



*Dedicated to Professor Ion Grosu
on the occasion of his 65th anniversary*

NEW STABLE 2,3-DICHLORO,1,3-DIPHOSPHAPROPENES; SYNTHESIS AND CHARACTERIZATION

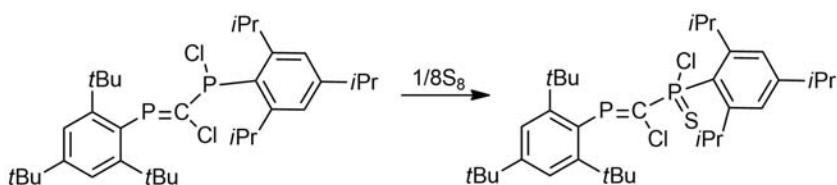
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Two novel diphosphapropenic compounds bearing two vicinal chlorine atoms on the P=C-P moiety have been obtained and completely characterized both through experimental (multinuclear NMR, HRMS, X-ray diffraction) and theoretical methods. These compounds are, due to their multiple coordination sites and the two halogen atoms, very interesting building blocks for new organometallic, cumulenenic and coordination derivatives.



INTRODUCTION

The chemistry of unsaturated compounds containing the phosphalkenyl $-P=C<$ moiety maintains its scientific interest due to the applications of these compounds, especially in obtaining coordinative compounds with applications in catalysis.^{1,2} If the symmetric carbodiphosphiranes with the general formula $R_3P=C=PR_3$ (where R is a bulky organic group) are well represented in the literature,³⁻⁷ the unsymmetrical derivatives containing a bicoordinated trivalent and a tricoordinated pentavalent phosphorus atom namely diphosphapropenes containing the $P=C-P(=E)$ backbone (when E is a group 16 element) are less studied.⁸ Almost

unknown remain 2,3-dihalogenated,1,3-diphosphapropenic derivatives, which represent effective building blocks for the synthesis of new organometallic and coordination compounds due to multiple reaction centers: the electron lone pairs, the halogen atoms and also the $P=C$ double bond. In this respect, some phosphalkenylphosphine oxides or thioxides $Mes^*P=C(Cl)-PCl(=E)R$ ($E = O, S$, $R = Mes^*$ (2,4,6-tri-*tert*-butylphenyl), tBu) were prepared and used as monodentate or chelating ligands;⁹ but their reactivity is yet to be established.

In order to stabilize the $P=C$ double bond by kinetic protection, the bulky organic group 2,4,6-tri-*tert*-butylphenyl (Mes^*) is the substituent of choice to be used on the phosphorus atom of the

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phosphaalkenyl unit.^{7–13} However, when used for stabilizing P=C=P=O cumulenic unit, a cyclisation of the supermesityl group was observed, even at low temperature, by addition of a methyl group from an *ortho*-*tert*-butyl unit to the C=P double bond of the C=P=O moiety, forming a five member saturated cycle.⁸ This behavior of the supermesityl group challenged as to find different stabilizing groups that offer sufficient steric hindrance but do not allow the cyclization of the cumulenic unit.

A theoretical study revealed that the presence of bulky organic groups connected to the P(V) atom induce a stabilizing effect but their electronic effects also play an important role in the stabilization of such compounds.^{14,15} For example the silyl group connected on the P(V) atom increases the stability of RP=C=P(=E)R derivatives. In contrast, the presence of electron-withdrawing groups leads to the decrease of the bond order in the –C=P(=E) fragment.

Following the research in this area, we present here the synthesis and complete characterization of two new 2,3-dichlorinated,1,3-diphosphapropenes bearing as stabilizing unit on the pentavalent phosphorus atom a 2,4,6-tri-*iso*-propylphenyl group in order to prevent the previously observed cyclisation and thus being able to act better as ligands for metals.

RESULTS AND DISCUSSION

Following a procedure similar to that previously used for the preparation of diphosphapropenic system containing a P=C–P(E) backbone,⁹ the preparation of the 3-chloro({chloro[(2,4,6-tri-*tert*-butylphenyl)phosphanylidene]methyl})[2,4,6-tris(propan-2-yl)phenyl]-λ⁵-phosphanethione **3** (Mes*P=C(Cl)–P(S)(Cl)Trip) (Scheme 1) was achieved in two stages: the synthesis of the new diphosphapropene Mes*P=C(Cl)–P(Cl)Trip **2** chloro({chloro[(2,4,6-tri-*tert*-butylphenyl)phosphanylidene]methyl})[2,4,6-tris-propan-2-yl]phenyl]phosphane followed by its oxidation with sulfur.

In the first step, the new derivative **2** was obtained by the addition of an equivalent of a phosphaalkenyllithium Mes*P=CClLi to a solution of 2,4,6-tri-*isopropyl*-dichlorophosphine at low temperature, as shown in the Scheme 1.

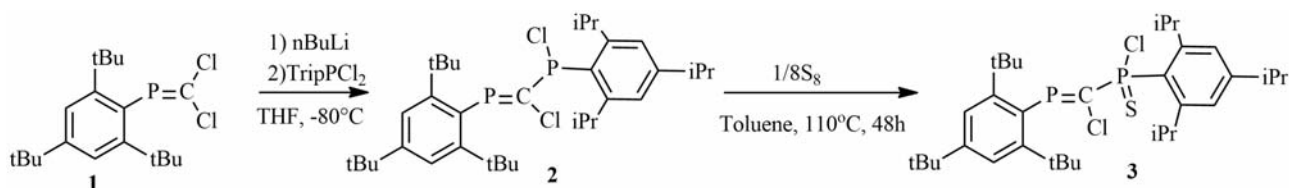
The diphosphapropene **2**, separated from the reaction mixture by filtration in pentane, was obtained as yellow crystals from diethyl ether. The newly formed compound was found to be air sensitive (it decomposes fast in reaction with water

or air) giving rise to a large number of decomposition compounds which could not be separated from the reaction mixture and characterized. **2** was completely characterized in solution through multinuclear spectroscopy and mass spectrometry. In the ³¹P and ³¹P{H} NMR spectra two doublets were observed at 83.9 (P–C) and 278.8 (P=C) ppm with a ²J_{PP} coupling constant of 125.2 Hz, in the expected ranges for phosphorus atoms involved in a P=C–P unit when compared to similar compounds.⁹ In the ¹³C{H} NMR, the central carbon atom of the P=C–P unit gives rise to a resonance signal at 155.5 ppm, as a doublet of doublets (with ²J_{PC} coupling constants of 77.3 and 89.1 Hz). All the resonance signals from the ¹H and ¹³C{H} NMR were assigned using two-dimensional experiments and show the non-equivalency of the carbon atoms of the supermesityl and tri-*iso*-propyl groups due to a hindered rotation.

The selective oxidation of derivative **2** with sulfur in refluxing toluene afforded the novel 2,3-dichloro,3-thio,1,3-diphosphapropene **3** (Scheme 1). The reaction undergoes with an almost quantitative conversion when using 100% excess of sulfur and was found to be complete after 48 hours (monitored through ³¹P NMR).

The new diphosphapropene **3** was separated after removal of excess sulfur (by precipitating it in pentane) as yellow crystals in diethyl ether. The derivative **3** is completely stable in argon and does not decompose at short exposures to air/moisture (decomposition products were observed only after exposure longer than 2 weeks). The structure of compound **3** was completely characterized in solution, through multinuclear NMR spectroscopy and mass spectrometry and in solid state, by X-ray diffraction.

The ³¹P NMR spectrum reveals two doublet signals, high field shifted when compared to those observed for the precursor **2**, at 79.5 (C–P=S) and 322.8 (P=C) with a ²J_{PP} coupling constant of 134.9 Hz. The ¹H and ¹³C{H} spectra show the specific resonance signals of all the protons and carbon atoms at the expected chemical shifts⁹ and their complete assignment was possible after 2D experiments. For instance, the central carbon atom of the P=C–P(=S) moiety gives rise to a doublet of doublets at 160.0 ppm (²J_{PC} = 67.5 and 85.0 Hz). A close analysis of the NMR data revealed that the rotation of both aromatic groups (supermesityl and tri-*iso*-propylphenyl) is hindered, causing the non-equivalence of the carbon and proton atoms as further detailed in the experimental part.



Scheme 1

Single crystals of **3** were obtained by recrystallization from diethylether. One crystal was mounted on a MiTeGen microMount cryoloop and data was collected on a Bruker D8 VENTURE diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a I μ S 3.0 micro focus source with multilayer optics, at low temperature (100 K). Further details on the data collection and refinement methods can be found in Table 1 and the experimental section.

Compound **3** crystallizes in the triclinic centrosymmetric space group with two molecules in the unit cell, related through an inversion center. Although one of the phosphorus atoms is chiral, the X-ray diffraction revealed that both the R_P and S_P isomers are found in the crystal in equal proportions, thus the crystal is actually a solid racemic mixture. The asymmetric unit consists of only one molecule (Figure 1).

Table 1

Crystal data and structure refinement for compound **3**

Compound	3
Empirical formula	C ₃₄ H ₅₂ Cl ₂ P ₂ S
Formula weight	625.65
Crystal size /(mm)	0.174 x 0.059 x 0.020
Crystal habit	light yellow needle
Wavelength (\AA)	0.71073
Temperature (K)	100.(2)
Crystal system	Triclinic
Space group	P
a (\AA)	6.2264(9)
b (\AA)	16.857(2)
c (\AA)	18.519(3)
a ($^\circ$)	66.614(5)
b ($^\circ$)	89.771(5)
g ($^\circ$)	81.688(5)
Volume (\AA^3)	1762.3(4)
Z	2
Density (calculated) (g cm^{-3})	1.179
Absorption coefficient (mm^{-1})	0.355
$F(000)$	672
θ range for data collections ($^\circ$)	2.23-25.05
$T_{\text{max}} / T_{\text{min}}$	0.647/ 0.746
Reflections collected	45288
Independent reflections, R_{int}	6236, 0.0407
Completeness to $\theta = 25.05^\circ$	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6236 / 0 / 367
Goodness-of-fit on F^2	1.181
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0601$
	$wR_2 = 0.1410$
R indices (all data)	$R_1 = 0.0646$
	$wR_2 = 0.1424$
Largest diff. peak and hole, e\AA^{-3}	0.887, -0.493
CCDC No.	1962766

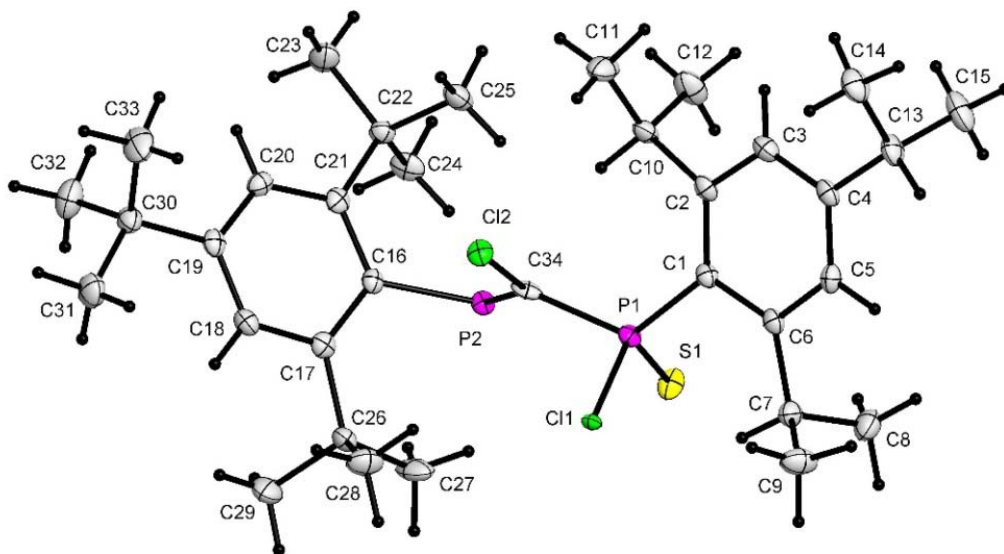


Fig. 1 – View of the (*R*)_{P1} isomer in the asymmetric unit in the crystal of **3**, shown with 50% probability ellipsoids.

Table 2

Selected bond lengths (Å) and angles (°) for compound **3**

Mes*(C)–P	1.846(4)	Mes*(C)–P=C	101.4(2)
P=C	1.687(4)	P=C–P	127.4(3)
C–Cl	1.720(4)	P=C–P	115.8(2)
C–P	1.825(5)	Cl–C–P	116.0(2)
P–Cl	2.108(1)	C–P–Cl	94.8(1)
P=S	1.925(1)	S=P–(C)Trip	114.5(1)
P–(C)Trip	1.831(4)	Mes*(C)–P=C–Cl	-7.6(3)
		Mes*(C)–P=C–P	161.9(2)
		Cl–C–P–Cl	55.1(2)

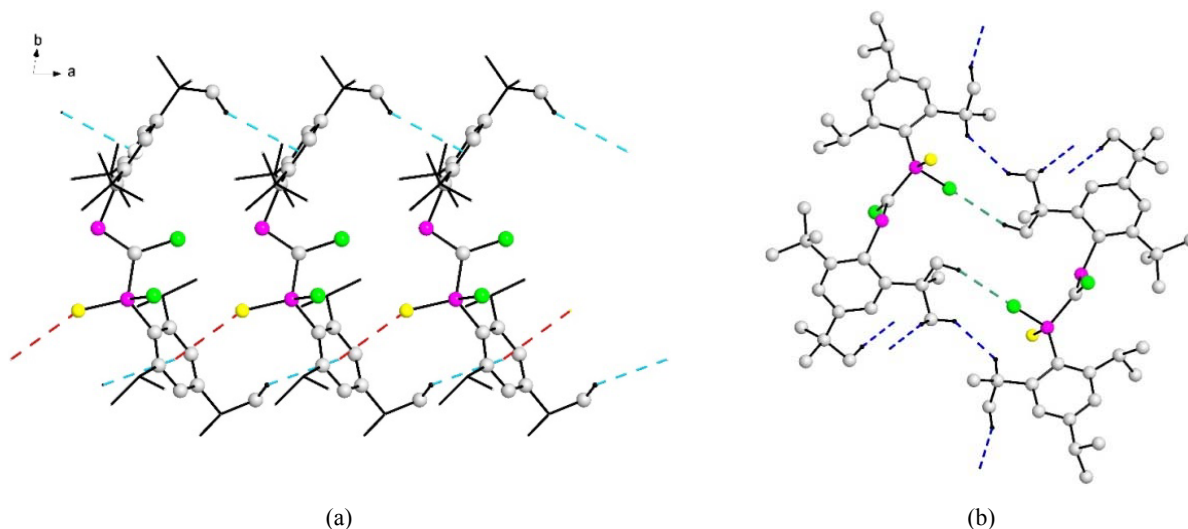


Fig. 2 – Intermolecular associations in the crystal of **3**, through (a) S \cdots π (red fragmented lines) and $\bar{C}H\cdots\pi$ (sky blue fragmented lines) contacts between (*R*)_{P1} isomers, (phosphorus atoms are highlighted in magenta, the sulfur atoms in yellow, the chlorine atoms in green, and the carbon ones in clear gray); (b) $\bar{C}H\cdots Cl$ (green fragmented lines) and dispersive type C–H \cdots H–C interactions (dark blue fragmented line) between (*R*)_{P1} and (*S*)_{P1} isomers. Hydrogen atoms not involved in such interactions are omitted for clarity.

In the asymmetric unit the two chlorine atoms are in a gauche arrangement, with the C11–P1–C34–Cl2 dihedral angle of 55.1(2)°. More

geometrical parameters related to the asymmetric unit are given in Table 2.

Table 3

Intermolecular contacts for compound **3**

C–H···Cl	d₁ (Å)	γ (°)	D
C27–H27B···Cl1 ^a	2.94	161.5	3.88(1)
C–H···H–C	d (Å)	α (°)	β (°)
C7–H7···H29C ^a –C29 ^a	2.50	140.8	139.2
C8–H8C···H8C ^b –C8 ^b	2.45	151.5	151.5
C29–H29A···H31B ^c –C31 ^c	2.36	161.0	170.7
C–H···plane	d₀ (Å)	α (°)	D_{pln} (Å)
C33–H33B···C(16-21) ^d	0.63	121.5(3)	3.12
S···plane	d₀ (Å)	α (°)	D_{pln} (Å)
S1···C(1-6) ^c	0.53	123.0(1)	3.46

Symmetry equivalent atoms are given by: a) -x, 1-y, 1-z; b) 1-x, -y, 1-z; c) -1+x, y, z; d) 1+x, y, z

Close inspection of the crystal packing in the search of intermolecular interactions has concluded that all existing interactions are really weak compared to the Van der Waals radii,¹⁶ due probably to the bulkiness of the substituted aryl groups which prevents molecules from getting closer. Thus, no $\pi\cdots\pi$ or $\text{Cl}\cdots\pi$ interactions were found considering a 4.1 Å cutoff for the $\text{Cg}\cdots\text{Cg}$ and $\text{Cg}\cdots\text{Cl}$ distances, where Cg is the center of gravity of the C_6H_2 aromatic groups.^{15,17} Also, no $\text{Cl}\cdots\text{Cl}$ intermolecular interactions were found in the crystal lattice.¹⁸ However, weak $\text{S}\cdots\pi$ and $\text{C–H}\cdots\pi$ interactions between same type of enantiomers were identified (Figure 2a).^{19,20} Considering only these interactions a chain like arrangement of molecules results. (Figure 2a).

In the crystal lattice further associations through $\text{C–H}\cdots\text{Cl}$ and dispersive type, $\text{C–H}\cdots\text{H–C}$ interactions between R_{P1} and S_{P1} isomers were found (Figure 2b).²⁰⁻²² When all these weak interactions (table 3) are considered a tridimensional supramolecular network results.

Relevant information regarding the weak intermolecular contacts is given in Table 3.

Additionally, a DFT study was performed on the diphosphapropenic moiety in order to determine additional structural and electronic properties.

Calculated structural features for species **2**, **3** and **4** (**4** represent the calculated specie $\text{Mes}^*\text{P}(\text{S})=\text{C}(\text{Cl})\text{–PCl}(\text{Trip})$) are presented in Table 4. In the case of **3**, a good agreement between calculated geometrical features and the experimental measured ones is observed (see Tables 2 and 4 for comparisons), while for **2**, calculations reassemble previously reported crystallographic data for similar systems.^{8,9,13} The Wiberg bond indices (WBI) are additionally illustrated for selected chemical bonds. NPA charges computed within the framework of the Natural Bond Orbital (NBO) analysis are also displayed for the P and C atoms (Table 4), highlighting an enhanced electrophilic character for the P atoms. Concerning the lone pair electrons (LP) on the two P atoms, NBO calculations reveal a mixed s - p AO character in all cases (about 55-65% s and 45-35% p), as previously revealed in other theoretical studies.¹⁴ In addition, the molecular structure of system **4** was investigated by DFT calculations, in order to assess the relative stability of the species with the $\text{P}=\text{S}$ bond involving the sp^2 P atom related to the experimental observed derivative **3**. Nonetheless, computed enthalpies indicate a higher stability for **3**, with a calculated gap ($\Delta H_{3,4}$) of about 5 kcal mol⁻¹.

Table 4

Selection of calculated structural features for derivatives **2**, **3** and calculated **4**. The WBI indices are displayed for selected chemical bonds. The calculated NPA charges for the P and C atoms of the $\text{P}=\text{C–P}$ unit are additionally presented

	P–C–P (°)	P=C (Å)	WBI (P=C)	C–P (Å)	WBI (P–C)	P–Cl (Å)	WBI (P–Cl)	P=S (Å)	WBI (P=S)	qP(sp³)	qP(sp²)	qC
2	120.6	1.684	1.58	1.811	0.95	2.077	0.88	-	-	0.86	0.73	-0.88
3	119.7	1.680	1.59	1.816	0.83	2.059	0.82	1.926	1.50	1.27	0.78	-0.92
4	127.8	1.675	1.34	1.815	0.91	2.080	0.89	1.924	1.50	0.88	1.18	-0.95

Due to the relatively high stability of the obtained compounds, they could not only be completely characterized, but are also very suitable to be tested in order to determine their coordination capacity.

EXPERIMENTAL

All the reactions have been carried out under inert conditions (argon) using Schlenk techniques. The solvents were used after purification through an MBraun automatic solvent purifying system and the THF was freshly distilled over Na/benzophenone. NMR experiments were performed on a Bruker Avance 400 MHz spectrometer in CDCl₃ at the following frequencies: 400.13 (reference TMS) for ¹H; 100.61 MHz (reference TMS) for ¹³C; 161.98 MHz (reference H₃PO₄) for ³¹P. High resolution mass spectra were obtained using a LTQ ORBITRAP XL spectrometer (ThermoScientific) using an atmospheric pressure chemical ionization (APCI) probe.

For structure solving and refinement of the X-ray structure the Bruker APEX3 software package was used.²³ The structure was solved by dual methods (SHELXT-2014/5)²⁴ and refined by full matrix least-squares procedures based on *F*² with all measured reflections (SHELXL-2018/3).²⁵ The structure was refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. The drawings were created with the Diamond program.²⁶ The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

All theoretical calculations were performed using the *Gaussian 09* package,²⁷ in the framework of the Density Functional Theory (DFT). Geometry optimizations were performed in the gas phase without symmetry constraints. The PBE0²⁸ hybrid functional was employed in all cases, along with the Def2-TZVP^{29,30} basis set. Optimization criteria were set to tight, while the integration grid used was of 99 radial shells and 950 angular points for each shell (99,950), precisely the "ultrafine" grid within *Gaussian 09*. Frequency analyses were performed in order to characterize the nature of the stationary points, and to compute the enthalpies for the investigated species. Natural Bond Orbital (NBO)³¹⁻³³ analyses were carried out on the optimized structures. The natural charges computed within the framework of the Natural Population Analysis (NPA) and the Wiberg bond indices (WBI) are discussed throughout this text. The *NBO 7.0 Program*³⁴ was used for all NBO calculations.

Synthesis of Mes*P=C(Cl)–P(Cl)Trip (2) A solution of *n*-butyllithium in hexane (2.27 M, 3.22 mL, 7.3 mmol) was added dropwise to a solution of Mes*P=C(Cl)₂ (2.79 g, 7.3 mmol) in THF (40 mL) at –80 °C and was stirred for an additional hour at the same temperature. The resulting solution was transferred to a solution of TripPCl₂ (2.37 g, 7.3 mmol) in THF (40 mL) at –80 °C. The brown reaction mixture was allowed to slowly warm to room temperature. After removal of volatile compounds under reduced pressure, pentane was added over the solid and the lithium salts were removed by filtration. The compound **2** was separated as a brown powder from pentane at low temperature (3 g, η = 70 %, m.p. = 167 °C).

¹H NMR (CDCl₃, 400.13 MHz): δ (ppm) = 1.28, d, ³J_{H,H} = 6.9 Hz, 6H, CH₃-*para*-isopropyl; 1.31 and 1.33 d, ³J_{H,H} = 2.6 and 4.2 Hz, 12H, CH₃-*ortho*-isopropyl; 1.34, s, 9H, CH₃-*para*-tertbutyl; 1.43 and 1.47, s, 18H, CH₃-*ortho*-tertbutyl; 2.92, septet, ³J_{H,H} = 6.8 Hz, 1H, CH-*para*-isopropyl; 3.86, septet, ³J_{H,H} = 6.1 Hz, 2H, CH-*ortho*-isopropyl; 7.10, d, ⁴J_{P,H} = 2.9 Hz, 2H, *H*_{arom}-Trip; 7.42, d, ⁴J_{P,H} = 4.7 Hz, 2H, *H*_{arom}-Mes*.

³¹P NMR (CDCl₃, 161.98 MHz): δ (ppm) = 83.9, d, ²J_{P,P} = 125.2 Hz, Trip-*P*-C, 278.8, d, ²J_{P,P} = 125.2 Hz, Mes*-*P*-C.

¹³C{H} NMR (CDCl₃, 100.61 MHz): δ (ppm) = 23.8, d, ⁶J_{P,C} = 2.2 Hz, C_H₃-*para*-isopropyl; 25.2 and 25.6 C_H₃-*ortho*-isopropyl; 31.5, C_H₃-*para*-tertbutyl; 32.1 and 32.4, C_H(CH₃)₂-*ortho*-isopropyl; 32.7 and 32.9, d, ⁴J_{P,C} = 6.1 Hz and ⁴J_{P,C} = 6.7 Hz, C_H₃-*ortho*-tertbutyl; 34.4, C_H(CH₃)₂-*para*-isopropyl; 35.2, C(CH₃)₃-*para*-tertbutyl; 37.9 and 38.1, C(CH₃)₃-*ortho*-tertbutyl; 122.0 and 122.6, C_{meta}-Mes*; 123.0, d, ³J_{P,C} = 4.4 Hz, C_{meta}-Trip; 126.7, d, ¹J_{P,C} = 45.5 Hz, ³J_{P,C} = 10.0 Hz, C_{ipso}-Trip, 135.6, d, ¹J_{P,C} = 63.0 Hz, C_{ipso}-Mes*, 151.1, C_{para}-Mes*, 153.1, d, ²J_{P,C} = 1.6 Hz, C_{ortho}-Trip, 153.3, d, ⁴J_{P,C} = 4.3 Hz, C_{para}-Trip, 155.5, d, ²J_{P,C} = 18.9 Hz, C_{ortho}-Mes*, 172.3, dd, ¹J_{P,C} = 77.3 Hz, ¹J_{P,C} = 89.1 Hz, P=C–P.

HRMS (APCI) (C₃₄H₅₂Cl₂P₂): calculated [M+1] 593.29996, found 593.29857.

Synthesis of Mes*P=C(Cl)–P(Cl)(S)Trip (3) An excess of sulfur (0.25 g, 7.82 mmol) was added to a solution of 1,3-diphosphapropene **2** (2.32 g, 3.91 mmol) in toluene (50 mL) and the mixture was heated under reflux for 5 days. The reaction was stopped when the conversion reached 100% (monitored through ³¹P{H} NMR). The solvent was removed under vacuum and compound **3** was obtained by recrystallization from diethyl ether as a yellow precipitate (1.54 g, η = 63%, m.p. = 187 °C).

¹H NMR (CDCl₃, 400.13 MHz): δ (ppm) = 1.23-1.26, m, 18H, CH₃-isopropyl (*ortho* and *para*); 1.35, s, 9H, CH₃-*para*-tertbutyl; 1.52, d, ³J_{P,H} = 11.8 Hz, 18H, CH₃-*ortho*-tertbutyl; 2.87, septet, ³J_{H,H} = 11.8 Hz, 1H, CH-*para*-isopropyl; 3.92, septet, ³J_{H,H} = 11.8 Hz, 2H, CH-*ortho*-isopropyl; 7.09, d, ⁴J_{P,H} = 6.0 Hz, 2H, *H*_{arom}-Trip; 7.45, d, ⁴J_{P,H} = 14.4 Hz, 2H, *H*_{arom}-Mes*.

³¹P NMR (CDCl₃, 161.98 MHz): δ (ppm) = 79.5, d, ²J_{P,P} = 134.9 Hz, Trip-*P*-C; 322.8, d, ²J_{P,P} = 134.9 Hz, Mes*-*P*-C

¹³C{H} NMR (CDCl₃, 100.61 MHz): δ (ppm) = 23.7, d, ⁶J_{P,C} = 3.0 Hz, C_H₃-*para*-isopropyl; 24.6 and 25.2 C_H₃-*ortho*-isopropyl; 31.4, C_H₃-*para*-tertbutyl; 32.0, d, ³J_{P,C} = 6.8 Hz, C_H(CH₃)₂-*ortho*-isopropyl; 33.6 and 33.8, d, ⁴J_{P,C} = 7.6 Hz and ⁴J_{P,C} = 6.7 Hz, C_H₃-*ortho*-tertbutyl; 34.2, C_H(CH₃)₂-*para*-isopropyl, 35.1 C(CH₃)₃-*para*-tertbutyl, 38.0 and 38.7 C(CH₃)₃-*ortho*-tertbutyl; 122.2 and 123.9 C_{meta}-Mes*; 123.3, d, ³J_{P,C} = 13.5 Hz C_{meta}-Trip; 128.9, d, ¹J_{P,C} = 98.1 Hz C_{ipso}-Trip; 151.5, C_{para}-Mes*; 152.4, d, ²J_{P,C} = 13.4 Hz, C_{ortho}-Trip; 152.8, d, ⁴J_{P,C} = 3.2 Hz, C_{para}-Trip; 154.2 and 154.0 d, ²J_{P,C} = 3.2 Hz and ²J_{P,C} = 2.4 Hz, C_{ortho}-Mes*; 160.0, dd, ¹J_{P,C} = 67.5 Hz, ¹J_{P,C} = 85.0 Hz P=C–P.

HRMS (APCI) (C₃₄H₅₂Cl₂P₂S): calculated [M+1] 625.27203, found 625.26688.

CONCLUSIONS

We obtained two novel dichlorinated 1,3-diphosphapropenes Mes*P=C(Cl)–P(Cl)Trip and Mes*P=C(Cl)–P(=S)(Cl)Trip (Mes*=2,4,6-tri-*tert*-

butylphenyl, Trip=2,4,6-tri-*iso*-propylphenyl). The newly obtained compounds proved to be stable for an indefinite time under argon and for several days in air/moisture. By using Trip instead of Mes* on the pentavalent phosphorus atom, the cyclization of the supermesityl group was prevented, as not to block the P(V) atom for potential future applications. These compounds are valuable building blocks as they have the lone pairs on the phosphorus and/or sulfur atoms, the double bond and the chlorine atoms available for modifications in view of future applications.

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