# Alkali-Metal Phthaloylphosphides: Easily Prepared Phosphide Reagents for Coordination and Main-Group Chemistry

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*Summary: A straightforward method for the preparation of alkali-metal phthaloylphosphide (isophosphindoline-1,3-dione(1−) ion) salts from phosphine, diethyl phthalate or its ring-substituted analogues, and an alkali-metal tert-alkoxide is described. Spectroscopic and physical characterizations are provided for three representative examples.*

## Introduction

Even though a few examples of P-substituted isophosphindoline-1,3-diones (phthaloylphosphines) have been known since the mid-1970s,[1a] relatively little chemistry has been reported for them or for other acylphosphines and acylphosphides,[1b−e] despite the enormous amount of research that has been done with other classes of phosphorus(III) compounds. One obvious area for investigation is the synthesis of coordination compounds of diacylphosphides. The few known examples of diacylphosphide coordination complexes fall into two categories: (1) O-coordinated chelate complexes of dibenzoylphosphide and dipivaloylphosphide[2] and (2) P-coordinated diacylphosphide complexes of osmium,[3a,b] ruthenium,[3c,d] and iron.[3e] P-coordinated tungsten complexes of hydridodiacylphosphines have also been prepared.[3f] In each of the latter cases, the diacylphosphide or diacylphosphine ligand was created within the metal coordination sphere by acylation of a bound dihydrogenphosphide, silylphosphide, or phosphaalkene ligand.

The work described in this Note opens a new route to diacylphosphido complexes by providing stable, easily accessible reagents for direct insertion of phthaloylphosphide[4] (or, after alkylation, phthaloylphosphine) ligands into a metal coordination sphere. This new procedure for the preparation of phthaloylphosphide ion and some of its ring-substituted analogues provides a group of compounds that has considerable potential for the development of new types of ligands for low-valent transition-metal chemistry and for discovery of new main-group chemistry. With regard to the latter area, the phthaloylphosphides might also be expected, by analogy with known properties of the structurally and electronically related dicyanophosphide,[5] to possess significant pseudohalide character. This work also provides new examples of heavy-alkali-metal phosphides, a group of compounds that is of theoretical interest with regard to the nature of interactions between the metal ion and the softer sites of the counterion.[6]

## Results and Discussion

During the course of our research on phthaloylphosphides and P-alkyl phthaloylphosphines, the need for the development of a short, convenient, general procedure for the preparation of a series of ring-substituted phthaloylphosphides became apparent. Such ring substitution can modify the solubility properties of the anions and their P-substituted derivatives and, in addition, provides a potential means for indirect "tuning" of the ligand behavior of the phosphorus atom. It is also expected that, in common with other highly electronegative groups,[7] the carbonyl groups of phthaloylphosphides and phthaloylphosphines will enhance the $\pi$-acceptor ability of the phosphorus atom. This property is subject to qualitative evaluation through examination of, for example, C−O stretching frequencies of iron carbonyl derivatives.[8] A single literature example

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(1) (a) For a review of early work in acylphosphine chemistry, including examples of phthaloylphosphine preparations, see: Becker, G.; Mundt, O. *Phosphorus Sulfur Relat. Elem.* **1983**, *14*, 267−283. (b) A single P-coordinated iron(0) tetracarbonyl complex of phenylphthaloylphosphine has been reported, along with examples of P−C cleavage and oxidation at the phosphorus atom: Barron, A. R.; Hall, S. W.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1753−1754. (c) Nickel(0) and iron(0) carbonyl complexes of 1-adamantyldipivaloylphosphine have been prepared: Goerlich, J. R.; Mueller, C.; Schmutzler, R. *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *85*, 193−205. (d) O'Brien, B. A. Ph.D. Thesis, Georgia Institute of Technology, 1980. (e) McLaughlin, M. L. Ph.D. Thesis, Georgia Institute of Technology, 1983.

(2) (a) Becker, G.; Rössler, M.; Uhl, G. *Z. Anorg. Allg. Chem.* **1982**, *495*, 73−88. (b) Becker, G.; Beck, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 741−742; *Angew. Chem.* **1980**, *92*, 756−757. (c) Becker, G.; Beck, H. P. *Z. Anorg. Allg. Chem.* **1982**, *430*, 91−109.

(3) (a) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1990**, *393*, 243−85. (b) Weber, L.; Bungardt, D. *J. Organomet. Chem.* **1986**, *311*, 269−280. (c) Weber, L.; Bungardt, D.; Reizig, K.; Boese, R. *Z. Naturforsch., B: Chem. Sci.* **1986**, *41B*, 1096−106. (d) Weber, L.; Reizig, K.; Boese, R. *Organometallics* **1985**, *4*, 1890−1891. (e) Weber, L.; Reizig, K.; Frebel, M. *Chem. Ber.* **1986**, *119*, 1857−1867. (f) Nief, F.; Mercier, F.; Mathey, F. *J. Organomet. Chem.* **1987**, *328*, 349−55.

(4) The IUPAC name is isophosphindoline-1,3-dione(1−) ion; the term "phthaloylphosphide" is, however, less cumbersome and more descriptive of the chemical nature of $C_6H_4(CO)_2P^-$ and will be used in the present discussion.

(5) (a) Schmidpeter, A.; Zwaschka, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 704−705; *Angew. Chem.* **1977**, *89*, 747−748. (b) Schmidpeter, A.; Zwaschka, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 411−412; *Angew. Chem.* **1979**, *91*, 441−442. (c) Sheldrick, W. S.; Kroner, J.; Zwaschka, F.; Schmidpeter, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 934−935; *Angew. Chem.* **1979**, *91*, 998−999. (d) Schmidpeter, A. *Inorg. Synth.* **1989**, *25*, 126−127.

(6) Smith, J. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2071−2073; *Angew. Chem.* **1998**, *37*, 2181−2183.

(7) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*; Wiley: New York, 1999; p 434.

**Scheme 1**



**Chart 1**
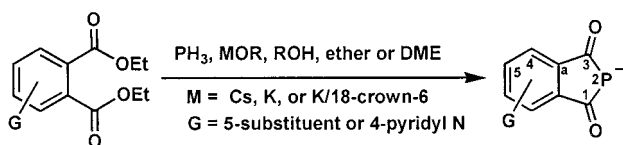


supports this contention: (1-adamantyldipivaloylphosphine)tetracarbonyliron(0) exhibits an A$_1$ stretch for coordinated CO at 2058 cm$^{-1}$.[1c] This value exceeds that observed for the analogous complex of trimethyl phosphite (2053 cm$^{-1}$),[9] a moderately strong $\pi$-acceptor, and thus it can be inferred that phthaloylphosphines will, in general, be reasonably strong $\pi$-acceptors. The magnitude of the $\pi$-acceptor ability of phthaloylphosphines and phthaloylphosphides should be subject to modification through substitution in the benzene ring of the ligand, as is the case for phosphines in which phosphorus is bonded directly to the aromatic ring.[8] Even though the phosphorus atoms in the phthaloyl compounds are two bonds removed from the $\pi$ system of the aromatic ring, the transmission of ring substituent effects to atoms in similar environments is very well-documented.[10]

The parent phthaloylphosphide ion was first prepared by reaction of potassium dihydrogenphosphide with diethyl phthalate in toluene in the presence of 1 molar equiv of 18-crown-6.[1d,11] The procedure is hazardous, cumbersome, and time-consuming, requiring the preparation (via K/PH$_3$/NH$_{3(l)}$),[12] storage, and glovebox handling of solid KPH$_2$. The procedure reported in the present Note (Scheme 1) relies on in situ generation and reaction of a synthetic equivalent of MPH$_2$[13] (M = Cs, K, K·18-crown-6) as needed, thus avoiding the hazards of handling and storage of the toxic, water-sensitive, pyrophoric alkali-metal dihydrogenphosphides. Preparations of phthaloylphosphide and its ring-substituted derivatives can be carried out with ease, and with much improved safety, through reaction of PH$_3$ with an alkali-metal *tert*-alkoxide in a mixed tertiary alcohol/ethereal solvent (with or without 18-crown-6) and a diethyl ester of a phthalic acid.[14] The syntheses are conveniently carried out on a ca. 10 mmol scale using a 15–100% molar excess of phosphine.[15]

The reaction of diethyl phthalate and ring-substituted diethyl phthalates with MOR/PH$_3$ proceeds readily, with

or without crown ether catalysis, for M = K, Cs, to produce the corresponding phthaloylphosphides. Yields are greater than 70% for the cesium phthaloylphosphides, which can be isolated from the reaction mixtures by filtration. Both *tert*-amyl alcohol/alkali-metal *tert*-amyloxide/PH$_3$ and *tert*-butyl alcohol/alkali-metal *tert*-butoxide/PH$_3$ in an ethereal solvent are effective synthetic reagents.

Spectral and analytical data are fully consistent with the proposed structures. The compounds exhibit low carbonyl stretches in their infrared spectra (1510–1530 cm$^{-1}$), with the symmetric and antisymmetric bands closely spaced. The $^{31}$P NMR resonances occur in the range $\delta$ 43–59. The $^{13}$C spectra are distinctive: one- and three-bond couplings of $^{31}$P to $^{13}$C are seen for each case, and the carbonyl absorptions are shifted strongly downfield ($\delta$ 228–231). Assignment of the aromatic ring carbon signals was facilitated by comparison of the spectra of the 5-methylphthaloyl- and 4-azaphthaloyl-phosphides (**2** and **3**): only one $^{31}$P-coupled aromatic carbon signal is seen for the 4-aza compound, whereas two are seen for the 5-methyl compound. Thus, the $^{31}$P-coupled carbons must be those that are *ortho* to the acyl groups. DEPT analysis of the two anions differentiated the tetrasubstituted carbons from those bearing a single hydrogen and, in addition, provided further support for the previous assignments.

While all of the phthaloylphosphides prepared so far are stable and relatively easy to handle, significant differences in properties relevant to their use in synthesis exist. Potassium phthaloylphosphide is deliquescent, whereas the cesium salt is less prone to water absorption. The 18-crown-6 complex of the potassium salt is less hygroscopic than the crown-free salt but easily forms a monohydrate.[11] The cesium phthaloylphosphides are recommended over the potassium compounds for use in synthesis, since their preparation is faster, isolation is simple, and use of a crown ether is not required for production of an easily handled material.

The phthaloylphosphides described here (see Chart 1), differing in ring substitution, not only illustrate the

(8) (a) Howell, J. A. S.; Lovatt, J. D.; Mcardle, P.; Cunningham, D.; Maimone, E.; Gottlieb, H. E.; Goldschmidt, Z. *Inorg. Chem. Commun.* **1998**, *1*, 118–120. (b) Howell, J. A. S.; Fey, N.; Lovatt, J. D.; Yates, P. C.; McArdle, P.; Cunningham, D.; Sadeh, E.; Gottlieb, H. E.; Goldschmidt, Z.; Hursthouse, M. B.; Light, M. E. *J. Chem. Soc., Dalton Trans.* **1999**, *17*, 3015–3028.

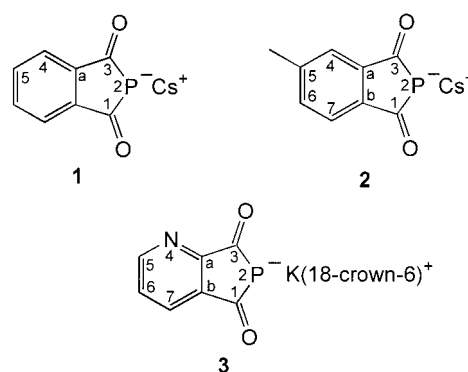(9) Albers, M. O.; Singleton, E.; Coville, N. J. *Inorg. Synth.* **1989**, *26*, 62.

(10) For example, the well-known Hammett constants, used in the study of ring substituent effects, are derived from ionization equilibria of substituted benzoic acids. For a thorough discussion, see: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987; pp 143–159.

(11) Liotta, C. L.; McLaughlin, M. L.; VanDerveer, D. G.; O'Brien, B. A. *Tetrahedron Lett.* **1984**, *25*, 1665–1668.

(12) (a) Jacobs, H.; Hassiepen, K. M. *Z. Anorg. Allg. Chem.* **1985**, *531*, 108–118. (b) Thompson, N. R. *J. Chem. Soc.* **1965**, 6288–6290. (c) Issleib, K. *Pure Appl. Chem.* **1964**, *9*, 205–223. (d) Wagner, R. J.; Burg, A. B. *J. Am. Chem. Soc.* **1953**, *75*, 3869–3871. (e) Watt, G. W.; Thompson, R. C. *J. Am. Chem. Soc.* **1948**, *70*, 2295.

(13) A synthetic equivalent of dihydrogenphosphide has been generated in situ in DMSO by reaction with KOH; in that case it is assumed that the deprotonation is facilitated through absorption, by excess KOH, of the water that is produced in the reaction: Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 124–126.

(14) This new method for generation of a synthetic equivalent of MPH$_2$ should prove to be of use in other areas of phosphorus chemistry. A reviewer suggested that, for preparation of potassium phthaloylphosphides, commercially available potassium *tert*-butoxide solution be used in preference to generation of the potassium *tert*-alkoxide by reaction of potassium metal with the alcohol.

(15) It is assumed that the actual phosphine pressure does not reach the upper limit calculated from the free volume of the reaction vessel, since phosphine has significant solubility in organic solvents: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1997; p 493.

success of the new synthetic method but also possess interesting chemical properties. All of these anionic phosphorus(III) compounds are unusually resistant to oxidation, especially in the solid state. For example, compounds **1** and **2** can be handled for reasonably long periods in dry air without significant degradation. The compounds are also significantly less basic than alkyl- or arylphosphides, as evidenced by their solubility in oxygen-free water with little protonation.[16]

## Experimental Section

The examples that follow are representative preparations. All operations were carried out in dry, deoxygenated solvents, either in a Schlenk vessel, in a vacuum line fitted with Kontes glass−Teflon stopcocks, or in a nitrogen-purged glovebox. Esters were dried over 3A molecular sieves and purged with nitrogen before use. Phosphine pressures were measured with a Matheson 63-5601 Bourdon tube gauge. NMR spectra were recorded at 300.1 MHz for ^{1}H, 121.5 MHz for ^{31}P, and 75.5 MHz for [13]C. [31]P chemical shifts were referenced against 85% $H_3PO_4$ in a sealed capillary placed in each sample; ^{13}C and ^{1}H chemical shifts were referenced against internal solvent signals. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Phosphine (*Caution!* toxic and pyrophoric) was prepared in ca. 100 mmol batches by pyrolysis of phosphorous acid,[17] passed through a −95 °C trap (toluene slush) and collected at −196 °C. The phosphine was distilled into a 304 stainless steel cylinder fitted with a Nupro SS-4JBR regulating valve. The valve was connected with Swagelok fittings via a 4 in. length of $^1/_4$ in. o.d. stainless steel tubing so as to allow cooling of the lower part of the cylinder in liquid nitrogen for condensation of the phosphine. 18-crown-6 was prepared from 2,2′-dichlorodiethyl ether, tetraethylene glycol, and KOH in THF.[18] Diethyl 4-methylphthalate and diethyl pyridine-2,3-dicarboxylate were prepared by esterification of the acids (Aldrich) in ethanol in the presence of, respectively, 10 mol % and 110 mol % of *p*-toluenesulfonic acid hydrate.

The preparations were carried out in a specially designed Schlenk flask of ca. 200 mL volume (a diagram of the reaction vessel is available as Supporting Information) capped by a Kontes vacuum stopcock attached through a 15 mm O-ring fitting. A vertical side arm, fused to the flask and isolated from the reaction flask by way of a second stopcock, had a third stopcock fused to its top for admission of phosphine. Cesium was purchased (Strem) in ampules that nominally contained 1 g of Cs; the empty ampules were weighed to find the exact mass of cesium contained.

**$Cs^+C_6H_4(CO)_2P^-$ (1).** In a nitrogen-purged glovebox, a weighed, opened ampule of cesium (1.50 g, 11.3 mmol) (*Caution!* pyrophoric) was added to the reaction vessel. The vessel was removed from the glovebox and attached to a Schlenk line. 1,2-Dimethoxyethane (DME) (30 mL) and *tert*-amyl alcohol (20 mL) were added to the flask under nitrogen flow by syringe, and stirring was begun. Stirring and periodic mild warming with a heat gun led to melting and dissolution of the cesium and formation of a clear, pale yellowish solution. The empty ampule was removed under nitrogen flow, using Nichrome wire hooks, and weighed. The calculated stoichiometric amount (based on Cs) of diethyl phthalate (2.51 g, 11.3 mmol) was added by syringe, producing a clear solution with a darker yellowish color. The flask and sidearm were then briefly

evacuated so as to remove noncondensable gases (this procedure also removed an inconsequential amount of solvent).

The stopcock connecting the side arm to the flask was closed; the side arm was then evacuated to remove nitrogen and solvent vapor, followed by cooling of the side arm to −196 °C with liquid nitrogen. Phosphine (13.0 mmol) (*Caution!* toxic and pyrophoric) was measured in the vacuum line, then condensed into the side arm. The liquid-nitrogen bath was removed from the side arm, immediately followed by opening of the connecting stopcock to the reaction mixture. The yellow color of the reaction mixture deepened quickly, and a dark maroon color developed within 30 min. A voluminous precipitate of **1** formed within 12 h.

The reaction vessel was evacuated for ca. 10 min through a slightly opened stopcock while the mixture was stirred, with the effluent gases (phosphine plus small amounts of *tert*-amyl alcohol and DME) being collected in a U-tube vacuum line trap cooled to −196 °C. This mixture was separated by trap-to-trap fractionation (−95 °C, *tert*-amyl alcohol and DME; −196 °C, phosphine). The phosphine was transferred to a cylinder as described above. The materials from the −95 °C trap were distilled out of the vacuum line into another U-tube, blanketed with nitrogen, and then treated with 5% aqueous NaOCl to destroy any remaining traces of phosphine.

The product was isolated by filtration under nitrogen on a sintered-glass frit, followed by washing with 5 mL of *tert*-amyl alcohol and three 30 mL portions of diethyl ether, followed by drying under vacuum. A dull maroon product was obtained (2.45 g, 73% yield). ^{1}H NMR showed that the sample had entrained small amounts of DME and *tert*-amyl alcohol. Recrystallization from acetonitrile at −32 °C provided analytically pure material, mp (sealed capillary under nitrogen, uncorrected) ∼160 °C dec. ^{1}H NMR (DMSO-$d_6$): δ 7.10−7.25 (m, 2H), 7.25−7.35 (m, 2H) ppm. ^{13}C NMR (DMSO-$d_6$): δ 115.5 (C4, d, $^3J_{C(4)-P}$ = 4.7 Hz), 130.2 (C5), 144.0 (Ca), 230.5 (C3=O, d, $^1J_{C(3)-P}$ = 59.5 Hz) ppm. ^{31}P NMR (DMSO-$d_6$): δ 43.4 ppm. IR (Fluorolube mull): 1512 cm$^{-1}$ (C=O max). Anal. Calcd (found): C, 32.46 (32.25); H, 1.36 (1.60).

**$Cs^+(5-CH_3)C_6H_3(CO)_2P^-$ (2).** Compound **2** was prepared by the procedure used for preparation of **1**, except that diethyl ether was used in place of DME, the *tert*-amyl alcohol rinsing step was omitted, and a larger excess of phosphine was used. Quantities of reactants were as follows: cesium, 1.58 g (11.3 mmol); diethyl 4-methylphthalate, 2.72 g (11.5 mmol); phosphine, 20.0 mmol. A maroon product was obtained (2.56 g, 71% yield). ^{1}H NMR showed that the sample had entrained a small amount of *tert*-amyl alcohol. Recrystallization in an H-tube by vapor diffusion of ether into a solution of **2** in acetonitrile provided analytically pure material, mp (sealed capillary under nitrogen, uncorrected) ∼100 °C dec. ^{1}H NMR (DMSO-$d_6$): δ 2.29 (CH₃), 6.96 (H4), 7.08 (H6, $J_{H(6)-H(7)}$ = 7.3 Hz), 7.03 (H7) ppm. ^{13}C NMR (DMSO-$d_6$): δ 21.0 (CH₃), 115.4, 116.2 (C4, C7, d, $^3J_{C(4,7)-P}$ = 3.0, 3.0 Hz), 139.7 (C5), 130.1 (C6), 141.2, 141.4 (C$_a$, C$_b$), 230.2, 230.1 (C1=O, C3=O, d, $^1J_{C(1,3)-P}$ = 59.3, 59.3 Hz) ppm. ^{31}P NMR (DMSO-$d_6$): δ 44.2 ppm. IR (Fluorolube mull): 1511 cm$^{-1}$ (C=O max). Anal. Calcd (found): C, 34.87 (35.09); H, 1.95 (2.20).

**$K(18\text{-}crown\text{-}6)^+4\text{-}C_5H_3N(CO)_2P^-$ (3).** Dry 18-crown-6 (2.64 g, 10.0 mmol) and a magnetic stirring bar were transferred to the reaction flask. The flask was held under dynamic vacuum, and the crown ether was melted with a heat gun and spread in a thin layer by rotation of the flask; after the layer solidified, evacuation was continued for ca. 12 h. *tert*-Amyl alcohol (30 mL) was transferred under nitrogen flow to the reaction flask. Stirring was begun, and after the 18-crown-6 had dissolved, small pieces of potassium (0.39 g, 10 mmol) were added under nitrogen flow. Stirring and periodic heating with a heat gun led to dissolution of the potassium and formation of a clear, pale yellowish solution. Diethyl 2,3-pyridinedicarboxylate (2.23 g, 10.0 mmol) was added, producing a clear solution with a darker yellowish color. The remainder of the procedure was

(16) The pH of a ca. 0.13 M solution of **1** in deoxygenated water is ca. 8.4. Addition of trifluoroacetic acid to such a solution causes precipitation of a pale orange-yellow solid that ^{31}P NMR indicates to be a complex mixture of products.

(17) Gokhale, S. D.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 56.

(18) Johns, G.; Ranson, C. J.; Reese, C. B. *Synthesis* **1976**, 515.

similar to that used for preparation of **1**, with 15.0 mmol of phosphine being used. A total of 1.94 g of a pinkish maroon product was obtained (1.94 g, 41% yield). Recrystallization from acetonitrile at −32 °C provided analytically pure material, mp (sealed capillary under nitrogen, uncorrected) 159−160 °C. $^1$H NMR (DMSO-$d_6$): δ 7.45 (H7, $J_{H(7)-H(6)}$ = 7.3, $J_{H(7)-H(5)}$ = 1.5 Hz), 7.21 (H6, $J_{H(5)-H(6)}$ = 4.7 Hz), 8.41 (H5) ppm. $^{13}$C NMR (DMSO-$d_6$): δ 121.9 (C7, d, $^3J_{C(7)-P}$ = 6.1 Hz), 123.4 (C6), 137.6 (C$_b$), 149.6 (C5), 160.8 (C$_a$), 226.6 (C1=O, d, $^1J_{C(1)-P}$ = 58.6 Hz), 228.2 (C3=O, d, $^1J_{C(3)-P}$ = 60.4 Hz) ppm. $^{31}$P NMR (DMSO-$d_6$): δ 58.8 ppm. IR (KBr pellet):1530 cm$^{-1}$ (C=O max). Anal. Calcd (found): C, 49.05 (48.81); H, 5.82 (5.99); N 3.00 (3.09).

**Test of Air Stability of Phthaloylphosphides.** In a qualitative test of air stability, ca. 0.12 g samples of **1** and **2** were left open to the air in aluminum weighing boats on balance pans. No significant change in mass or appearance was noted for either sample over a period of ca. 3.5 h. After ca. 36 h, the color of **2** had mostly faded to light tan, and the mass had increased, whereas **1** had experienced only a slight mass increase and the color was unchanged.

On two occasions, samples of substituted cesium phthaloylphosphides have unexpectedly and spontaneously ignited under such conditions. A reviewer suggested that these incidents might have been caused by microscopic particles of unreacted cesium, invisible to the eye. It is thus recommended that the preparations be carried out with at least a 50:1 molar ratio of alcohol to cesium in order to ensure complete consumption of metallic cesium.

**Supporting Information Available:** A detailed diagram of the reaction vessel used for preparation of the phthaloylphosphides. This material is available free of charge via the Internet at http://pubs.acs.rg.

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