Journal of Organometallic Chemistry, 475 (1994) 25–30

Invited Lecture

Recent advances in the chemistry of phospholide and polyphospholide ions

François Mathey

Laboratoire "Hétéroéléments et Coordination" URA CNRS 1499 DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex (France)

(Received November 24, 1993)

Abstract

Several aspects of the chemistry of phospholide and polyphospholide ions under current development are described briefly. They include: the synthesis of flexible tetraphosphorus macrocycles from 2,2′-biphospholide ions; the synthesis of functional phospholide, 1,3-arsaphospholide and 1,2,3-triphospholide ions; the description of new coordination modes of η^5-phospholyl complexes involving the metal d electrons.

Key words: Phosphorus; Phospholide; Polyphospholide; Arsenic; Arsaphospholide; Macrocycle, polyphospha-

1. Introduction

Together with phosphinines, phospholide and polyphospholide anions are the only known carbon–phosphorus heterocycles where an extensive electronic delocalization has been demonstrated. In Scheme 1, we quote some data of Padma Malar [1] which clearly establish that these ions are comparable to cyclopentadienide anions as far as aromaticity is concerned. Whatever the precise meaning of these figures, they indisputably show that these ions are one of the most interesting classes of carbon–phosphorus rings. In this report, we discuss the recent advances of our group in their chemistry.

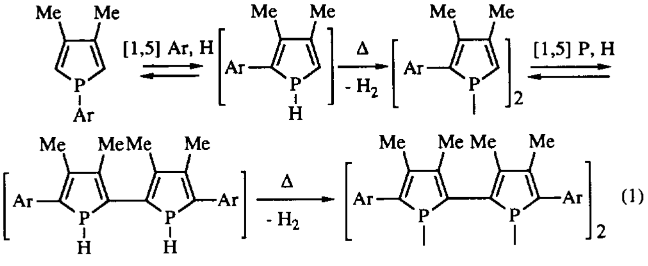
2. 2,2′-Biphospholide ions as starting points for the synthesis of flexible tetraphosphorus macrocycles

Polyphosphorus macrocycles have been the subject of relatively few investigations in spite of their obvious interest in coordination chemistry [2]. Besides the classical difficulties associated with the synthesis of any macrocycle, an additional specific drawback of tervalent polyphosphorus macrocycles lies in the high pyramidal inversion barrier of phosphorus, *ca.* 30–35 kcal/mol. Thus, at room temperature, a tervalent polyphosphorus macrocycle generally exists as a complex mixture of diastereomers which result from the different relative orientations of the phosphorus lone pairs. Since these diastereomers display different coordination behavior, it is necessary to carry out cumbersome separations in order to obtain useful ligands for further use in transition metal chemistry. However, tervalent phospholes are known to have an exceptionally low pyramidal inversion barrier, due to the extensive electronic delocalization which exists in the transient planar state [3]. With a barrier in the range of 16 kcal/mol, the phosphorus of phospholes readily inverts close to room temperature. Hence, a polyphosphamacrocycle in which all the phosphorus atoms were incorporated in adjacent phosphole rings would exist as a mixture of interconverting isomers slightly above 25°C and would "select" its best isomer in view of the stereochemical requirements of any metal to be complexed. As a consequence, no separation of the diastereomers would be needed.

In order to investigate these ideas, we selected the phosphole tetramers which result from the prolonged thermolysis of 1-aryl-3,4-dimethylphospholes [4] as starting points. (eqn. (1)).

The mechanism of these tetramerizations involves several concerted [1,5] shifts of aryl, hydrogen and phosphorus functionalities, plus two dehydrogenation steps which are not completely understood. During our work, we discovered by chance that 4-bromo-*N*,*N*-dimethylaniline acts as a promoter for this tetrameriza-

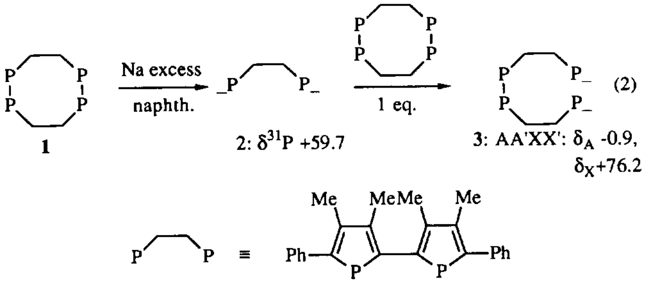
0022-328X/94/$7.00
SSDI 0022-328X(94)24511-G



1: Ar = Ph : 5 days, 170°C, 20-25%

with 4-Br-C_6H_4-NMe_2 : 18 h, 40-45%

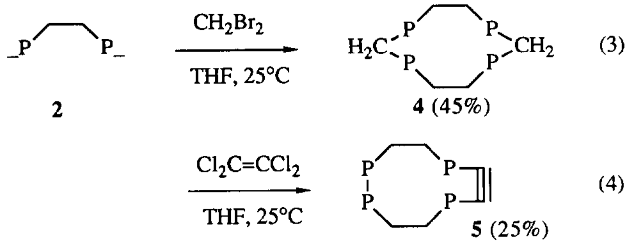
tion and dramatically enhances both the speed and the yield of the reaction. Two phospholide ions, **2** and **3** can be obtained by cleavage of one or two P–P bonds of the tetraphenyl-substituted tetramer, **1**, as shown in eqn. (2) [5].



2: $\delta^{31}P$ +59.7

3: AA'XX': δ_A -0.9, δ_X+76.2

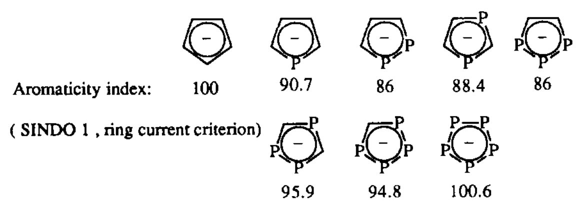
The symmetrical dianion **2** can be used to prepare two original 10-membered macrocycles, **4** and **5**, by reaction with dibromomethane and tetrachloroethylene (eqns. (3), (4)).



4 (45%)

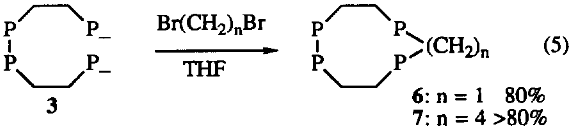
5 (25%)

In the second case, unexpected redox reactions take place leading to P–P and P–C≡C–P bridges. This acetylenic macrocycle has been characterized by X-ray crystal structure analysis. Some strain is present in the ring as shown by the values of the P–C≡C angles (170.2(8)° and 173.5(6)°).



Scheme 1. The aromaticity of phospholide and polyphospholide ions.

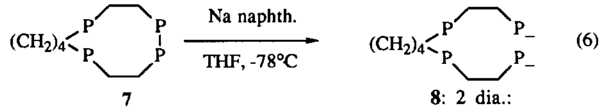
Macrocycles **6** and **7** are obtained in better yields from the quadricyclic dianion **3** as shown in eqn. (5).



6: n = 1 80%

7: n = 4 >80%

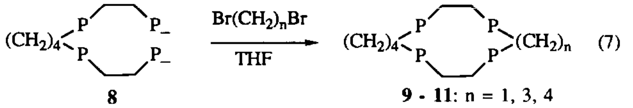
In the resulting macrocycles, the remaining P–P bond can be selectively cleaved by naphthalene-sodium in THF at low temperature (eqn. (6)). The new dianions thus obtained can in turn be used to prepare larger macrocycles as shown in eqn. (7).



8: 2 dia.:

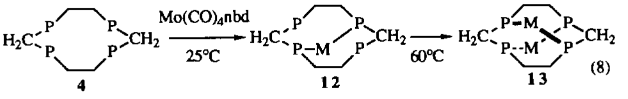
$\delta^{31}P$ +13.9 and +79.9, ^3J = 76 Hz

+13.7 and +79.2, ^3J = 74.5 Hz



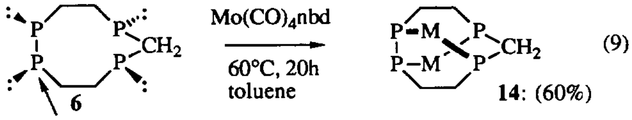
9 - 11: n = 1, 3, 4

The flexibility of these phosphole-based macrocycles was clearly demonstrated by a preliminary study of the coordination chemistry of **4** and **6**. The interaction of **4** with a source of $Mo(CO)_4$ at room temperature yields a mono-complex **12** whose X-ray crystal structure shows that the two lone pairs of the non-complexed phosphorus atoms point towards molybdenum. Nevertheless, at 60°C, these two phosphorus atoms readily invert and become able to chelate a second molybdenum to give the bis-complex **13** (eqn. (8)).



M ≡ $Mo(CO)_4$

Similarly, **6**, whose conformation was established by ^{31}P NMR analysis (all the four phosphorus atoms are inequivalent), is able to give a bis-chelate (eqn. (9)) and this result necessarily means that at least one phosphorus atom has undergone a pyramidal inversion.



14: (60%)

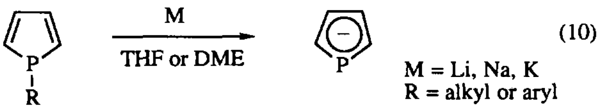
inversion is necessary before chelation

Complex **14** has a cage-like structure with a molybdenum–molybdenum distance of 5.883 Å, and is well adapted for the bimetallic activation of small molecules.

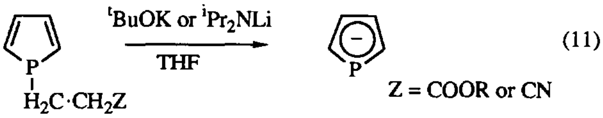
We are currently expanding this first series of results, with special emphasis on the building of macrocycles where the phosphole sub-units are connected *via* the α and α' carbons of the ring.

3. Towards functional phospholide ions

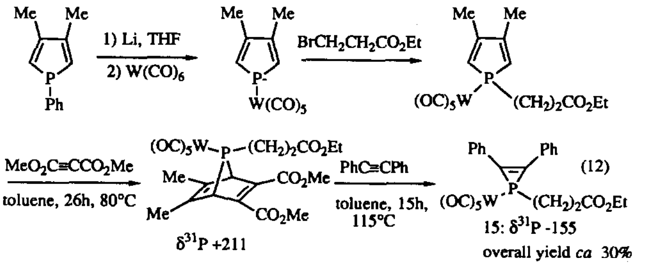
We have already commented upon the high electronic delocalization that exists in phospholide ions. In spite of this delocalization, all known chemistry of these ions takes place at the phosphorus, as a consequence of the strong negative charge which is borne by this heteroatom. In order to pave the way for a chemistry at the carbons of the ring, we studied the synthesis of C-functional derivatives of these species. The classical preparation of these ions involves the cleavage of the exocyclic P–R bonds of phospholes by alkali metals [6] (eqn. (10)).



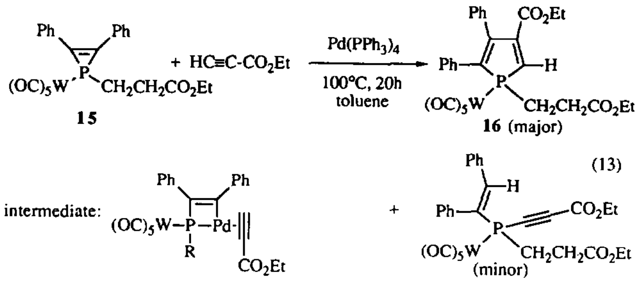
This technique is obviously not compatible with many reactive organic functionalities. We have found an alternative technique which relies on the base-induced cleavage of a P–CH_2CH_2Z bond [7] (eqn. (11)).



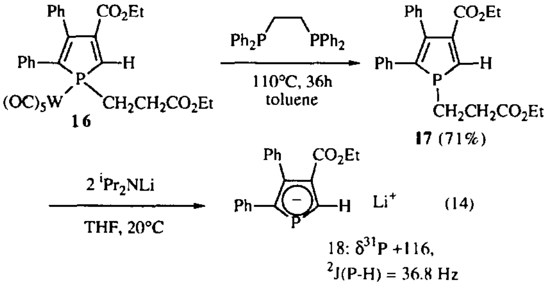
The problem, then, was to build a phosphole incorporating both the P–CH_2CH_2Z bond and the functionality at the ring carbon. We finally chose a multistep approach involving the combination of a functional alkyne with a non-functional alkyne and a phosphinidene unit. The phosphirene ring resulting from the combination of the last two units was first built using well-known chemistry [8] (eqn. (12)).



Palladium-catalysed insertion of ethyl propiolate into the ring of **15** following an earlier report [9] then afforded the required phosphole (eqn. (13)).



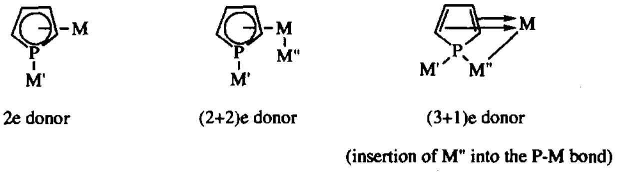
Complex **16** was finally transformed into the corresponding 3-ethoxycarbonylphospholide ion **18** as shown in eqn. (14).



This chemistry is too complex to be of practical use, but it nevertheless demonstrates that functional phospholide ions do exist, and can be the starting points of an extensive series of new organic and organometallic compounds.

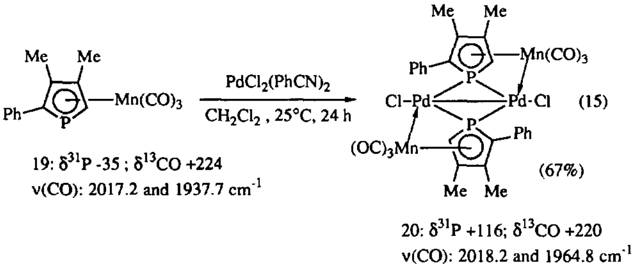
4. New coordination modes of phospholide ions

The ability of phospholide ions to give a wide range of stable η^5-complexes with transition metals is now well established [10]. These η^5-complexes can in turn be used as ligands via their lone pairs at phosphorus. As P-ligands, they generally behave as good π-acceptors because the LUMOs are significantly localized at phosphorus. Another characteristic feature of their electronic structure concerns the high-lying occupied orbitals. The HOMOs are systematically localized at the η^5-coordinated metal and are basically a combination of metallic d atomic orbitals. On this basis, it seems possible to use the metal as a donor towards another metal. Two possibilities exist *a priori*, M donation and P–M insertion as shown in Scheme 2.



Scheme 2. The coordination chemistry of η^5-phospholyl complexes.

These two possibilities have been demonstrated for phosphacymantrenes whose HOMOs are indeed localized at manganese [11]. Phosphacymantrene (**19**) readily reacts at room temperature with palladium chloride to give the tetrametallic complex **20** (eqn. (15)).

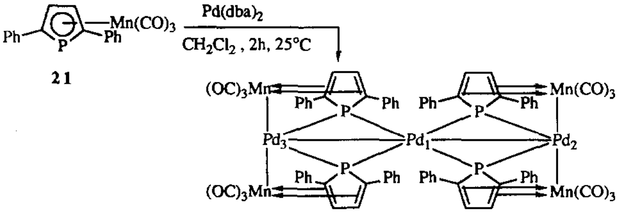


19: $\delta^{31}P$ -35 ; $\delta^{13}CO$ +224
ν(CO): 2017.2 and 1937.7 cm^{-1}

20: $\delta^{31}P$ +116; $\delta^{13}CO$ +220
ν(CO): 2018.2 and 1964.8 cm^{-1}

In this complex, the $Mn_2Pd_2Cl_2P_2$ core is strictly planar and the Mn–Pd and Pd–Pd separations are in the normal ranges for such bonds. The P–Mn separation at 2.3712 (9) Å is shorter than the P–Mn bond of phosphacymantrene (**21**) (2.392(1) Å). The electronic transfer from manganese to palladium is confirmed by the ^{13}C NMR data and the shift of the CO stretches towards higher frequencies when going from **19** to **20**.

With palladium(0), the outcome of the reaction is entirely different. Phosphacymantrene (**21**) gives a heptametallic complex **22** directly (eqn. (16)).



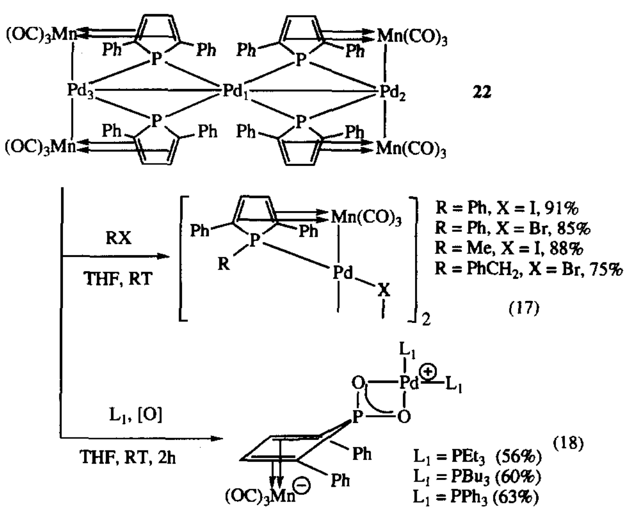
22: $\delta^{31}P$ +12 (77%) (16)

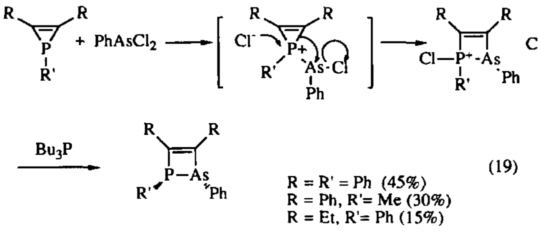
Here, an insertion of palladium into the P–Mn bond of **21** has taken place, as shown by the longer P ··· Mn separations between 2.470(2) and 2.489(1) Å. The phospholyl rings now act as (4 + 3) donors *via* their dienic systems and their phosphorus atoms. This leads to an umpolung at phosphorus which shifts from being electrophilic to nucleophilic. The nucleophilic reactivity of phosphorus is illustrated in eqns. (17) and (18) which depict the reactions of **22** with alkylating and arylating agents and with oxygen. All this chemistry proceeds in high yield at room temperature.

These two examples [12] clearly demonstrate that η^5-phospholyl complexes have an unexpectedly rich and varied coordination chemistry.

5. Synthesis of 1,3-arsaphospholide ions

Whereas the first arsolide ion was discovered as early as its phosphorus counterpart [6], the chemistry of these species has not been developed to any significant extent since then. The situation is even worse for the mixed species containing both phosphorus and arsenic. Apart from a preliminary report by the group of Nixon describing a 4-arsa-1,2-diphospholide ion [13], no other data are available from the literature. Therefore, we have attempted to transpose our previous results on the chemistry of 1,3-diphospholide ions [14]. As a first step, we prepared the unknown 1,2-dihydro-1,2-arsaphosphetes [15] by ring-expansion of phosphirenes (eqn. (19)), using an approach already applied to the synthesis of 1,2-dihydro-1,2-diphosphetes [16].

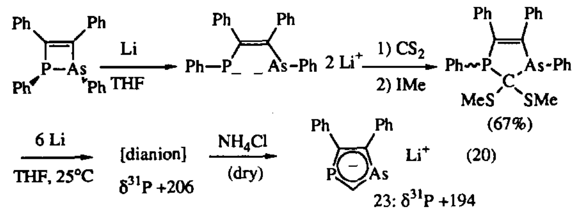




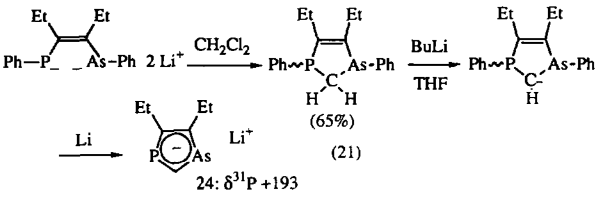
Then, we inserted a carbon unit into the P–As bond of these 4-membered rings and cleaved the exocyclic P–Ph and As–Ph bonds as shown in eqns. (20) and (21) to obtain the required 1,3-arsaphospholide ions **23** and **24**.

In the second case, the P–CH_2–As unit is strengthened by metallation, which delocalizes the negative charge over the three atoms. This precludes the collapse of the ring during the cleavage of the two exocyclic bonds.

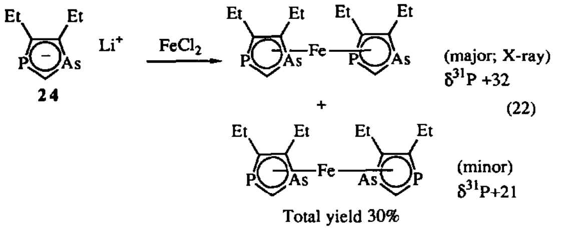
The arsaphospholide ion **24** proved to be a satisfactory pentahapto-ligand as shown in eqn. (22).



(20)



(21)

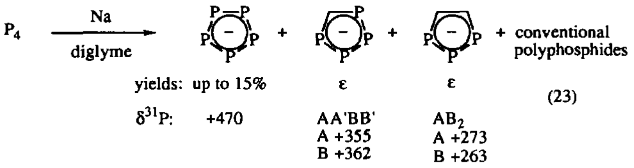


(22)

The introduction of arsenic as a substitute for phosphorus further expands the potential of polyphospholide ions in coordination chemistry.

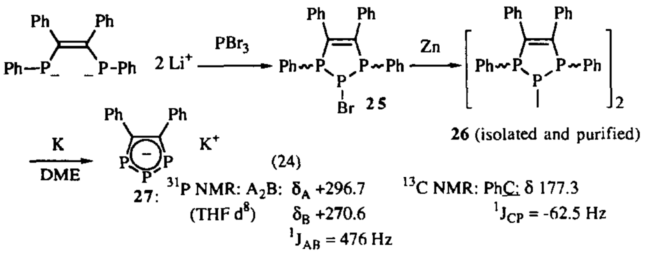
6. Synthesis of 1,2,3-triphospholide ions

At the moment, satisfactory routes exist for the synthesis of 1,3-di-, 1,3,4-tri- and 1,2,3,4,5-penta-phospholide ions. Two of the three other possible ions (see Scheme 1) have been observed by the group of Baudler [17] as minor components of complex mixtures obtained by reduction of elemental phosphorus with alkali metals (eqn. (23)).



(23)

Very recently, we have been able to devise a synthetic scheme which selectively gives a 1,2,3-triphospholide ion [18]. A PBr unit is first inserted into the P–P bond of a 1,2-dihydro-1,2-diphosphete as shown in eqn. (24).



(24)

The resulting 1,2,3-triphospholene (**25**) is purified as its P_2–$P_{2'}$ dimer, **26**. The reaction of **26** with potassium then affords the triphospholide ion **27**. Very probably, the alkali metal first cleaves the P_2–$P_{2'}$ bond of **26** to give a delocalized P-anion whose delocalization strengthens the P–P–P unit and prevents the collapse of the ring during the cleavage of the two exocyclic P–Ph bonds. At the moment, the triphospholide ion **27** has been characterized by NMR and negative ion mass spectrometry. Its chemistry remains to be explored.

7. Conclusion

The aim of this progress report is to underline the various possible facets of the chemistry of phospholide and polyphospholide ions. In our opinion, it is not extravagant to say that these ions represent one of the most powerful classes of ligands in organophosphorus chemistry. Their analogy with the ubiquitous cyclopentadienyl ligand and the additional possibilities resulting from the presence of the phosphorus lone pairs suffice to forecast their extensive use in coordination chemistry. In such a context, it may be quite encouraging for newcomers to the field to see that a lot remains to be done.

Acknowledgements

The work reported here has been ably performed by several co-workers and students, including: Lionel Brunet, Claude Charrier, Bernard Deschamps, Arturo Espinosa-Ferao, Frank Laporte, Nicole Maigrot, François Mercier, and Mike Sierra. The X-ray crystal structure analyses were performed by Louis Ricard. Financial support was provided by CNRS and Ecole Polytechnique.

References

1 E.J. Padma Malar, *J. Org. Chem.*, 57 (1992) 8694.
2 Reviews: O. Stelzer and K.-P. Langhans, in F.R. Hartley (ed.), *The Chemistry of Organophosphorus Compounds*, Vol. 1, Wiley, Chichester, 1990, pp. 226–233; C.A. McAuliffe, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, Vol. 2, Pergamon, Oxford, 1987, pp. 995–1004.

3 W. Egan, R. Tang, G. Zon and K. Mislow, *J. Am. Chem. Soc., 93* (1971) 6205.

4 M.-O. Bevierre, F. Mercier, L. Ricard and F. Mathey, *Bull. Soc. Chim. Fr., 129* (1992) 1.

5 F. Laporte, F. Mercier, L. Ricard and F. Mathey, *J. Am. Chem. Soc.*, in press.

6 E.H. Braye, I. Caplier and R. Saussez, *Tetrahedron, 27* (1971) 5523.

7 A. Espinosa-Ferao, B. Deschamps and F. Mathey, *Bull. Soc. Chim. Fr., 130* (1993) 695.

8 A. Marinetti, F. Mathey, J. Fischer and A. Mitschler, *J. Am. Chem. Soc., 104* (1982) 4484.

9 A. Marinetti and F. Mathey, *Tetrahedron Lett., 28* (1987) 5021.

10 F. Mathey, *Coord. Chem. Rev.*, in press.

11 C. Guimon, G. Pfister-Guillouzo and F. Mathey, *Nouv. J. Chim., 3* (1979) 725.

12 L. Brunet, F. Mercier, L. Ricard and F. Mathey, *Angew. Chem.*, in press.

13 R. Bartsch, J.A. Johnson and J.F. Nixon, *Phosphorus, Sulfur, Silicon, 77* (1993) 275.

14 N. Maigrot, L. Ricard, C. Charrier and F. Mathey, *Angew. Chem., Int. Ed. Engl., 29* (1990) 534; N. Maigrot, M.L. Sierra, C. Charrier, L. Ricard and F. Mathey, *Polyhedron, 11* (1992) 601.

15 M.L. Sierra, C. Charrier, L. Ricard and F. Mathey, *Bull Soc. Chim. Fr., 130* (1993) 521.

16 L. Ricard, N. Maigrot, C. Charrier and F. Mathey, *Angew. Chem., Int. Ed. Engl., 26* (1987) 548.

17 M. Baudler and J. Hahn, *Z. Naturforsch., 45B* (1990) 1139.

18 N. Maigrot, M.L. Sierra, C. Charrier and F. Mathey, *Bull. Soc. Chim. Fr.*, in press.