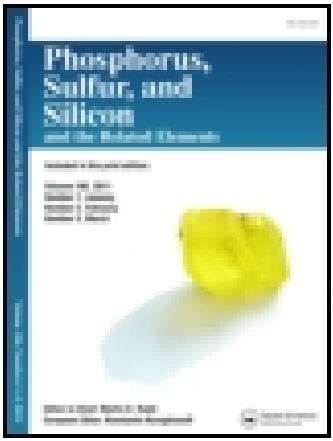


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

NOVEL ISOLABLE C,C-DICHLOROPHOSPHAALKENES RP=CCl_2 OWING TO THE USE OF NEW HUGE STABILIZING GROUPS

L. Rigon [a] , H. Ranaivonjatovo [a] & J. Escudie [a]
[a] UPRES A 5069, Hétérochimie Fondamentale et Appliquée , Université Paul Sabatier , 118 route de Narbonne, 31062, Toulouse, Cedex 4, France
Published online: 24 Sep 2006.

To cite this article: L. Rigon , H. Ranaivonjatovo & J. Escudie (1999) NOVEL ISOLABLE C,C-DICHLOROPHOSPHAALKENES RP=CCl_2 OWING TO THE USE OF NEW HUGE STABILIZING GROUPS, Phosphorus, Sulfur, and Silicon and the Related Elements, 152:1, 153-167, DOI: 10.1080/10426509908031627

To link to this article: http://dx.doi.org/10.1080/10426509908031627

Phosphorus, Sulfur and Silicon, 1999, Vol. 152, pp. 153-167
Reprints available directly from the publisher
Photocopying permitted by license only

NOVEL ISOLABLE *C,C*-DICHLOROPHOSPHAALKENES $RP{=}CCl_2$ OWING TO THE USE OF NEW HUGE STABILIZING GROUPS

L. RIGON, H. RANAIVONJATOVO and J. ESCUDIE*

UPRES A 5069, Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 4, France

(Received 09 February, 1999)

Three new *C,C*-dichlorophosphaalkenes $RP{=}CCl_2$ **18–20** have been synthesized from the corresponding dichlorophosphines $RPCl_2$ **11–13**. Compounds **18–20** are stabilized owing to the use of the very bulky new groups R^1 [2,6-bis(4-methylphenyl)-4-methylphenyl] and R^3 [2,6-bis(2-methoxyphenyl)-4-methylphenyl] and the known 2,6-dimesityl-4-methylphenyl (R^2). The compounds with a R^3 group (R^3I: **4**, R^3PCl_2: **13**, R^3PH_2: **17** and $R^3P{=}CCl_2$: **20**) exist in the form of two conformational isomers on the NMR time scale. A ^1H and ^{31}P NMR dynamic study (for **4** and **13** respectively) allowed the determination of the ΔG^* of this phenomenon, respectively 18.5 and 18.2 kcal/mol.

Keywords: *C,C*-Dichlorophosphaalkenes; $RP{=}CCl_2$; NMR-data

INTRODUCTION

A remarkable progress has been made very recently in the chemistry of stable or marginally stable allenic derivatives of group 14 elements such as >Si=C=X (X: C,[1] N,[2] P,[3]), >Ge=C=X (X: C,[4] P[5]) and >Sn=C=N-[6]. Although some metallaallenes >M=C=C< (M: Si, Ge) have been isolated, this is not the case for the metallaphosphaallenes >M=C=P- which dimerize above −20°C or −30°C despite the use of bulky 2,4,6-tri-tert-butylphenyl (Ar), 2,4,6-triisopropylphenyl (Tip) or mesityl (Mes) groups.[3,5] Moreover heavy allenes such as >M=C=M< or

* Correspondence Author.

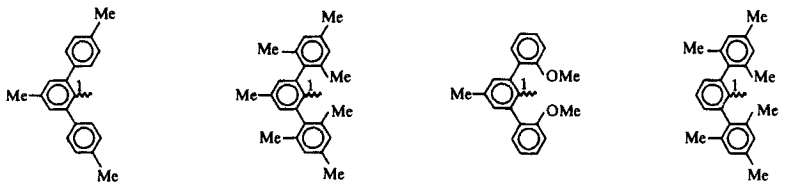
>C=M=C< are still unknown as well as heavy alkynes -M≡Y (Y: C, Si, Ge, Sn, P, As), which have never been isolated nor physicochemically characterized. In order to isolate such still unknown species it is of course necessary to use new stabilizing groups, particularly huge groups since it is well known that the steric effects play the main role in the stabilization of doubly bonded species. However intermolecular or intramolecular complexation particularly by alkoxy or amino groups are also good ways to stabilize highly oligomerizable low coordinate species.

The phosphaalkene $ArP{=}CCl_2$, bearing the bulky 2,4,6-tri-tert-butylphenyl (Ar) group has been prepared by Appel[7a] and Bickelhaupt,[7b] but no other *C,C*-dichlorophosphaalkene has been isolated until now. Such unsaturated derivatives constitute very good synthons in doubly bonded phosphorus chemistry due to the presence of two easily substituable halogens on the sp^2 carbon (they allowed for example the preparation of sila- or germaphosphaallenes[3,5]) and thus the synthesis of new derivatives of this type presents a great interest.

In this paper we describe the synthesis and the stabilization of three new *C,C*-dichlorophosphaalkenes owing to the use of novel huge groups R^1 and R^3 and also the known 2,6-dimesityl-4-methylphenyl group[8,9] which are potentially able to stabilize other multiply bonded species of groups 14 and 15 elements.

RESULTS AND DISCUSSION

Due to the presence of aromatic substituents in position 2 and 6, the R^1-R^3 groups have the particularity to present a large steric hindrance at a rather long distance from the atom bonded to the phenyl in position 1 (scheme 1).



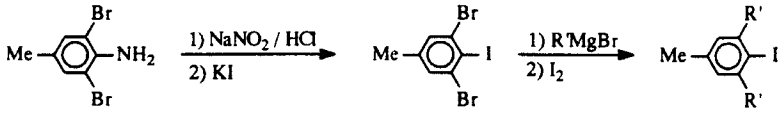
R¹ **R²** **R³** **R⁴**

SCHEME 1

The 2,6-dimesitylphenyl group R^4 has been previously used, particularly by Power[10] and also by some other authors,[11] for the successful stabilization of various reactive species generally unstable. The similar R^2 group has been recently prepared by Shah[8] and employed for the stabilization of the diphosphene[8] $R^2P{=}PR^2$ and of the arsaphosphene[9] $R^2P{=}AsR^2$. These three groups R^1, R^2 and R^3 should have different stabilizing properties, since in R^1 the 4-methylphenyl group presents a less important steric hindrance than a t-Bu group at a short distance from the atom bonded to the phenyl in position 1, but a larger steric hindrance at a long distance. R^2 and R^3 should be bulkier than the Ar group, both close and at a long distance from X and thus should present good stabilizing properties for derivatives with two cumulative double bonds >M=C=X or a triple bond -M≡Y without substituents on the triply bonded Y atom.

a) Synthesis of RH and $RPCl_2$

The synthesis of the 2,6-dibromo-4-methyliodobenzene **1** has been previously described by Shah[8] according to the general procedure described by Du.[12] The reaction of **1** with excess of Grignard reagents and the quenching with iodine afforded R^2I[8,9] **3** and the new derivatives R^1I **2** and R^3I **4** respectively (scheme 2).



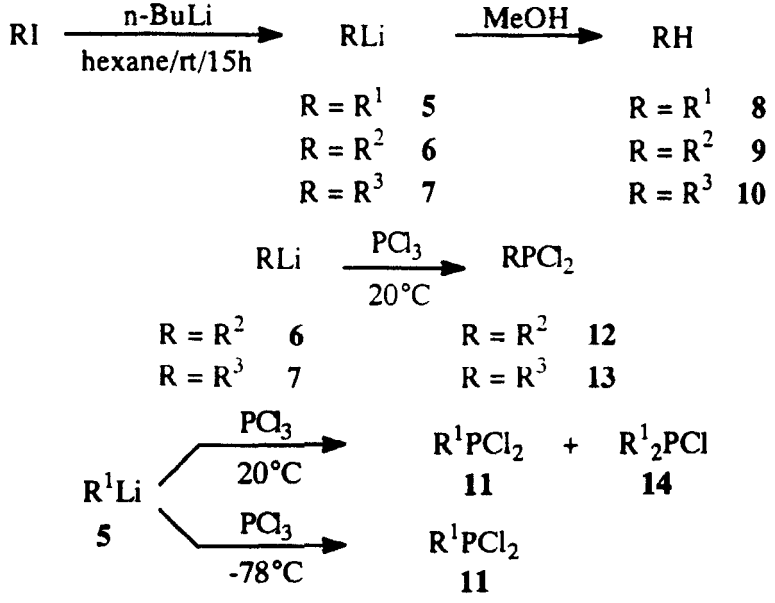
1

R'		
p-MePh	**2**	(R^1I)
Mes	**3**	(R^2I)
o-MeOPh	**4**	(R^3I)

SCHEME 2

The lithium compounds RLi **5–7** are obtained by stirring overnight a solution of RI with n-butyllithium in hexane at room temperature; quenching with methanol affords the new RH compounds **8–10** in good yields and proves the formation of the expected lithium compounds **5–7.** Addition of PCl_3 to a suspension of **6** and **7** at 20°C leads to the expected dichlorophosphines $RPCl_2$ **12**[8,9] and **13** in good yields. By contrast, addi-

tion of PCl_3 to R^1Li gives a mixture (60/40) of dichlorophosphine **11** and chlorophosphine **14.** However, **11** was obtained in pure form when the addition of phosphorus trichloride was performed to a suspension of R^1Li **5** cooled at – 78°C (scheme 3).



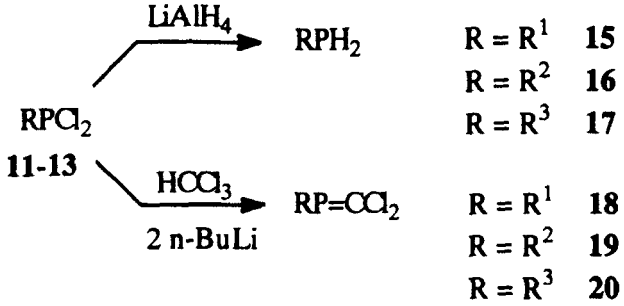
SCHEME 3

The fact that the disubstitution of phosphorus occurs when $R = R^1$ proves that this group does not present, as expected, a high steric hindrance close to the phosphorus atom. It should be noted that, in the case of the 2,4,6-tri-tert-butylphenyl group (Ar), the diarylchlorophosphine Ar_2PCl cannot be formed.

b) Synthesis of RPH_2 and $RP{=}CCl_2$

The reduction of **11–13** with lithium aluminium hydride in Et_2O affords quantitatively the corresponding phosphines **15–17** which should be useful starting materials for doubly bonded phosphorus compounds. Addition of chloroform and of two equivalents of n-butyllithium at -110°C to the

dichlorophosphines $RPCl_2$ **11–13,** according to the process previously described by Bickelhaupt[7b] for $ArP{=}CCl_2$, afforded the dichlorophosphaalkenes **18–20** (scheme 4).



SCHEME 4

The three new *C,C*-dichlorophosphaalkenes **18–20,** which are obtained in a one-pot synthesis, are stable at room temperature and can be handled in air without decomposition. All the new compounds **2, 4, 11, 13–20,** have been characterized by ^1H and ^{13}C NMR and also by ^{31}P NMR spectroscopy for **11, 13–20.** In mass spectrometry, the molecular peak has been observed in all compounds containing the $R^1$and R^2 groups. By contrast in the derivatives with the R^3 group it is observed only for R^3H and R^3I. Loss of OMe occurs in R^3PCl_2 and R^3PH_2.

For the phosphorus compounds **13, 17** and **20** containing the R^3 group, two close signals are surprisingly observed in the ^{31}P NMR spectrum, in the approximate ratio 55/45. The same phenomenon is observed in the ^1H NMR spectrum for the methoxy groups in R^3I **4,** R^3PH_2 **17** and $R^3P{=}CCl_2$ **20** with two signals; for the methyl on carbon 4 two signals are also observed in the case of R^3I and $R^3P{=}CCl_2$. By contrast, only one signal appeared as expected for the methoxy groups in R^3H and in R^3PCl_2. In the ^{13}C NMR spectrum, the methoxy groups resonate also in the form of two signals in all compounds except R^3H. Such a phenomenon can only be understood by the existence of two conformational isomers on the NMR time scale due to the huge steric hindrance caused by the two 2-methoxyphenyl groups. A similar phenomenon has been reported by Okazaki et al[13] in the cis-disilene RRSi=SiRR' (R: mesityl, R': 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl: Tbt): four signals are observed in ^{29}Si NMR,

instead of one expected, due to the presence of four conformations caused by the great steric hindrance of the Tbt groups.

The presence of two observable conformations at 25 °C was proved by a NMR study at various temperatures. For R^3I **4** a dynamic ^1H NMR study was performed between room temperature and 80°C and showed a coalescence for the two signals of the methyl group on carbon 4 and also for those of the methoxy groups which each collapse to a singlet; the free energy of activation for this phenomenon could be calculated:

$$Me,\ T_c:\ 334\ K,\ \Delta\nu:\ 2.8\ Hz,\ \Delta G^* = 18.4\ \text{kcal/mol}.$$
$$OMe,\ T_c: 342\ K,\ \Delta\nu:\ 4.0\ Hz,\ \Delta G^* = 18.6\ \text{kcal/mol}.$$

In the case of the dichlorophosphine **13** a dynamic ^{31}P NMR spectroscopy was performed. The coalescence temperature was in this case 350 K leading to a ΔG^* of 18.2 kcal/mol, very close to the value obtained for **4.** These ΔG^* are high for such a phenomenon of conformational isomers and prove the high steric hindrance of the R^3 group.

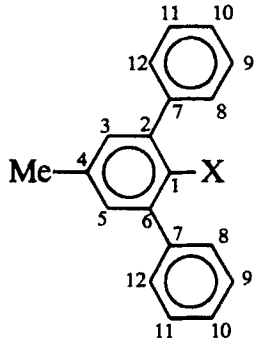
CONCLUSION

The three new isolable dichlorophosphaalkenes **18–20** and particularly **20,** are very interesting since they should be the precursors of various phosphaalkenes by substitution of one or two chlorine atoms and of phosphaallenes -P=C=X. Our efforts are now directed towards the synthesis of stable sila-, germa- and stannaphosphaallenes >M=C=P- (M: Si, Ge, Sn). Such groups R^1, R^2 and R^3 are also potentially very promising to stabilize various types of doubly bonded and even triply bonded silicon, germanium or tin derivatives.

EXPERIMENTAL SECTION

All experiments were carried out in flame-dried glassware under an atmosphere of nitrogen. Hexane was distilled over $LiAlH_4$ and THF was distilled from sodium/benzophenone prior to use. NMR spectra were recorded on the following spectrometers: ^1H, Bruker AC 80 (80.13 MHz) and Bruker AC 200 (200.13 MHz); ^{13}C, Bruker AC 200 (50.32 MHz) (ref-

erence TMS); ^{31}P, Bruker AC 200 (80.01 MHz) (reference: H_3PO_4 85%). The NMR solvent was always $CDCl_3$ except for **4** (C_7D_8). Melting points were determined on a Leitz 350 apparatus. Mass spectra were collected on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV. IR spectra were recorded on a Perkin Elmer 1600 FT instrument. Elemental analysis were performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse"; all of them present an error of less than 0.4 % and are not reported.



Synthesis of 2,6-dibromo-4-methyliodobenzene 1

Compound **1** was synthesized according to the procedure of Shah[8] and identified by its melting point and its ^1H NMR spectrum. ^{13}C NMR and mass spectrometry to determine the fragmentation pattern of **1,** not yet reported, have been performed.

^{13}C NMR: 20.6 (Me), 105.0 (C-I), 130.8 (C-Br), 132.0 (C-Me), 141.2 (C-H).

MS: 376 (M, 100), 297 (M – Br, 33), 249 (M – I, 8), 127 (I, 46), 89 (M – I – 2 Br, 84).

Synthesis of 2,6-bis(4-methylphenyl)-4-methyliodobenzene (R^1I) 2

R^1I **2** was synthesized according to the procedure used by Lüning[14] for the synthesis of 2,6-bis(2,6-dimethylphenyl)iodobenzene. A solution of **1** (5.00 g, 13.30 mmol) in THF (40 ml) was slowly added to a solution of p-MePhMgBr prepared from p-MePhBr (9.10 g, 53.22 mmol) and Mg (1.3 g, 53.22 mmol) in THF (50 ml). After 3 h stirring at room tempera-

ture, the reaction mixture was cooled at 0°C and then 14.9 g of iodine (4.4 eq) in THF (150 ml) were added. Stirring was maintained overnight then excess of iodine was destroyed by a saturated solution of Na_2SO_3. THF was removed under vacuum and Et_2O was added. The two layers were separated and the organic layer was dried over Na_2SO_4. After one night, Et_2O was removed under vacuum, hexane was added and white crystals of **2** precipitated. The crystals were isolated by filtration and dried under vacuum (4.20 g, 81 %, mp: 177°C).

^{1}H NMR: 2.35 (t, $^4J_{HH}$: 0.7 Hz, 3 H, MeC_4), 2.43 (s, 6 H, MeC_{10}), 7.08 (q, $^4J_{HH}$: 0.7 Hz, 2 H, arom H on C_3C_5), 7.26 (s, 8 H, arom H of p-tolyl).

^{13}C NMR: 20.8 ($\underline{Me}C_4$), 21.4 ($\underline{Me}C_{10}$), 100.0 (C_1), 128.6 and 129.3 (C_8C_{12} and C_9C_{11}), 129.7 (C_3C_5), 137.2 (C_{10}), 137.5 (C_4), 142.9 (C_7), 147.7 (C_2C_6).

MS: 398 (M, 100), 271 (M – I, 25), 256 (M – I – Me, 37), 239 (M – I – 2Me – 2, 20), 127 (I, 8).

Synthesis of 2,6-dimesityl-4-methyliodobenzene (R^2I) 3

Compound **3** was synthesized by the same procedure as R^1I and identified by its melting point and ^{1}H NMR spectrum according to the literature data.[8]

^{13}C NMR: 20.4 ($\underline{Me}C_8C_{12}$), 21.1 ($\underline{Me}C4$), 21.3 ($\underline{Me}C_{10}$), 104.2 (C_1), 128.1 (C_9C_{11}), 128.7 (C_3C_5), 135.5 (C_8C_{12}), 137.1 (C_{10}), 138.7 (C_4), 142.1 (C_7), 146.9 (C_2C_6).

MS: 454 (M, 100), 327 (M – I, 56), 312 (M – I – Me, 73), 297 (M – I – 2Me, 34).

Synthesis of 2,6-bis(2-methoxyphenyl)-4-methyliodobenzene (R^3I) 4

R^3I **4** was prepared according to the same procedure as R^1I **2** using 9.95 g (53.22 mmol) of 2-methoxybromobenzene, 1.3 g (53.22 mmol) of magnesium, 50 ml of THF, 5.00 g (13.29 mmol) of **1** and 14.9 g (58.00 mmol) of iodine. After distillation of 2-methoxyiodobenzene, recrystallization from Et_2O afforded white crystals of **4** (8.7 g, 78 %, mp: 103°C).

^{1}H NMR (200.13 MHz, toluene-d_8): 2.01 and 2.03 (2s, 3 H, MeC_4), 3.32 and 3.35 (2s, 3H, OMe), 6.59–7.17 (m, 10 H, arom H).

^{13}C NMR: 21.0 (Me), 55.7 and 55.8 (OMe), 103.3 (C_1), 111.1 and 111.2 (C_9), 120.4 and 120.7 (C_{11}), 129.2, 129.6, 129.8, 129.9, 130.7 and 131.0

(C_3C_5, C_{10}, C_{12}), 134.7, 134.8 and 137.3 (C_4, C_7), 144.6 (C_2C_6), 158.4 (C_8).

MS:430 (M, 47), 303 (M – I, 29), 288 (M – I – Me, 100), 273 (M – I – 2Me, 24), 258 (M – I - 3Me, 24).

Synthesis of R^1H 8

To a solution of 0.87 g (2.18 mmol) of R^1I **2** in hexane (7 ml) at room temperature was added by syringe a solution of n-BuLi 1.6 M in hexane (1.37 ml, 2.18 mmol). A white precipitate appeared almost immediately. The reaction mixture was stirred overnight leading to an abundant precipitate of R^1Li. In all the experiments involving this lithium compound no further purification was necessary. Addition of an excess of methanol immediately afforded a clear solution. After removal of the volatile material (BuI, hexane and methanol) pentane (30 ml) was added. The lithium salts were removed by filtration. Crystallization from pentane afforded 0.45 g (75%) of a white powder of R^1H (mp: 98°C).

^{1}H NMR: 2.48 (s, 6 H, MeC_{10}), 2.56 (t, $^4J_{HH}$: 0.5 Hz, 3 H, MeC_4), 7.27–7.69 (m, 11 H, arom H).

^{13}C NMR: 21.3 ($\underline{Me}C_{10}$), 21.8 ($\underline{Me}C_4$), 123.2 (C_1), 126.7 (C_3C_5), 127.3 and 129.8 (C_8, C_9, C_{11}, C_{12}), 137.2, 138.6, 138.8, 141.8 (C_2C_6, C_4, C_7 and C_{10}).

MS: 272 (M, 100), 257 (M – Me, 10), 242 (M – 2Me, 8), 165 (M – MePh – Me – 1, 14), 91 (MePh, 15).

Synthesis of R^2H 9 and R^3H 10

R^2H and R^3H were prepared according to the experimental procedure previously described for R^1H.

R^2H

R^2I **3** (0.50 g, 1.10 mmol), hexane (5 ml), n-BuLi 1.6 M in hexane (0.75 ml, 1.20 mmol). White powder (0.3 g, 83 %, mp: 85°C).

^{1}H NMR: 2.16 (s, 12 H, MeC_8C_{12}), 2.42 (s, 6 H, MeC_{10}), 2.43 (s, 3 H, MeC_4), 6.73 (broad s, 1 H, HC_1), 6.94 (broad s, 6 H, arom H).

^{13}C NMR: 20.9 ($\underline{Me}C_8C_{12}$), 21.2 ($\underline{Me}C_{10}$), 21.7 ($\underline{Me}C_4$), 127.4 (C_1), 128.1 (C_9C_{11}), 128.3 (C_3C_5), 135.9, 136.4, 137.9, 139.3 and 141.1 (C_2C_6, C_4, C_7, C_8C_{12}, C_{10}).

MS: 328 (M, 100), 313 (M – Me, 45), 298 (M – 2Me, 15), 283 (M – 3Me, 12), 209 (M - Mes, 10), 194 (M - Mes - Me, 8).

R^3H

R^3I **4** (2.11 g, 4.91 mmol), hexane (20 ml), n-BuLi 1.6 M in hexane (3.4 ml, 5.00 mmol). White powder (0.89 g, 59 %, mp: 107°C).

^{1}H NMR: 2.44 (s, 3 H, MeC_4), 3.81 (s, 6 H, OMe), 6.91–7.40 (m, 11 H, arom H).

^{13}C NMR: 21.8 (s, $\underline{Me}C_4$), 55.7 (OMe), 111.3 (C_9), 120.9 (C_{11}), 128.3 (C_1), 128.6, 129.2 and 131.2 (C_3C_5, C_{10}, C_{12}), 137.2, 138.3 and 144.7 (C_1, C_2C_6, C_7), 156.7 ($\underline{C}_8OMe$).

MS: 304 (M, 100), 289 (M – 15, 20), 274 (M – 2Me, 11), 273 (M – OMe, 12).

Synthesis of R^1PCl_2 11

To a suspension of R^1Li (prepared from 3.00 g (7.54 mmol) of R^1I, 5.18 ml of n-BuLi 1.6 M in hexane (8.29 mmol) and 20 ml of hexane) cooled at – 80°C were added 3 equivalents of PCl_3 (3.11 g, 22.62 mmol). The reaction mixture was stirred for 15 min at – 60°C then gradually warmed to room temperature and refluxed for 1 h. After removal of the excess of PCl_3 and hexane under vacuum, 30 ml of Et_2O and 30 ml of pentane were added. LiCl was filtered out; crystallization from Et_2O/pentane (50/50) afforded **8** as yellow crystals (2.5 g, 89%, mp: 75°C).

^{1}H NMR: 2.46 (s, 9 H, MeC_4 and MeC_{10}), 7.17–7.50 (m, 10 H, arom H).

^{13}C NMR: 21.4 ($\underline{Me}C_4$ and $\underline{Me}C_{10}$), 128.7 (C_9C_{11}), 130.2 (d, $^4J_{CP}$: 3.5 Hz, C_8C_{12}), 131.7 (C_3C_5), 137.8 (d, $^3J_{CP}$: 7.8 Hz, C_7), 138.0 (C_{10}), 142.3 (C_1), 148.7 (d, $^2J_{CP}$: 28.0 Hz, C_2C_6).

^{31}P NMR: 157.8.

MS:371 (M – 1, 100), 336 (M – Cl – 1, 23), 301 (M – 2Cl – 1, 81), 271 (M – PCl_2, 43).

Synthesis of $(R^1)_2PCl$ 14

The lithium compound R^1Li **5** was prepared as previously described using 2.00 g (5.02 mmol) of R^1I, 3.45 ml (5.52 mmol) of n-BuLi 1.6 M in hexane and 20 ml of hexane. The addition of PCl_3 (0.69 g, 5.02 mmol) was carried out at room temperature. The reaction was exothermic. After removal of volatile materials and addition of 50 ml of pentane, LiCl was filtered out. Crystallization from Et_2O/pentane afforded 1.37 g (45%, mp: 228°C) of **14** in the form of a yellow powder.

^{1}H NMR: 2.28 (broad d, $^4J_{HH}$: 0.5 Hz, MeC_4), 2.44 (s, MeC_{10}), 6.64 (dd, $^4J_{HP}$: 3.0 Hz, $^4J_{HH}$: 0.5 Hz, 2 H, HC_3C_5), 6.94 and 7.02 (AB like spectrum, $^3J_{HH}$: 11.8 Hz, 8 H, C_8C_{12} and C_9C_{11}).

^{13}C NMR: 20.9 ($\underline{Me}C_1$), 21.4 ($\underline{Me}C_{10}$), 128.1 (C_9C_{11}), 129.5 (C_8C_{12}), 131.2 (C_3C_5), 133.3 (d, $^1J_{CP}$: 51.3 Hz, C_1), 136.0 (C_{10}), 138.4 (C_4), 139.6 (d, $^3J_{CP}$: 3.4 Hz, C_7), 147.5 (d, $^2J_{CP}$: 27.0 Hz, C_2C_6).

^{31}P NMR: 93.6.

MS: 608 (M, 25), 571 (M – Cl – 2, 100), 517 (M – PhMe, 7), 481 (M – PhMe – Cl – 1, 11), 391 (M – 2 PhMe – Cl, 2), 301 (M – R^1 – Cl – 1, 53), 272 (R^1H, 83), 91 (PhMe, 44).

Synthesis of R^2PCl_2 12

R^2PCl_2 **12** has been prepared as previously described[8] and crystallized from pentane (mp: 162°C). It was identified owing to its ^{1}H and ^{31}P NMR data[8], and also by its ^{13}C data and the fragmentation in mass spectrometry which were not given.

^{13}C NMR: 21.3 and 21.5 (Me), 128.7 (C_9C_{11}), 131.4 (C_3C_5), 136.3, 136.5, 136.6 and 137.6 (C_7, C_8C_{12}, C_{10}), 143.7 (C_4), 146.7 (d, $^2J_{CP}$: 29.0 Hz, C_2C_6).

MS: 428 (M, 18), 413 (M – 15, 100), 327 (M – PCl_2, 32), 312 (M – PCl_2 – Me, 33).

Synthesis of R^3PCl_2 13

The lithium compound R^3Li was prepared as previously described by addition of a slight excess of n-BuLi 1.6 M in hexane (3.4 ml, 5.00 mmol) to a solution of R^3I (2.11 g, 4.91 mmol) in hexane (20 ml). After stirring overnight at room temperature an excess of PCl_3 (2.02 g, 3 eq) was added

by syringe. The reaction mixture was then refluxed for 1h30. After removal of LiCl by filtration, hexane and the excess of PCl_3 were eliminated under vacuum. Crude **10** was crystallized from Et_2O/pentane (50/50) leading to 1.7 g (86%) of a light-yellow powder (mp: 78°C).

^{1}H NMR: 2.41 (s, 3 H, MeC_4), 3.78 (s, 6 H, OMe), 6.87–7.42 (m, 10 H, arom H).

^{13}C NMR: 21.5 (Me), 55.3 and 55.4 (OMe), 110.0 and 110.1 (C_9), 119.8 and 119.9 (C_{11}), 129.6, 132.3, 132.4 and 132.5 (C_2C_6, C_{10}, C_{12}), 156.9 and 157.0 (C_8).

^{31}P NMR: 160.6 and 161.2.

MS: 373 (M – OMe, 100).

Synthesis of R^1PH_2 15

A solution of R^1PCl_2 (4.09 g, 10.96 mmol) in Et_2O (30 ml) was added dropwise to a suspension of $LiAlH_4$ (1 g, 26.31 mmol) in Et_2O (30 ml). The reaction mixture was then refluxed for 1 h then stirred two supplementary hours at room temperature. The excess of $LiAlH_4$ was carefully hydrolyzed with oxygen-free water. The organic layer was dried overnight over Na_2SO_4. After removal of Et_2O, recrystallization from pentane gave a white powder but the ^{1}H and ^{13}C NMR spectrum showed the presence of R^1I which could not be eliminated. **12** was identified by ^{31}P NMR, IR, and mass spectrometry.

^{31}P NMR: -131.9 (t, $^1J_{PH}$: 194.0 Hz).

IR: ν PH: 2362 cm^{-1}

MS: 304 (M, 100), 289 (M – Me, 14), 271 (M – PH_2, 22), 256 (M – PH_2 – Me, 23).

Synthesis of R^2PH_2 16 and R^3PH_2 17

The same experimental procedure was used for **16** and **17:**

R^2PCl_2 (1.6 g, 2.49 mmol) in a mixture Et_2O/THF (50/50) (30 ml), excess of $LiAlH_4$ (0.30 g), 20 min reflux; recrystallization of **16** from pentane afforded a white powder (0.8 g, 89%, mp: 190°C).

R^2PH_2

^{1}H NMR: 1.97 (s, 12 H, MeC_8C_{12}), 2.32 (s, 9 H, MeC_4C_{10}), 3.00 (d, $^1J_{HP}$: 209.0 Hz, 2 H, PH), 6.65–6.93 (m, 6 H, arom H).

^{13}C NMR: 20.4 ($\underline{Me}C_9C_{12}$), 21.1 (MeC_4), 21.3 ($\underline{Me}C_{10}$), 128.2 and 128.6 (arom. CH), 135.7, 135.8, 135.9, 136.4, 136.5, 138.1 and 140.4 (arom. C).

^{31}P NMR: -147.7 (t, $^1J_{PH}$: 209.0 Hz),

IR: ν PH: 2298 cm^{-1}.

MS: 360 (M, 18), 345 (M – Me, 100), 327 (M – PH_2, 10), 297 (M – PH_2 – 2Me, 9).

R^3PCl_2 (1.40 g, 3.48 mmol) in a mixture Et_2O/THF (50/50) (30 ml), $LiAlH_4$ (0.26 g, 2 eq, 6.96 mmol), 30 min reflux; recrystallisation of the residue from Et_2O/pentane (50/50) afforded a white powder of **17** (1.05 g, 90 %, mp: 50°C).

R^3PH_2

^{1}H NMR: 2.34 and 2.37 (2s, MeC_4), 3.20 (d, $^1J_{PH}$: 206 Hz, 2 H, PH), 3.79 and 3.80 (2s, OMe), 6.90–7.58 (m, 10 H, arom. H).

^{13}C NMR: 21.4 ($\underline{Me}C_4$), 55.6 and 55.7 (OMe), 110.9 and 111.30 (C_9), 120.8 and 121.0 (C_{11}), 130.0–132.0 (other arom. CH), 131.2–143.1 (arom. C), 158.7 and 158.8 (C_8).

^{31}P NMR: -140.7 (t, $^1J_{PH}$: 207.0 Hz) and –141.2 (t, $^1J_{PH}$: 206.0 Hz)

IR: ν PH: 2302 cm^{-1}.

MS: 305 (M – OMe, 100), 288 (M – PH_2 – Me, 43), 273 (M – PH_2 – 2Me, 16).

Synthesis of $R^2P{=}CCl_2$ 19

To a solution of R^2PCl_2 **12** (1.35 g, 3.15 mmol), chloroform (0.38 g, 3.15 mmol) and THF (10 ml) cooled at – 110°C was slowly added by syringe a solution of n-BuLi 1.6 M in hexane (4.33 ml, 2.2 eq). The brown reaction mixture was stirred for 30 min at – 100°C then gradually warmed to room temperature. After removal of the lithium salts by filtration and of the solvents under vacuum, crude **19** was recrystallized from pentane/methanol (50/50) as a white-yellow powder (3.36 g, 86 %, mp: 65°C).

^{1}H NMR: 2.12 (s, 12 H, MeC_8C_{12}), 2.30 (s, 3H, MeC_{10}), 2.41 (s, 3H, MeC_4), 6.91 (broad s, HC_9C_{11}), 6.97 (broad s, 2 H, HC_3C_5).

^{13}C NMR: 20.95–21.54 ($\underline{Me}C_1$, $\underline{Me}C_8$, $\underline{Me}C_{10}$, $\underline{Me}C_{12}$), 128.5 (C_9C_{11}), 130.0 (C_3C_5), 136.1, 137.1, and 140.5 (arom. C), 145.2 (d, $^2J_{CP}$: 7.4 Hz, C_2C_6), 162.2 (d, $^1J_{CP}$: 47.0 Hz, P=C).

^{31}P NMR: 231.3.

MS: 440 (M, 7), 425 (M – Me, 8), 405 (M – Cl, 100), 370 (M – 2Cl, 7).

Synthesis of $R^1P{=}CCl_2$ 18 and $R^3P{=}CCl_2$ 20

Compounds **18** and **20** were obtained by the same procedure.

$R^1P{=}CCl_2$

R^1PCl_2 (2.80 g, 7.54 mmol), $CHCl_3$ (0.90 g, 7.54 mmol), THF (25 ml), n-BuLi 1.6 M in hexane (10.0 ml, 2.1 eq). The ^{31}P NMR study proved the formation of $R^1P{=}CCl_2$ (δ ^{31}P: 232.1 ppm) in a rather good yield (~50%) with unidentified products. Attempts of crystallization in various solvents to have pure **18** failed. However crude solutions of **18** could be used for further experiments.

$R^3P{=}CCl_2$

R^3PCl_2 (3.80 g, 9.30 mmol), $CHCl_3$ (1.11 g, 9.30 mmol), THF (35 ml), n-BuLi 1.6 M in hexane (11.0 ml, 1.89 eq). Yellow crystals of **20** were obtained from pentane: 3.29 g, 85 %, mp: 62°C.

^{1}H NMR: 2.42 and 2.45 (2s, 3 H, MeC_4), 3.77 and 3.78 (2s, 6 H, OMe), 6.75–7.65 (m, 10 H arom. H).

^{13}C NMR: 21.6 and 21.8 ($\underline{Me}C_4$), 55.0 and 55.4 (OMe), 111.20 (C_9), 120.8 (C_{11}), 128.2–131.1 (other arom. CH), 134.7, 137.1, 138.2, 139.1, 144.6 (arom. C), 156.6 (C_8).

^{31}P NMR: 225.2 (45%) and 228.7 (55%).

MS: 303 (M – $P{=}CCl_2$, 100).

References

[1] a) G. E. Miracle, J.L. Ball, D.R. Powell and R. West, *J. Am. Chem. Soc.*, **115,** 11598 (1993).
b) M. Trommer, G. E. Miracle, B. E. Eichler, D. R. Powell and R. West, *Organometallics*, **16**, 5737 (1997).

[2] N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki and S. Nagase, *J. Am. Chem. Soc.*, **119,** 1456 (1997).

[3] L. Rigon, H. Ranaivonjatovo, J. Escudié, A. Dubourg and J.-P. Declercq, *Chem. Eur. J.*, **5,** 774 (1999).
[4] a) B. E. Eichler, D. R. Powell and R. West, *Organometallics,* **17,** 2147 (1998).
b) N. Tokitoh, K. Kishikawa and R. Okazaki, *Chem. Lett.*, 811 (1998).
[5] H. Ramdane, H. Ranaivonjatovo, J. Escudié and S. Mathieu, *Organometallics,* **15,** 3070 (1996).
[6] H. Grützmacher, S. Freitag, R. Erbst-Irmer and G.S. Sheldrick, *Angew. Chem. Int. Ed. Engl.*, **31,** 437 (1992).
[7] a) R. Appel, C. Casser and M. Immenkeppel, *Tetrahedron Lett.*, **26,** 3551 (1985).
b) S. J. Goede and F. Bickelhaupt, *Chem. Ber.,* **124**, 2677 (1991).
c) M. Van Der Sluis, J. B. Wit and F. Bickelhaupt, *Organometallics,* **15**, 174 (1996).
[8] S. Shah, S. C. Burdette, S. Swavey, F. L. Urbach and J. D. Protasiewicz, *Organometallics,* **16,** 3395 (1997).
[9] K. Tsuji, Y. Fujii, S. Sasaki and M. Yoshifuji, *Chem. Lett., 855* (1997).
[10] a) J. J. Ellison and P. P. Power, *Inorg. Chem.*, **33,** 4231 (1994).
b) K. Ruhlandt-Senge, J.J. Ellison, R. J. Wehmschulte, F. Pauer and P. P. Power, *J. Am. Chem. Soc.*, **115,** 11353 (1993).
c) R. S. Simons, L. Ru, M. M. Olmstead and P. P. Power, *Organometallics,* **16,** 1920 (1997).
d) W. J. Grigsby and P. P. Power, *J. Am. Chem. Soc.*, **118**, 7981 (1996).
e) J. J. Ellison, K. Ruhlandt-Senge, H. H. Hope and P. P. Power, *Inorg. Chem.*, **34**, 49 (1995).
f) J. J. Ellison, K. Ruhlandt-Senge and P. P. Power, *Angew. Chem. Int. Ed. Engl.*, **33,** 1178 (1994).
g) R. S. Simons and P. P. Power, *J. Am. Chem. Soc.*, **118,** 11966 (1996).
[11] a) X. W. Li, W. T. Pennington and G. H. Robinson, *J. Am. Chem. Soc.*, **117**, 7578 (1995) and *Organometallics,* **14**, 2109 (1995).
b) E. Urzenius and J. D. Protasiewicz, *Main Group Chem.*, **1**, 369 (1996).
[12] C.-J. Du, H. Hart and K.-K. D. Ng, *J. Org. Chem.*, **51**, 3162 (1986).
[13] H. Suzuki, N. Tokitoh, R. Okazaki, J. Harada, K. Ogawa, S. Tomoda and M. Goto, *Organometallics,* **14,** 1016 (1995).
[14] U. Lüning, C. Wangnick, K. Peters and H. G. Von Schnering, *Chem. Ber.,* **124,** 397 (1991).