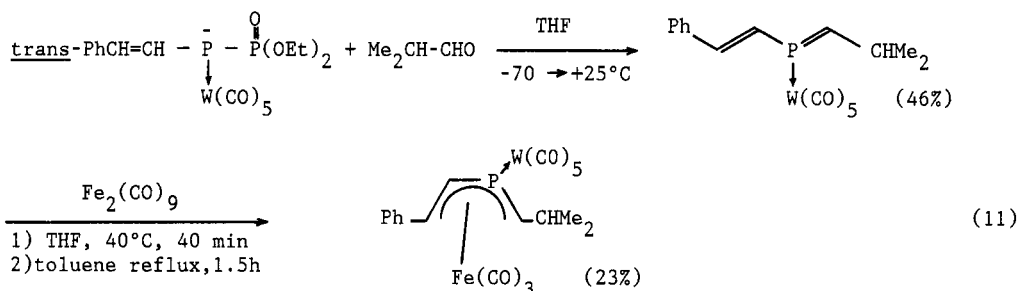
The reaction is quantitative and takes place with retention of stereochemistry. According to the X-ray structural analysis of one of these oxaphosphirane complexes, the plane of the 3-membered ring is almost perpendicular to the plane of the former phosphalkene complex. The ring is strained as expected (C-P-O = 50.9°, P-O-C = 68.8°) and is readily opened by reaction with RO⁻.

The phospho-Wittig reaction also provides a ready access to electron-poor P=C double bonds. The corresponding phosphalkene complexes are extremely reactive and give [2+2] cycloadducts with electron-rich alkenes and alkynes (ref.11) (eq.9)



Finally, it is also possible to use the phospho-Wittig reactions to prepare 1- and 2-phospha-butadiene complexes (ref.12,13). Some representative examples are given in eq.(10)-(11)





These new complexes were characterized by X-ray crystal structure analysis. The 2-phosphabutadiene P-W(CO)₅ complex displays a planar transoid phosphadiene unit. The W(CO)₅ complexing group lies in the plane of the diene. The diene unit is not delocalized: P-C: 1.800(8) Å, P=C: 1.626(7) Å, C=C: 1.33(1) Å. The corresponding η⁴-Fe(CO)₃ complex shows a planar cisoid phosphadiene unit. Full delocalization is now operative: P-C: 1.743 and 1.753(4) Å, C=C: 1.397(6) Å. According to P-W bond lengths and ¹J(P-W) coupling constants, the 2-phosphadienes appear to be better ligands and better acceptors toward W(CO)₅ than the 1-phosphadienes. From another standpoint, the Fe(CO)₃ moiety is an efficient protecting group for the phosphadiene units. A normal chemistry can be performed with the aldehyde derivative. Numerous other applications of this "phospha-Wittig" chemistry are currently being developed.

REFERENCES

1. G. Becker, *Z. Anorg. Chem.*, **423**, 242 (1976)
2. See for example: W.W. Schoeller, *J. Chem. Soc., Chem. Commun.*, 334 (1985); H. Bock and M. Bankmann, *Angew. Chem., Int. Ed. Engl.*, **25**, 265 (1986); S. Lacombe, D. Gonbeau, J.-L. Cabioch, B. Pellerin, J.-M. Denis, and G. Pfister-Guillouzo, *J. Am. Chem. Soc.*, **110**, 6964 (1988)
3. A.B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **83**, 2388 (1961); D. Weber and E. Fluck, *Z. Anorg. Allg. Chem.*, **424**, 103 (1976); A. Schmidpeter and S. Lochschmidt, *Angew. Chem., Int. Ed. Engl.*, **25**, 253 (1986); F. Zurmühlen and M. Regitz, *Angew. Chem., Int. Ed. Engl.*, **26**, 83 (1987); *New. J. Chem.*, **13**, 335 (1989)
4. P. Le Floch, A. Marinetti, L. Ricard, and F. Mathey, *J. Am. Chem. Soc.*, **112**, 2407 (1990)
5. P. Le Floch and F. Mathey, *Synlett*, 171 (1990)
6. A. Marinetti and F. Mathey, *Tetrahedron*, **45**, 3061 (1989)
7. A. Marinetti, S. Bauer, L. Ricard, and F. Mathey, *Organometallics*, **9**, 793 (1990)
8. A. Marinetti and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, **27**, 1382 (1988)
9. Th. A. van der Knaap, Th. C. Klebach, R. Lourens, M. Vos, and F. Bickelhaupt, *J. Am. Chem. Soc.*, **105**, 4026, (1983)
10. S. Bauer, A. Marinetti, L. Ricard, and F. Mathey, to be published
11. A. Marinetti and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 153 (1990)
12. A. Marinetti, L. Ricard, and F. Mathey, *Organometallics*, **9**, 788 (1990)
13. A. Marinetti, S. Bauer, L. Ricard, and F. Mathey, to be published