

First synthesis of chloroformylphosphane complexes^{*,**}

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Abstract: An approach to novel *P*-functional chloroformylphosphane complexes is described using the synthetic potential of lithium/halogeno phosphinidenoid tungsten(0) complexes. Similarly to transition-metal-free chloroformylphosphanes, the obtained complexes tend to eliminate CO via P–C bond cleavage to give the corresponding *P*-chlorophosphane complex derivatives. Nevertheless, this method allowed the isolation of the first complex derivatives, which will open new synthetic perspectives in organophosphorus chemistry.

Keywords: acyl phosphanes; P–C bond cleavage; phosgenation; transition-metal complexes; tungsten.

INTRODUCTION

Phosgenation reactions play an important role in industry as they are employed in the production of isocyanates, ureas, carbamates, organic carbonates, and more [1]. In organophosphorus chemistry, phosgenation has been known since 1879 [2], but it is limited (mainly) to the chlorination of phosphane derivatives due to the instability of the P–C bond of chloroformyl derivatives and their tendency to liberate carbon monoxide [3]. Although other organoacylphosphane derivatives do not tend to eliminate carbon monoxide, their weak P–C bonds are susceptible to cleavage, which can be synthetically useful, i.e., organoacylphosphane oxides possessing relatively stable P–C bond can be cleaved homolytically under photochemical conditions to give corresponding radicals; this protocol is practically used for photoinitiators [4]. The knowledge about P^{III}-functional chloroformylphosphanes is extremely scarce, e.g., *P*-silylated derivatives are known as intermediates in the preparation of phosphaketenes [5], and only two derivatives having a triphenylmethyl group bound to phosphorus [6] have been described as relatively stable compounds. We became attracted to this intriguing class of phosphorus compounds having a weak P–C bond [7], and are thus trying to evaluate the influence of transition-metal complex formation on stability of the species. Here, we describe the first syntheses of *P*-functional chloroformylphosphane complexes based on reactions of lithium/halogen phosphinidenoid tungsten(0) complexes with phosgene.

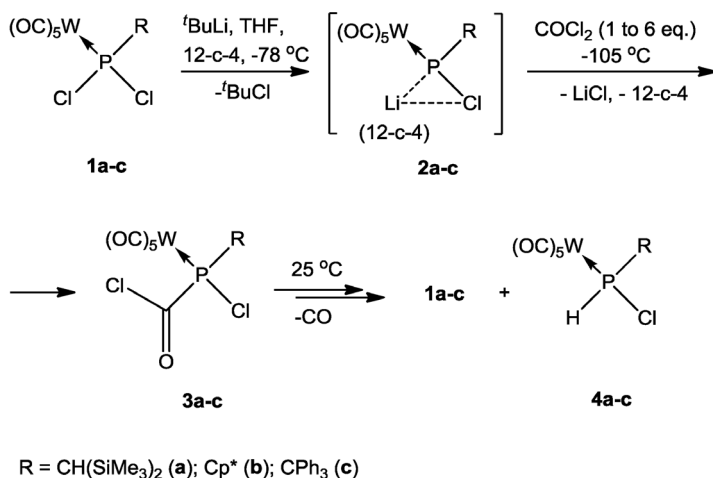
RESULTS AND DISCUSSION

Dichlorophosphane complexes **1a–c** [8–10] were lithiated with ^tBuLi in tetrahydrofuran (THF) at –78 °C in the presence of 12-crown-4 to give corresponding Li/Cl phosphinidenoid complexes **2a–c**,

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Scheme 1 Reactions of Li/Cl phosphinidenoid complexes **2a–c** with phosgene.

which were reacted in situ with phosgene at -105°C to give *P*-chloro chloroformylphosphane complexes **3a–c** and chlorophosphanes **1a–c** and **4a–c** in different ratio, depending on the reaction conditions applied (Scheme 1).

The formation and stability of chloroformylphosphane complexes **3a–c** was found to be largely dependent on the nature of the substituents at phosphorus, the amounts of phosgene solution employed, and the temperature regime. When phosphinidenoid complex **2a** [11] [$\text{X} = \text{Cl}$, $\text{R} = \text{CH}(\text{SiMe}_3)_2$] was reacted with nearly equimolar amounts of phosgene (20 % solution in toluene) in conditions similar to reported for preparation of analogous organylacylphosphane tungsten(0) complexes [12], no selective formation of the corresponding chloroformylphosphane complex **3a** was observed. Instead, rapid formation of dichlorophosphane complex **1a** [$\delta(^{31}\text{P}) = 157.6$ ppm, $^1J_{\text{P,W}} = 330.8$ Hz] and some by-products assigned to the chloroformylphosphane complex **3a** [$\delta(^{31}\text{P}) = 129.6$ ppm, $^1J_{\text{P,W}} = 296.3$ Hz], chlorophosphane complex **4a** [13] [$\delta(^{31}\text{P}) = 53.7$ ppm, $^1J_{\text{P,W}} = 268.8$ Hz, $^1J_{\text{P,H}} = 349.4$ Hz], and non-identified species was observed. Significant improvement was achieved by increasing the stoichiometry of phosgene to 3 equiv, which led to a higher content of the desired phosphane **3a** in the reaction mixture. Finally, selective formation of **3a** was possible to achieve only by adding the cooled THF solution of thermally labile complex **2a** to a toluene solution of phosgene and applying a larger excess (6 equiv) of the latter. In this case, isolation of pure chloroformylphosphane complex **3a**, a viscous oil at ambient temperature, was achieved after separation of LiCl and evaporation of volatiles.

Under optimized conditions, the outcome for the reaction of Cp*-substituted Li/Cl phosphinidenoid complex **2b** [9] (Scheme 1) was different. The reaction was not selective and gave two main products (ratio $\sim 1.4:1$) of which one was assigned to the chloroformylphosphane complex **3b** [$\delta(^{31}\text{P}) = 127.9$ ppm, $^1J_{\text{P,W}} = 297.5$ Hz] and the starting dichlorophosphane complex **1b** [$\delta(^{31}\text{P}) = 153.2$ ppm, $^1J_{\text{P,W}} = 329.3$ Hz].

Phosgenation of triphenylmethyl substituted Li/Cl phosphinidenoid complex **2c** [10] under the same conditions led instead to a selective formation of corresponding chloroformylphosphane **3c** [$\delta(^{31}\text{P}) = 148.6$ ppm, $^1J_{\text{P,W}} = 278.5$ Hz]; the compound was obtained as a light-yellow solid after crystallization from diethyl ether and fully characterized.

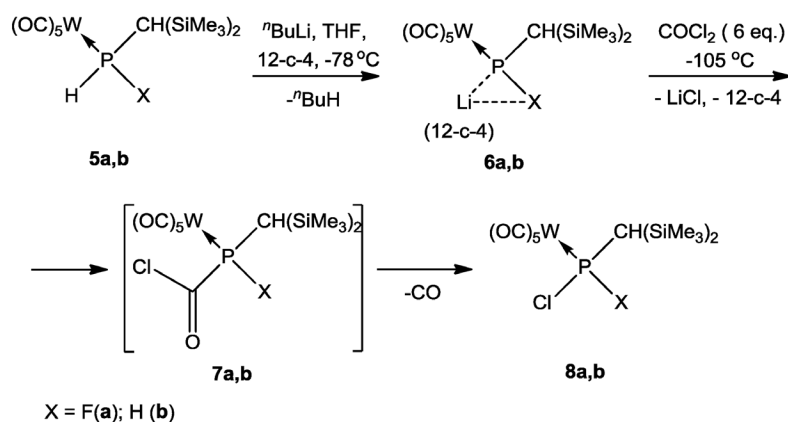
The ^{31}P NMR data of **3a** and **3c** showed chemical shifts that are upfield relative to those of the dichlorophosphanes **1a** and **1c**, respectively, and a diminished tungsten-phosphorus coupling constant which is also structurally indicative. For example, **3a** possesses a value inbetween those of the dichlorophosphane **1a** and the corresponding benzoylphosphane complex [$\delta(^{31}\text{P}) = 113.8$ ppm, $^1J_{\text{P,W}} = 267.0$ Hz] [12] in which the phenyl group is bonded to the carbonyl carbon instead of chlorine. In the

^{13}C NMR spectra signals of carbonyl carbon atoms of chloroformyl moieties for **3a** and **3c** were observed as a singlet (at $-60\text{ }^{\circ}\text{C}$) and as a doublet [$^1J(\text{C},\text{P}) = 13.6\text{ Hz}$; $25\text{ }^{\circ}\text{C}$] at 176.9 ppm , respectively. The IR absorption bands of these carbonyl groups were observed at 1772 cm^{-1} (**3a**) and 1747 cm^{-1} (**3c**).

The structure of chloroformylphosphane complex **3c** was confirmed by single-crystal X-ray diffraction studies [14], representing thus the first structurally characterized compound containing a chloroformylphosphane unit. An important structural feature of **3c** in the solid state is the presence of two elongated P–C bonds: 1.899 and 1.945 \AA for P–C(O)Cl and P–CPh₃ units, respectively. The P–C bond of the P–C(O)Cl group in **3c** is elongated as expected for such bonds in acylphosphanes [cf.12]. The P–C bond between phosphorus atom and triphenylmethyl moiety preserves elongation compared to the starting dichlorophosphane complex **1d** [10], where it is equal to 1.955 \AA .

The stability of trityl-substituted chloroformylphosphane complex **3c** in solution was found to be similar to **3a** complex bearing bis(trimethylsilyl) substituent. The stability of obtained chloroformyl derivatives is significantly increased by using a less polar media. For example, half-lifetime of **3a** at $25\text{ }^{\circ}\text{C}$ selectively obtained under optimized conditions in the reaction mixture is roughly 1 day and decreases in more polar reaction mixtures, while for the neat compound in toluene it is about 6 days; a similar tendency was observed before for noncoordinated phosphanes [cf.6]. In the solid state under inert atmosphere, complex **3c** is stable for months ($25\text{ }^{\circ}\text{C}$) and for longer periods of time at lower temperatures (e.g., $-40\text{ }^{\circ}\text{C}$).

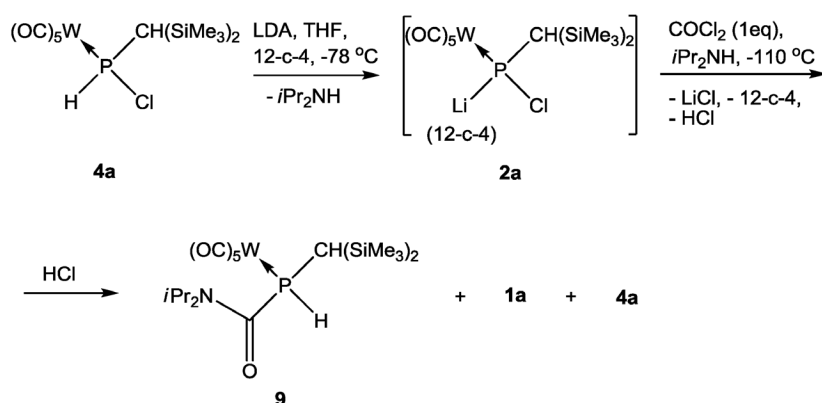
To evaluate the influence of the halogeno substituent at the phosphorus atom on stability of chloroformyl derivatives, complexes **5a,b** were phosgenated under optimized conditions (Scheme 2).



Scheme 2 Reaction of Li phosphinidenoid complexes **6a,b** with phosgene.

Compared to corresponding *P*-chloro derivative **3a**, the *P*-F or the *P*-H substitution in **7** gives rise to a significant decrease of stability of the chloroformylphosphanes. Phosgenation of **6a** [15] (X = F, Scheme 2) led to selective formation of the desired complex **7b** [$\delta(^{31}\text{P}) = 190.3\text{ ppm}$, $^1J(\text{P},\text{F}) = 915.5\text{ Hz}$, $^1J_{\text{PW}} = 310.2\text{ Hz}$]. Here, the half-lifetime in the reaction mixture at $25\text{ }^{\circ}\text{C}$ was ca. 4 h and further quantitative formation of complex **8a** [16] was observed. When in situ formed lithium phosphinide **6b** [X = H; $\delta(^{31}\text{P}) = -174.7\text{ ppm}$, $^1J_{\text{PH}} = 164.0\text{ Hz}$, $^1J_{\text{PW}} = 80.1\text{ Hz}$] was reacted with phosgene, it led to the formation of a mixture of the corresponding chlorophosphane complex **8b** and complex **5b** (ratio ~ 2:1) (Scheme 2) and the desired chloroformylphosphane complex **7b** was not observed.

Interestingly, reaction of Li/Cl phosphinidenoid complex **2a**, prepared via lithiation of the chlorophosphane complex **4a** with lithium diisopropylamide (LDA), with equimolecular amounts of phosgene led to formation of a mixture of phosphane complexes **9**, **1a**, and **4a** in ratio: 2:1:1



Scheme 3 Reactions of Li/Cl phosphinidenoid complex **2a** with phosgene in the presence of $i\text{Pr}_2\text{NH}$.

(Scheme 3). Using column chromatography at low temperature enabled the isolation of the diisopropylamidoyl-phosphane complex **9** as a white stable solid in 27 % yield.

We suppose that complex **9** is formed in the reaction of the intermediate chloroformylphosphane complex **3a** with diisopropylamine (present in the reaction mixture) and subsequent reaction of the *P*-chloro *P*-amido substituted phosphane complex in a σ -bond methathesis-type reaction to furnish **9** as the final product. Thus, the reaction itself can be considered as the first example of reactivity of *P*-chloro substituted chloroformylphosphane complex **3a**.

The molecular structure of complex **9** [14] was confirmed by single-crystal X-ray diffraction studies. The phosphorus atom in **9** as ligand has a pyramidal geometry [within the ligand the sum of bond angles at P(1) is 300.8°] with a slightly elongated P–C bond of 1.888(4) in PC(O)N unit Å. The unit C2,C5–N–C1 is planar as expected for dialkylamides.

CONCLUSION

It has been demonstrated that reactions of Li/X phosphinidenoid complexes can be used for the preparation of corresponding *P*-functional chloroformylphosphane complexes being unstable in solution. Their stability largely depends on the nature of substituents at phosphorus atom and the polarity of the reaction media. The effect of the presence of the transition-metal center on the stability of such compounds is rather small, but in some cases sufficient enough for the isolation of pure compounds. Reactivity studies on the chloroformyl derivatives **3a,c** are currently in progress.

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of purified argon using standard vacuum, Schlenk, and glove-box techniques. Solvents were dried and degassed by standard procedures.

Preparation of chloroformylphosphane complexes **3a,c**. General procedure:

To a stirred solution of phosphane complex **1a,c** (0.7 mmol) and 12-crown-4 (0.77 mmol) in 10 mL of THF at -78°C was added dropwise solution of $t\text{BuLi}$ in *n*-hexane (1.6 M, 0.49 mL). After 20 min obtained yellow solution was cooled down to -90°C and quickly transferred via cooled double-needle to cooled (-105°C) intensively stirred solution of phosgene (ca. 20 % in toluene, d 0.94, 2.21 mL). The

mixture was warmed to $-20\text{ }^{\circ}\text{C}$ in a cooling bath and the volatiles were evaporated in vacuo. The residue was cooled to $-20\text{ }^{\circ}\text{C}$ and extracted with appropriate solvent at this temperature.

3a: the product was extracted with *n*-pentane (25 mL), to give after evaporation of the solvent desired product as light-brown oil, yield: 87 %. ^1H NMR (300 MHz, toluene- d_8): δ = 0.15 (d, 9H, $^4J_{\text{H,P}}$ = 0.4 Hz, $\text{Si}(\text{CH}_3)_3$), 0.20 (d, 9H, $^4J_{\text{H,P}}$ = 0.6 Hz, $\text{Si}(\text{CH}_3)_3$), 2.11 (d, 1H, $^2J_{\text{H,P}}$ = 10.4 Hz, PCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, toluene- d_8 , $-60\text{ }^{\circ}\text{C}$): δ = 1.88 (d, $^3J_{\text{C,P}}$ = 3.2 Hz, $\text{Si}(\text{CH}_3)_3$), 2.36 (d, $^3J_{\text{C,P}}$ = 2.6 Hz, $\text{Si}(\text{CH}_3)_3$), 30.2 (d, $^1J_{\text{C,P}}$ = 24.6 Hz, PCH), 176.9 (s, $\text{C}(\text{O})\text{P}$), 195.7 (d_{sat}, $^2J_{\text{C,P}}$ = 6.5 Hz, $^1J_{\text{C,W}}$ = 123.5 Hz, *cis*-CO), 196.2 (d, $^2J_{\text{C,P}}$ = 34.9 Hz, *trans*-CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, toluene- d_8): δ = 129.6 (s_{sat}, $^1J_{\text{P,W}}$ = 296.3 Hz). IR (toluene; $\nu_{\text{max}}/\text{cm}^{-1}$): 1772 (s, CO), 1974 (s, CO), 2050 (m, CO).

3c: the product was extracted with diethyl ether (40 mL). After removing of the solvent in vacuo, solid residue was washed with diethyl ether (3 \times 3 mL) at $-20\text{ }^{\circ}\text{C}$ to give **4** as a light-yellow powder, yield: 74 %. ^1H NMR (300 MHz, C_6D_6): 6.91–7.47 (m, 15H, 3Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): 74.63 (d, $^1J_{\text{C,P}}$ = 3.6 Hz, PCPh_3), 128.65–128.94 (m, Ph), 129.63 (d, $J_{\text{C,P}}$ = 3.2 Hz, Ph), 130.80 (d, $J_{\text{C,P}}$ = 6.9 Hz, Ph), 133.33 (d, $J_{\text{C,P}}$ = 7.9 Hz, Ph), 141.17 (s, *ipso*-Ph), 141.4 (d, $^2J_{\text{C,P}}$ = 6.1 Hz, *ipso*-Ph), 141.89 (d, $^2J_{\text{C,P}}$ = 5.7 Hz, *ipso*-Ph), 176.94 (d, $^1J_{\text{C,P}}$ = 13.6 Hz, PCO), 195.06 (d_{sat}, $^2J_{\text{C,P}}$ = 5.9 Hz, $^1J_{\text{C,W}}$ = 127.4 Hz, *cis*-CO), 197.1 (d, $^2J_{\text{C,P}}$ = 37.4 Hz, *trans*-CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): 148.6 (s_{sat}, $^1J_{\text{P,W}}$ = 278.5 Hz). IR (KBr; $\nu_{\text{max}}/\text{cm}^{-1}$): 1747 (m, CO), 1942 (vs, CO), 1959 (vs, CO), 2078 (s, CO).

Preparation of diisopropylamidoylphosphane complex 9

Cooled solution ($-40\text{ }^{\circ}\text{C}$) of complex **4a** (495 mg, 0.9 mmol) and 12-crown-4 (0.16 mL, 1.0 mmol) in THF (7.2 mL) was added dropwise to a stirred solution of freshly prepared LDA (1.0 mmol) in THF (10.8 mL) at $-80\text{ }^{\circ}\text{C}$. After 30 min, the solution was cooled down to $-110\text{ }^{\circ}\text{C}$ and phosgene (20 % in toluene, 0.26 mL, 0.99 mmol) was added and reaction solution was allowed to warm up within two hours to $-20\text{ }^{\circ}\text{C}$ in a cooling bath. Volatiles were evaporated in vacuo, the residue was extracted with *n*-pentane. The solvent was removed in vacuo, and the product was subjected to column chromatography (silica gel, $-20\text{ }^{\circ}\text{C}$, petroleum ether/diethyl ether). Elution of the second yellow band (petroleum ether/diethyl ether = 10/0.5) and evaporation of the volatiles gave light-yellow oil. The product was crystallized from *n*-pentane at $-60\text{ }^{\circ}\text{C}$, to give complex **9** as a white solid. Yield: 27 %. ^1H NMR (300 MHz, CDCl_3): δ = 0.16 (d, 9H, $^4J_{\text{H,P}}$ = 0.4 Hz $\text{Si}(\text{CH}_3)_3$), 0.31 (d, 9H, $^4J_{\text{H,P}}$ = 0.4 Hz, $\text{Si}(\text{CH}_3)_3$), 0.41 (d, 1H, $^2J_{\text{H,P}}$ = 1.9 Hz, PCH), 1.29 (*pseudo-t*, 6H, $^3J_{\text{H,H}}$ = 6.8 Hz, $\text{NCH}(\text{CH}_3)_2$), 1.41 (d, 3H, $^3J_{\text{H,H}}$ = 6.8 Hz, $\text{NCH}(\text{CH}_3)_2$), 1.42 (dd, 3H, $^3J_{\text{H,H}}$ = 6.8 Hz, $^5J_{\text{H,P}}$ = 0.7 Hz, $\text{NCH}(\text{CH}_3)_2$), 3.44 (sd, 1H, $^3J_{\text{H,H}}$ = 6.8 Hz, $^4J_{\text{H,P}}$ = 4.1 Hz, $\text{NCH}(\text{CH}_3)_2$), 4.01 (sd, 1H, $^3J_{\text{H,H}}$ = 6.6 Hz, $^4J_{\text{H,P}}$ = 2.8 Hz, $\text{NCH}(\text{CH}_3)_2$), 5.82 (d, 1H, $^1J_{\text{H,P}}$ = 313.7 Hz, PH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ = 0.23 [d_{sat}, $^3J_{\text{C,P}}$ = 2.6 Hz, $^1J_{\text{C,Si}}$ = 53.0 Hz, $\text{Si}(\text{CH}_3)_3$], 3.82 [d_{sat}, $^3J_{\text{C,P}}$ = 2.6 Hz, $^1J_{\text{C,Si}}$ = 54.9 Hz, $\text{Si}(\text{CH}_3)_3$], 15.91 (d, $^1J_{\text{C,P}}$ = 14.2 Hz, PCH), 20.34 (s, CH_3), 20.47 (s, CH_3), 20.78 (s, CH_3), 21.32 (s, CH_3), 48.03 (d, $^2J_{\text{C,P}}$ = 1.3 Hz, NCH), 50.79 (d, $^2J_{\text{C,P}}$ = 7.1 Hz, NCH), 168.67 [s, $^1J_{\text{C,P}}$ = 47.8 Hz, $\text{C}(\text{O})\text{P}$], 197.2 (d_{sat}, $^2J_{\text{C,P}}$ = 6.5 Hz, $^1J_{\text{C,W}}$ = 126.1 Hz, *cis*-CO), 198.9 (d, $^2J_{\text{C,P}}$ = 22.6 Hz, *trans*-CO). ^{31}P NMR (121.5, CDCl_3): δ = -47.9 (d_{sat}, $^1J_{\text{P,W}}$ = 215.5 Hz, $^1J_{\text{P,H}}$ = 313.6 Hz). IR (KBr; $\nu_{\text{max}}/\text{cm}^{-1}$): 1631 (m), 1917 (vs), 1938 (vs), 2071 (m).

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