

A Simple Straightforward Synthesis of Phenylphosphane and the Photoinitiator Bis(mesityl)phenylphosphane Oxide (IRGACURE 819)

Hansjörg Grützmacher^{*a}, Jens Geier^a, Daniel Stein^a, Timo Ott^a, Hartmut Schönberg^a, Reinhard H. Sommerlade^b, Souad Boulmaaz^b, Jean-Pierre Wolf^c, Peter Murer^c, and Thomas Ulrich^d

Abstract: A straightforward high-yield synthesis for the photoinitiator bis(2,4,6-trimethylbenzoyl)phenylphosphane oxide (**16**, IRGACURE 819) involves: i) the reaction of phenyldichlorophosphane, PhPCl_2 , with sodium to give $[\text{Na}_2(\text{P}_2\text{Ph}_2)(\text{tmeda})]_6$ (**5**); ii) protonation of **5** with *tert*-butanol to give 1,2-diphenyldiphosphane, PhHP-PHPh (**12**); iii) reduction of **12** by sodium to yield $[\text{Na}(\text{PHPh})]_x$ (**13**); iv) protonation of **13** with *tert*-butanol to give phenylphosphane PhPH_2 (**14**) in excellent yields; v) reaction of **14** with 2,4,6-trimethylbenzoylchloride (MesCOCl) in presence of the NaOt-Bu formed in steps ii and iv to give bis(2,4,6-trimethylbenzoyl)phenylphosphane **7**; vi) oxygenation of **7** with 30% aqueous hydrogen peroxide to give the final product **16**. This reaction can be performed in toluene with about 4 vol-% of tmeda as an activator in a one-pot synthesis without changing the solvent. The structures determined by X-ray diffraction of the unique hexameric aggregate **5** and **16** are reported.

Keywords: Acylphosphanes · Ion triples · Phosphanes · Phosphorus · Photoinitiators · Sodium

1. Introduction

Bis(acyl)phosphanoxides (BAPOs) are very potent photoinitiators for a wide variety of polymerization, coating, and curing processes and have been intensively investigated over the last two decades.^[1] Commonly they are synthesized from a primary phosphane and two equivalents of

acylchloride in presence of a base which leads to bis(acyl)phosphanes (BAPs) in the first step (Eqn. (1), Scheme 1). Oxidation with hydrogen peroxide subsequently leads to the corresponding BAPO. However, due to its pyrophoric and toxic properties, phenylphosphane is no longer available in bulk quantities. Alternatively, the reaction of bis-metallated phosphandiides, $[\text{M}_2\text{PR}]$, with acylchlorides was proposed (Eqn. (2)). The 'M₂PR' compounds were believed to be formed in the reaction of organyl phosphorus dichlorides, RPCl_2 , with alkali metals $\text{M} = \text{Li}, \text{Na}, \text{K}$. Specifically, the commercially available bis(2,4,6-trimethylbenzoyl)phenylphosphane oxide IRGACURE 819 has been prepared from PhPCl_2 , lithium, and 2,4,6-trimethylbenzoylchloride (MesCOCl) in THF as solvent (Scheme 1).^[2] Disad-

vantages in this preparation are the use of lithium as reducing metal and the necessity to change the solvent before the oxygenation with H_2O_2 .

Hence, the development of a protocol for the synthesis of IRGACURE 819 in hydrocarbon solvents and employing sodium as a cheaper reducing metal was desirable. With this aim in mind, we started to investigate the reaction of phenyldichlorophosphane, PhPCl_2 (IUPAC: phenylphosphonous acid dichloride) with sodium in toluene or xylene in the presence of small amounts of tetramethylethylenediamine, tmeda, as an activator. In this report, we describe the tmeda complex of disodium diphenyldiphosphandiide, $[\text{Na}_2(\text{P}_2\text{Ph}_2)(\text{tmeda})]_6$, whose structure we finally could determine, and a convenient one-pot synthesis of IRGACURE

*Correspondence: Prof. Dr. H. Grützmacher^a

Tel.: +41 1 632 28 55

Fax: +41 1 633 10 32

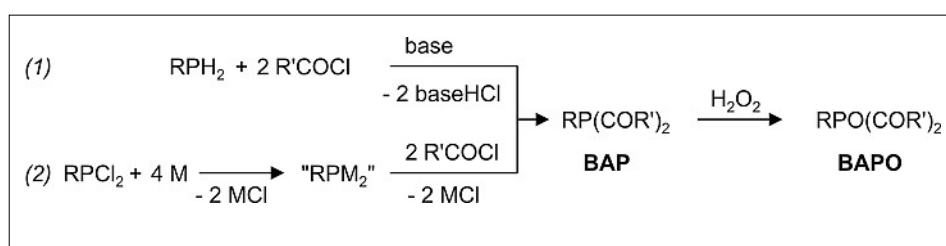
E-mail: hgruetzmacher@ethz.ch

^aDepartment of Chemistry and Applied Biosciences
 ETH Zürich, Wolfgang-Pauli-Strasse 10
 CH-8093 Zürich

^bProcess Research, Coating Effects Segment
 Ciba Inc., P.O. Box, CH-4002 Basel

^cR&D, Coating Effects Segment, Ciba Inc., P.O. Box
 CH-4002 Basel

^dProcess Optimization, Coating Effects Segment
 Ciba Inc., P.O. Box, CH-4002 Basel



Scheme 1. Synthetic routes to bis(acyl)phosphane oxides

819 from PhPCl_2 , sodium, and MesCOCl in a hydrocarbon solvent.

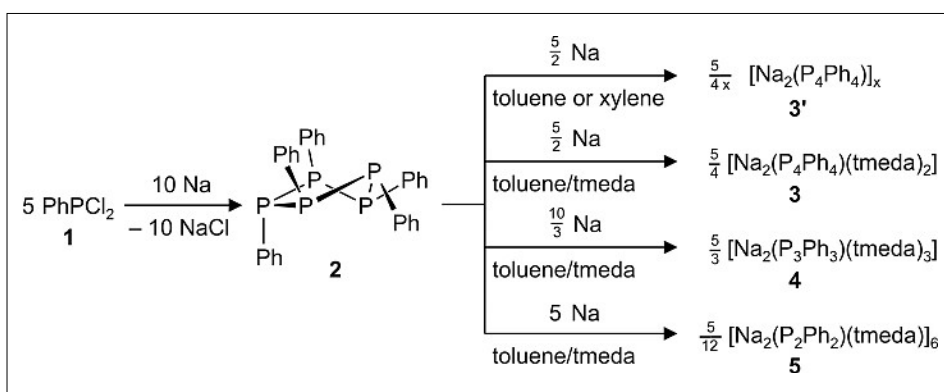
2. Results and Discussion

In the first steps of the reaction of PhPCl_2 with sodium, the cyclic pentaphenylcyclopentaphosphane, $(\text{PhP})_5$, is obtained in reductive bond-forming reactions without the detection of any other intermediates.^[3]

In the following steps, P–P bonds are reductively cleaved (a reaction typical for compounds containing bonds between heavier main group elements, *c.f.* sulfur, silanes, *etc.*) and depending on the reaction conditions the 1,2,3,4-tetraphenyltetraphosphane-1,4-diide, $[\text{Na}_2(\text{P}_4\text{Ph}_4)(\text{tmeda})_2]$ (**3**),^[4] 1,2,3-triphenyltriphosphane-1,3-diide, $[\text{Na}_2(\text{P}_3\text{Ph}_3)(\text{tmeda})_3]$ (**4**),^[4] or 1,2-diphenyldiphosphane-1,2-diide $[\text{Na}_2(\text{P}_2\text{Ph}_2)(\text{tmeda})_6]$ (**5**) were obtained (Scheme 2). In Fig. 1, simplified sketches of the structures of **3** and **4** and the dimethoxyethane (dme) solvate $[\text{Na}(\text{dme})_3]^+[\text{Na}_5(\text{P}_2\text{Ph}_2)_3(\text{dme})_3]^-$, which was obtained previously by crystallization from dme,^[4] are displayed ($\bullet = \text{P}$, $\oplus = \text{Na}$, $\circ = \text{C}$). Especially tetraphosphandiides, $[\text{M}_2(\text{P}_4\text{Ph}_4)(\text{sol})_x]^-$, were intensively investigated and a number of X-ray diffraction studies were performed to elucidate their structures.^[5]

Due to dynamic processes and the fact that relatively small changes in their conformations provoke large variations in the ^{31}P , ^{31}P coupling constants, the ^{31}P NMR spectra of $\text{M}_2(\text{P}_4\text{R}_4)$ species in solution are complicated and ill-defined very broad resonances at room temperature are frequently observed.^[6,7] However, these data allowed us to identify the yellow almost insoluble compound obtained in the reaction between $(\text{PhP})_5$ (or PhPCl_2) with sodium in toluene or xylene *in the absence of tmeda* as the almost solvent-free tetraphosphandiide, $[\text{Na}_2(\text{P}_4\text{Ph}_4)]_x$ (**3'**). This compound is not further degraded to smaller dianions in the absence of additives like tmeda. The triphosphandiide $[\text{Na}_2(\text{P}_3\text{Ph}_3)(\text{tmeda})_3]$ (**4**) is a rare example of a structurally characterized compound.^[8] Remarkably, **4** is not formed by reductive degradation of the tetraphosphandiide $[\text{Na}_2(\text{P}_4\text{Ph}_4)(\text{tmeda})_2]$ (**3**) but by a synproportionation reaction between **3** and $[\text{Na}_2(\text{P}_2\text{Ph}_2)(\text{tmeda})_6]$.^[5d] Note that we were not able to detect any species which may be formulated as $[\text{Na}_2\text{PPh}]$ under any of our reaction conditions (hydrocarbon/tmeda solvents, T up to 140 °C).

The dme solvate $[\text{Na}(\text{dme})_3]^+[\text{Na}_5(\text{P}_2\text{Ph}_2)_3(\text{dme})_3]^-$ (see Fig. 1C)^[5a] and $[\text{Li}_2(\text{P}_2\text{Ph}_2)(\text{tmeda})_2]$ ^[6] are the only compounds known to date which contain the vicinal dianion $[\text{P}_2\text{Ph}_2]^{2-}$. We were now able to determine the structure of the tmeda complex **5** by an X-ray diffraction study. This shows **5** to be a hexameric ionic aggregate with a unique structure (Fig. 2).



Scheme 2. Synthesis of disodium oligo(phenyl)phosphandiides **3–5** in hydrocarbon solvents

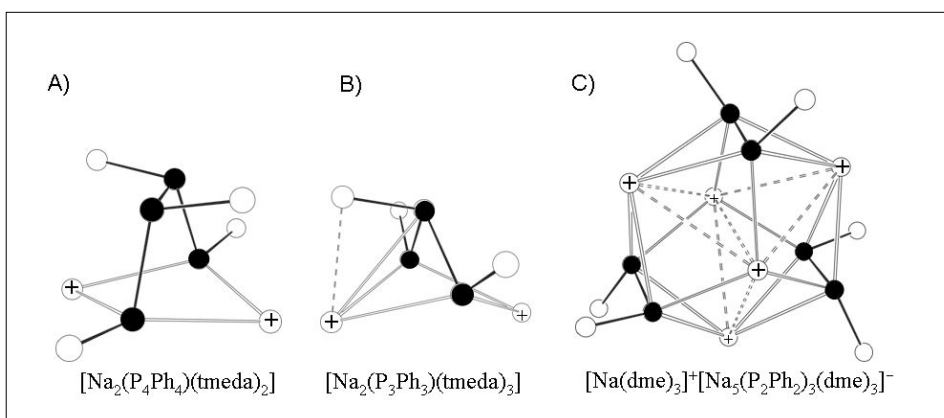


Fig. 1. Schematic representations of $[\text{Na}_2(\text{P}_4\text{Ph}_4)(\text{tmeda})_2]$ (**3**), $[\text{Na}_2(\text{P}_3\text{Ph}_3)(\text{tmeda})_3]$ (**4**), and $[\text{Na}(\text{dme})_3]^+[\text{Na}_5(\text{P}_2\text{Ph}_2)_3(\text{dme})_3]^-$ highlighting the core-structures composed from the P atoms (\bullet), the sodium cations (\oplus) and *ipso*-carbons of the phenyl rings (\circ).

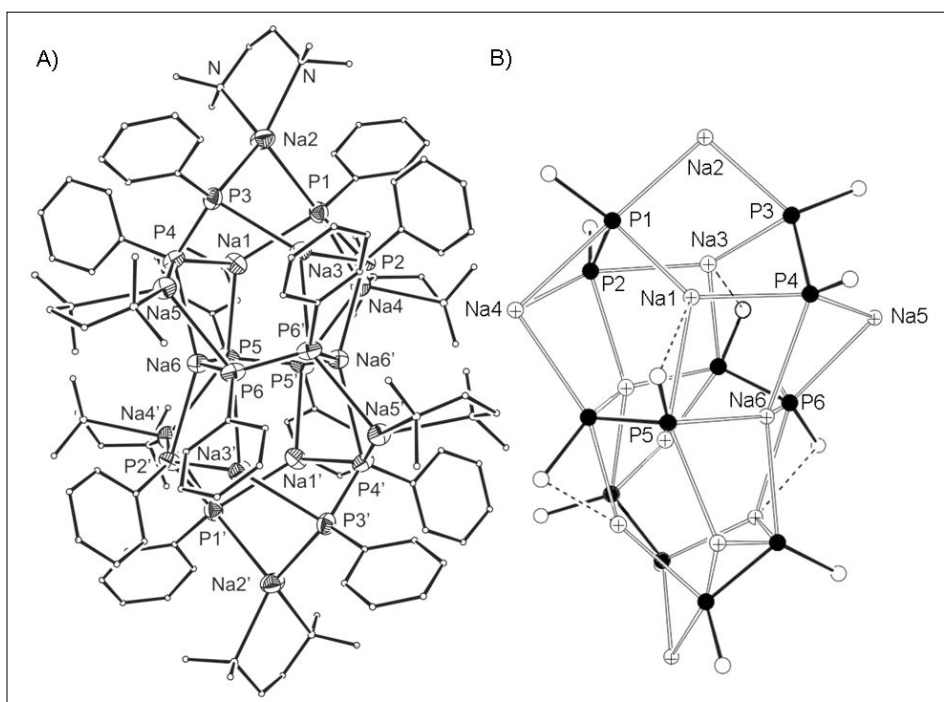
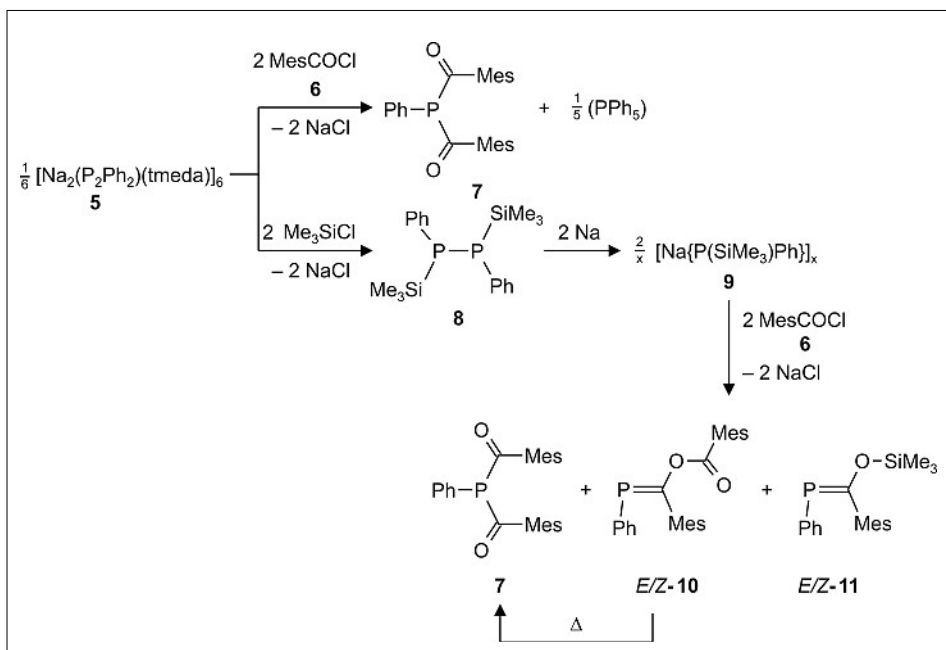


Fig. 2. Structure of $[\text{Na}_2(\text{P}_2\text{Ph}_2)(\text{tmeda})_6]$ (**5**). A) Hydrogen atoms are omitted for clarity. B) Schematic representation of **5** highlighting the core structure composed from the P atoms (\bullet), the sodium cations (\oplus) and *ipso*-carbons of the phenyl rings (\circ). Selected bond lengths [Å] and angles [°]: Na1–P1 2.796(4), Na1–P4 2.939(4), Na1–P5 2.911(4), Na2–P1 2.870(4), Na2–P3 2.852(4), Na3–P3 2.837(4), Na3–P2 2.965(4), Na3–P6' 2.920(4), Na4–P1 3.043(4), Na4–P2 2.911(4), Na4–P5' 2.974(4), Na5–P4 2.970(4), Na5–P6 2.998(4), Na6–P2' 2.935(4), Na6–P4 3.013(4), Na6–P6 2.927(4), Na6–P5 2.982(4), P1–P2 2.160(3), P3–P4 2.148(3), P5–P5' 2.170(5), P6–P6' 2.152(5), Na1...C25 2.750(9), Na3...C31' 2.804(8), C1–P1–P2–C7 71.5(4), C13–P3–P4–C19 74.2(4), C25–P5–P5'–C25' –92.3(6), C31–P6–P6'–C31' –86.6(5).

In this C_2 -symmetric species, only six of the twelve sodium cations (Na2, Na4, Na5 and their symmetry equivalents) are coordinated to tmeda molecules. Na2 and Na5 reside in slightly distorted tetrahedral coordination spheres (two nitrogen, two phosphorus centers) while Na4 is pentacoordinated to three phosphorus atoms and one tmeda molecule. The other sodium cations, Na1, Na3, and Na6, are tmeda free. The Na1 and Na3 ions are coordinated to three phosphorus centers and show an additional long contact (2.750 Å and 2.804 Å, respectively) to one *ipso*-carbon of an adjacent phenyl group (see dotted lines in Fig. 2B). Na6 resides in a strongly flattened tetrahedral coordination sphere spanned by four P atoms. The Na–P distances (2.796–3.043 Å) lie within the usual range (for a listing see ref. [6]). The P–P bond distances (2.148–2.170 Å) in the $[\text{Ph}_2\text{P}_2]^{2-}$ dianions which all have a *gauche* conformation (IC-P-P-CI 71.5–92.3°) are remarkably short compared to the previously reported values (>2.2 Å).^[5a,6] The aggregate **5** is the first we observe that is not composed from $\{(\text{Na}^+)_2(\text{P}_x\text{Ph}_x)^{2-}\}$ ion triples. In such an ion triple, the Na^+ cations bridge the negatively charged phosphorus atoms in form of a (flat or modestly folded) parallelogram which is an especially stable arrangement for electrostatic reasons (see discussion in ref.[6]). In **5**, only the sodium cation Na4 resides in such a bridging position over one $[\text{P}_2\text{Ph}_2]^{2-}$ dianion, all other sodium cations take bridging positions between different $[\text{P}_2\text{Ph}_2]^{2-}$ dianions. We assume that the increased steric bulk of the tmeda as co-ligand^[9] is responsible for the formation of a larger cluster than with dme. The steric encumbrance lowers the coordination enthalpies of the sodium cations which in turn search additional (longer) contacts to phosphorus or carbon centers whereby the aggregation state increases. It is likely that larger aggregates are generally observed with the heavier alkali cations ($\text{M}^+ = \text{Na}^+ - \text{Cs}^+$) and diphosphandiides as counter-dianions. In the corresponding lithium compounds, the Li^+ , P^- distances are short (≈ 2.6 Å) which gives rise to a sufficiently high electrostatic stabilization energy (ESP) even in a simple archetypical ion triple as $[\text{Li}_2(\text{P}_2\text{Ph}_2)(\text{tmeda})_2]$.^[6]

In aggregates with $\text{M} = \text{Na} - \text{Cs}$, the longer M^+ , P^- contacts do not sufficiently stabilize a small aggregate which is relatively more destabilized especially by the repulsive P^-, P^- interaction. Note that the number of attractive M^+ , P^- contacts per additional incorporation of a $\text{M}_2(\text{P}_2\text{Ph}_2)$ unit increases more rapidly than the repulsive M^+, M^+ , and P^-, P^- interactions (the exact ratio depends on the structural details^[6]).

When **5** is reacted with MesCOCl (**6**), a 50% yield of the BAP compound **7** is obtained and not the expected bis(acyl)diphosphane, $(\text{MesCO})\text{PhP}-\text{PPh}(\text{COMes})$.



Scheme 3. Reactions of **5** with 2,4,6-trimethylbenzoylchloride (MesCOCl) **6** and Me_3SiCl and synthesis of BAP **7**

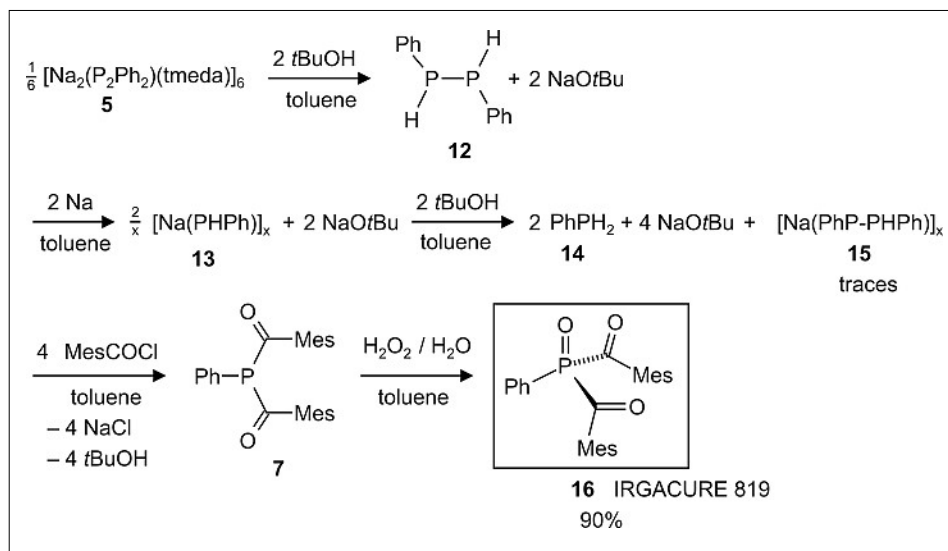
Obviously, the monoacylated product, $[(\text{MesCO})\text{PhP}-\text{PPh}]^-$ undergoes a fast fragmentation into the phosphoenolate $[\text{PhP}=\text{CO}(\text{Mes})]^-$ which is immediately intercepted by a second equivalent of the acid chloride **6**. The other product of this fragmentation, phenylphosphinidene PhP, immediately oligomerizes to $(\text{PhP})_5$ which is the other observed species (Scheme 3).

On the other hand, trimethylsilylchloride as electrophile reacts cleanly with **5** to yield the expected 1,2-diphenyl-1,2-disilyl-diphosphane **8** (^{31}P NMR: $\delta = -108$ ppm^[10]). The P–P bond in **8** is easily reductively cleaved by sodium in toluene and gives the soluble monosilylated phenylphosphanide sodium salt **9** (aggregation state x unknown) (^{31}P NMR: $\delta = -156$ ppm^[11]). Without isolation, **9** was further reacted with MesCOCl to give the desired bis(acyl)phosphane **7** as the main product. Further by-products are the phosphoenols **10** and **11**, which were obtained as *E*- and *Z*- isomers and identified by their typical ^{31}P NMR chemical shifts (*E*-**10**: $\delta = 196.0$ ppm, *Z*-**10**: $\delta = 189$ ppm; *E*-**11**: $\delta = 149$ ppm, *Z*-**11**: $\delta = 134$ ppm^[12]). The O-acyl phosphoenols *E/Z*-**10** undergo a remarkable 1,2-acyl shift reaction to BAP **7** upon warming in toluene, however, the O-silyl enolates *E/Z*-**11** cannot be further converted to **7** even at elevated temperature and excess of MesCOCl. Because the content of *E/Z*-**11** amounts to about 15–20% of the product and furthermore Me_3SiCl is needed, this process for the preparation of **7** was abandoned.

Brandtsma *et al.* published a series of papers describing the synthesis of alkali metal phosphides, $[\text{M}(\text{PH}_2)]$, from elemental phosphorus or PCl_3 and lithium or sodium metal

in liquid ammonia in the presence of *tert*-butanol as proton source.^[13] We wondered whether the addition of *tert*-butanol under our reaction conditions would likewise allow the *in situ* preparation of phenylphosphane **14**. To test this hypothesis, we reacted the disodium diphosphanediide **5** with two equiv. of *tert*-butanol which cleanly led to the diphosphane **12** (^{31}P NMR: $\delta = -68$ and -72 ppm for the *meso*- and *rac*-form, respectively^[14]) (Scheme 4). At $T = 100$ °C, **12** reacts quantitatively with sodium metal to give sodium(phenylphosphide) **13** (^{31}P NMR: $\delta = -121$ ppm^[15]), which is protonated by another two equiv. of *tert*-butanol to give phenylphosphane in almost quantitative yield (^{31}P NMR: $\delta = -123$ ppm, triplet, $^1J_{\text{PH}} = 197.4$ Hz)^[16]. Only traces (<3%) of the monosodium salt $[\text{Na}(\text{P}_2\text{Ph}_2\text{H})(\text{solv})]_x$ **15** are observed.^[17]

When MesCOCl is added slowly to this reaction mixture and the temperature is kept below 70 °C an almost quantitative yield of BAP **7** is obtained. Note that the reaction mixture contains exactly the amount of NaOtBu needed as base to promote the reaction between PhPH₂, **14** and the sterically congested MesCOCl **6**. Weaker bases like NEt_3 are ineffective. Because the reaction of *t*-BuOH with sodium is slower than the reductive cleavage of the P–P bond in **12** even at elevated temperatures, the synthesis of BAP **7** can be performed as a one-pot procedure: PhPCl_2 is reacted with four equiv. of sodium in a toluene/tmeda mixture (100/4 by volume) at $T = 120$ °C until **5** precipitates as bright yellow powder. Subsequently, two equivalents *t*-BuOH are added, the reaction kept at 120 °C until the remaining sodium completely dissolved, and addition



Scheme 4. Efficient synthesis of phenylphosphane **14** and the bis(acyl)phosphane oxide IRGACURE 819 (**16**)

of MesCOCl discloses the synthesis (>90% yield of **7**). Subsequently, the added tmeda is neutralized with a stoichiometric amount of conc. H₂SO₄ acid before 30% aqueous H₂O₂ is added (3 equiv.) at 40–50 °C to oxygenate BAP **7** to the final product IRGACURE 819 (**16**). Under optimized conditions, overall yields as high as 90% can be obtained.

3. Structure Determination of IRGACURE 819 (**16**)

To our knowledge, no X-ray diffraction study has been performed to elucidate the structure of a bis(acyl)phosphane or bis(acyl)phosphane oxide derivative. The structures of several mono(acyl) substituted phosphorus compounds are known.^[17] We have performed an X-ray diffraction study with a crystal of **16** grown from a saturated toluene solution. A plot of the structure is given in Fig. 3, selected bond lengths and angles are given in the Fig. legend.

Of interest are the phosphorus acyl carbon bond lengths, P1–C7 and P1–C17, which are broken in the photolytic process.^[1a–h]

These bonds in **16** are indeed remarkably long (1.895(3)/1.896(3) Å) especially when compared to the distance between P1 and the *ipso*-carbon atom C1 of the phenyl group, which is likewise sp² hybridized: the P1–C1 bond (1.797(3) Å) is about 0.1 Å shorter and in the expected range. In other monoacylphosphane oxides the corresponding P–C_{acyl} bonds (1.808–1.872 Å^[17]) are also elongated but slightly shorter than in **16**. The CO–PO–CO chromophore in **16** has a *syn,anti*-conformation, *i.e.* the C7=O₂ group points to the same side as the P1=O₁ bond (torsion angle 63.9°) while the C17=O₃ group points to the opposite side (torsion angle –174.4°). It remains to be seen, in how far these ground state properties, *i.e.*

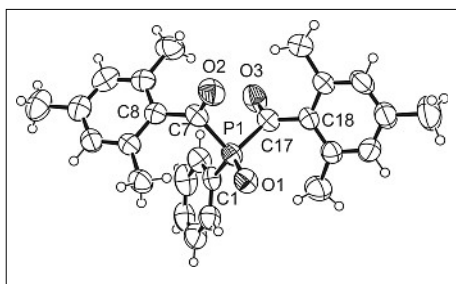


Fig. 3. Structure of PhPO(COMes)₂ (**16**). Selected bond lengths [Å] and angles [°]: P1–O1 1.475(2), P1–C1 1.797(3), P1–C7 1.895(3), P1–C17 1.896(3), C7–O2 1.210(3), C17–O3 1.226(3), C7–C8 1.491(4), C17–C18 1.487(4), O1–P1–C1 114.7(2), O1–P1–C7 111.9(1), O1–P1–C17 116.3(1), C1–P1–C7 110.1(1), C1–P1–C17 105.9(1), C7–P1–C17 96.3(1), O2–C7–P1–O1 63.9(1), O3–C17–P1–O1 –174.4(1).

the lengthening of the P–C_{acyl} bonds and the special arrangement of the CO–PO–CO chromophore, relate to the efficiency by which the reactive excited triplet state is populated and decays in an α -cleavage reaction.

4. Conclusion

In summary, a straightforward one-pot synthesis of bis(2,4,6-trimethylbenzoyl) phenyl phosphane oxide **16**, the commercial photoinitiator IRGACURE[®] 819TM, could be developed. The new protocol avoids the use of ethereal solvents and employs sodium as metal of lower ecotoxicity compared to lithium. Furthermore, the yield could be improved significantly. The detailed knowledge of the molecular components like the hexameric ion aggregate $[\text{Na}_2(\text{P}_2\text{Ph}_2)(\text{tmeda})]_6$ (**5**) which are encountered along the complex reaction path when PhPCl₂ reacts with sodium in consecutive reductive bond

forming and cleavage reactions, served as basis for the successful development of a new more environmentally friendly IRGACURE synthesis. We are currently extending the synthetic method reported here to the preparation of a broader range of BAPO type photoinitiators.

5. Experimental Part

5.1. General Techniques

All syntheses were performed in flame-dried glassware under an atmosphere of argon using standard Schlenk techniques. Toluene or xylene was freshly distilled from sodium/tetraglyme/benzophenone and tmeda was dried over calcium hydride prior to use. Air-sensitive compounds were stored and weighed in an argon filled glove box (Braun MB 150 B-G system) and reactions on small scale were performed directly in the glove box.

NMR spectra were recorded on Bruker Avance 700, 500, 400, 300, 250, 200 spectrometers. The chemical shifts (δ) are measured according to IUPAC^[18] and expressed in ppm relative to TMS, or H₃PO₄ for ¹H, ¹³C and ³¹P, respectively. Coupling constants *J* are given in Hertz [Hz] as absolute values, unless specifically stated. Where a first order analysis is appropriate, the multiplicity of the signals is indicated as s, d, or m for singlets, doublets, or multiplets, respectively. Aromatic carbons are indicated as C_{ar} when not noted otherwise.

5.2. Synthesis of Bis(2,4,6-trimethylbenzoyl)phenylphosphane Oxide (**16**)

Toluene (100 ml) and tmeda (4.0 ml, 26.68 mmol) are mixed and deoxygenated. Na (2.06 g, 89.52 mmol) is added and the mixture is heated for 30 min. at T = 120 °C. Subsequently, PhPCl₂ (4.01 g, 22.41 mmol) is added in one portion. The mixture turns pale yellow and a colorless precipitate starts to form. The mixture is heated (3–5 h) until a bright-yellow substance precipitates and the supernatant solution is colorless. To this suspension, *t*-BuOH (3.32 g, 44.85 mmol, 2 equiv.) is added drop-wise over a period of 30 min at T = 100 °C. The yellow precipitate dissolves and the solution turns orange. After about 20 min heating at 120 °C, all sodium metal is consumed. A ³¹P NMR spectrum indicates the presence of >95% PhPH₂ (**14**) as phosphorus-containing species which is reacted with 2,4,6-trimethylbenzoylchloride **6** (8.19 g, 44.8 mmol) such that the temperature is kept below 70 °C. Subsequently, conc. H₂SO₄ (1.48 ml, 26.68 mmol) is slowly added at room temperature in order to neutralize tmeda. In the final step of the synthesis, 30% aqueous hydrogen peroxide (6.9 ml, 67.5 mmol, 3 equiv) is added whereby the temperature is kept at 45–55 °C. For work up of the reaction mixture, H₂O (10 ml) is added,

the organic phase is separated and washed twice with a 10% sodium hydrogencarbonate solution (10 ml) and subsequently twice with H₂O (10 ml). The organic phase is dried over anhydrous sodium sulfate and all volatile materials are evaporated under vacuum. The initially formed thick yellow oil starts to solidify to give a brightly yellow substance which is washed with hexanes and subsequently dried under vacuum to give crude **16** (7.9–8.4 g, 85–90% yield, >95% pure by ¹H-NMR). An analytical pure sample (5.88 g = 62.7% yield) can be obtained by recrystallization from a concentrated THF solution. ¹H-NMR (CDCl₃): δ = 7.88 (m, 2 H, Ph H(2,6)), 7.53 (m, 1 H, Ph H(4)), 7.43 (m, 2 H, Ph H(3,5)), 6.79 (s, 4 H, Mes H_{ar}), 2.25 (s, 6 H, *p*-CH₃), 2.15 (s, 12 H, *o*-CH₃). ¹³C-NMR (CDCl₃): δ = 216.5 (d, ¹J_{CP} = 59.5 Hz, CO), 141.4 (d, ⁵J_{CP} = 0.8 Hz, Mes C4), 136.0 (d, ²J_{CP} = 41.9 Hz, Mes C1), 133.2 (d, ⁴J_{CP} = 3.0 Hz, Ph C4), 132.5 (d, ²J_{CP} = 8.1 Hz, Ph C2,6), 129.3 (d, ⁴J_{CP} = 0.9 Hz, Mes C3,5), 128.8 (d, ³J_{CP} = 11.2 Hz, Ph C3,5), 126.2 (d, ¹J_{CP} = 75.7 Hz, Ph C1), 20.0 (s, *o*-CH₃), 21.6 (s, *p*-CH₃). ³¹P-NMR (CDCl₃): δ = 8.1.

5.3. Crystal Structure Determinations:

Single crystals of **5** were obtained as yellow cuboids by slow cooling of a filtered, saturated (50 °C) solution of Na₂(P₂Ph₂)^[4] in neat tmeda from 50 °C to room temperature. M_r = 2270.28 g cm⁻³; crystal size 0.31 × 0.28 × 0.26 mm; orthorhombic, space group Pbcn; a = 24.37(2), b = 25.18(2), c = 21.91(2) Å; V = 13442(19) Å³; Z = 4; T = 293 K; 2θ_{max} = 36.83°, 4953 independent reflections, 649 parameters, R₁ = 0.0494 for 2849 reflections with I > 2σ(I), wR₂ = 0.1292 for all data, GOF = 0.999. Crystals of **16** were obtained by slow evaporation of a hexane solution. M_r = 418.17; crystal size 0.79 × 0.75 × 0.38 mm; monoclinic, space group P2₁/c; a = 18.2045(3), b = 15.0554(2), c = 8.6688(1) Å, α = 90.000(0), β = 103.156(4), γ = 90.000(0); V = 2313.55 Å³; Z = 2; T = 273 K; 2θ max = 46.51°; 11510 independent reflections, R₁ = 0.0446 for 2321 reflections with I > 2σ(I) and wR₂ = 0.1242, 277 parameters. Both crystals were measured on a 'Bruker APEX' diffractometer with CCD area detector using MoK_α radiation (0.71073 Å). The refinement against F² (full matrix - least squares) was performed with SHELXTL (ver. 6.12) and SHELXL-97. Empirical absorption correction was done with SADABS (ver. 2.03). All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. CCDC-666662 (**16**) and CCDC-667787 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from www.ccdc.

cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Acknowledgements

This work is the result of a fruitful collaboration between the ETH Zürich and the Ciba Specialty Chemicals Inc which funded this research.

Received: November 29, 2007

- [1] For investigations of the photophysical properties of acylphosphaneoxides see: a) T. N. Makarov, A. N. Savitsky, K. Möbius, D. Beckert, H. Paul, *J. Phys. Chem. A* **2005**, *109*, 2254; b) M. Weber, N. J. Turro, *J. Phys. Chem. A* **2003**, *107*, 3326; c) I. Gatlik, P. Rzadek, G. Gescheidt, G. Rist, B. Hellrung, J. Wirz, K. Dietliker, G. Hug, M. Kunz, J.-P. Wolf, *J. Am. Chem. Soc.* **1999**, *121*, 8332; d) S. Jockusch, N. J. Turro, *J. Am. Chem. Soc.* **1998**, *120*, 11773; e) S. Jockusch, I. V. Koptuyug, P. F. McGarry, G. W. Sluggett, N. J. Turro, D. M. Watkins, *J. Am. Chem. Soc.* **1997**, *119*, 11495; f) U. Kolczak, G. Rist, K. Dietliker, J. Wirz, *J. Am. Chem. Soc.* **1996**, *118*, 6477; g) G. W. Sluggett, C. Turro, M. G. George, I. V. Koptuyug, N. J. Turro, *J. Am. Chem. Soc.* **1995**, *117*, 5148; h) M. Kamachi, K. Kuwata, T. Sumiyoshi, W. Schnabel, *J. Chem. Soc., Perkin Trans. 2* **1988**, 961. For reviews see: i) K. Dietliker, 'A Compilation of Photoinitiators, Commercially available for UV today', SITA Series In Surface Coatings Technologies, Edinburgh, London UK, **2002**, pp. 63; j) W. Rutsch, K. Dietliker, D. Leppard, M. Koehler, L. Misev, U. Kolczak, G. Rist, *Prog. Org. Coat.* **1996**, *27*, 227 and references therein.
- [2] D. G. Leppard, M. Koehler, G. Hug, PCT Int. Appl. **1996**, WO 9607662 A1 19960314 CAN 125:11716 AN 1996:346073.
- [3] M. Scherer, D. Stein, F. Breher, J. Geier, H. Schönberg, H. Grützmaier, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2770.
- [4] J. Geier, H. Rügger, M. Wörle, H. Grützmaier, *Angew. Chem.* **2003**, *115*, 4081, *Angew. Chem., Int. Ed.* **2003**, *42*, 3951.
- [5] a) J. Geier, J. Harmer, H. Grützmaier, *Angew. Chem.* **2004**, *116*, 4185; *Angew. Chem., Int. Ed.* **2004**, *4*, 4093; b) R. Wolf, A. Schisler, P. Lönnecke, C. Jones, E. Hey-Hawkins, *Eur. J. Inorg. Chem.* **2004**, *16*, 3277; c) For some structures of potassium salts, [K₂(P₄Ph₄)(solvent)_x] see: R. Wolf, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **2006**, *632*, 727; d) D. Stein, J. Geier, H. Schönberg, H. Grützmaier, *CHIMIA* **2005**, *59*, 119.
- [6] D. Stein, A. Dransfeld, M. Flock, H. Rügger, H. Grützmaier, *Eur. J. Inorg. Chem.* **2006**, 4157. This reference cites also a number of earlier articles describing the reaction of PhPCl₂ with reducing metals.
- [7] For a computational analysis of M₂(P₄R₄) species see: M. Kaupp, A. Patrakov, R. Reviakine, O. L. Malkina, *Chem. Eur. J.* **2005**, *11*, 2773.
- [8] For the structure of the parent dianion [P₃H₃]²⁻ see: N. Korber, J. Aschenbrenner, *J. Chem. Soc., Dalton Trans.* **2001**, 1165.
- [9] D. B. Collum, *Acc. Chem. Res.* **1992**, *25*, 448.
- [10] H. Schumann, R. Fischer, *J. Organomet. Chem.* **1975**, *88*, C13.
- [11] U. Englich, K. Hassler, K. Ruhlandt-Senge, F. Uhlig, *Inorg. Chem.* **1998**, *37*, 3532.
- [12] V. A. Wright, D. P. Derek, *Angew. Chem., Int. Ed.* **2002**, *41*, 2389.
- [13] a) L. Brandsma, N. Gusarova, S. Arbuzaova, B. Trofimov, *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *111*, 807; b) L. Brandsma, N. K. Gusarova, A. V. Gusarov, H. D. Verkruisje, B. A. Trofimov, *Synth. Commun.* **1994**, *24*, 3219; c) L. Brandsma, J. A. Vandoorn, R. J. Delang, N. K. Gusarova, B. A. Trofimov, *Mendeleev Commun.* **1995**, *14*; d) M. C. J. M. Van Hooijdonk, Dissertation thesis, Universit at Utrecht, **1999**.
- [14] J.-P. Albrand, J.-B. Robert, *J. Chem. Soc., Chem. Commun.* **1976**, *21*, 876.
- [15] R. Batchelor, T. Birchall, *J. Am. Chem. Soc.* **1982**, *104*, 674.
- [16] J. W. Akitt, R. H. Cragg, N. N. Greenwood, *Chem. Commun.* **1966**, *5*, 135. These authors give a slightly smaller PH coupling, ¹J_{PH} = 194 Hz.
- [17] K. P. Langhans, O. Stelzer, *Chem. Ber.* **1987**, *120*, 1707.
- [18] a) J.-M. Huang, R.-Y. Chen, H. Chen, H.-G. Wang, *Jiegou Huaxue (Chin.)(Chin. J. Struct. Chem.)* **2001**, *20*, 349; b) W. Honggen, W. Ruji, Y. Xinkan, C. Leifeng, C. Ruyun, *Jiegou Huaxue (Chin.)(Chin. J. Struct. Chem.)* **1987**, *6*, 139; c) C. Leifeng, C. Ruyun, W. Honggen, W. Ruji, *Jiegou Huaxue (Chin.)(Chin. J. Struct. Chem.)* **1988**, *7*, 70; d) H. Nakazawa, H. Nosaka, Y. Kushi, H. Yoneda, *J. Organomet.* **1990**, *9*, 1958; e) J. Huang, H. Chen, R. Chen, *J. Chem. Cryst.* **2001**, *31*, 445; f) J. Huang, H. Chen, R. Chen, *Heteroatom. Chem.* **2002**, *13*, 63; g) J. M. Huang, R. Y. Chen, *Chin. Chem. Lett.* **2001**, *12*, 1071; h) K. A. Lyssenko, I. L. Odinets, P. V. Kazakov, M. P. Pasechnik, M. Y. Antipin, *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.)(Russ. Chem. Bull.)* **2005**, 553; i) R. R. Naqvi, P. J. Wheatley, E. Foresti Serantoni, *J. Chem. Soc. A* **1971**, 2751; j) I. Forristal, J. Lowman, K. Afarinkia, J. W. Steed, *Cryst. Eng. Comm.* **2001**, *3*, 53; k) D. V. Griffiths, J. E. Harris, J. R. Miller, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1997**, *53*, 1462; l) P. G. Jones, O. Kennard, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *34*, 2309; m) C. Ru-Yu, L. Hui-Ying, W. Hong-Gen, W. Ru-Ji, *Jiegou Huaxue (Chin.)(Chin. J. Struct. Chem.)* **1996**, *15*, 273; n) S. Cohen, Y. Katz, R. Reich, E. Breuer, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *61*, 3008; o) C. Meier, W. H. G. Laux, J. W. Bats, *Lieb. Ann.* **1995**, 1963; p) P. G. Jones, H. Thonnessen, private communication, **2006**.
- [19] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* **2001**, *73*, 1795.