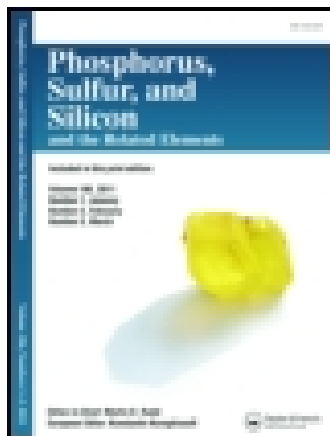


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AN IMPROVED SYNTHETIC METHOD FOR DIPHENYL-1-PYRENYLPHOSPHINE AND THE PROPERTIES AND STRUCTURE OF ITS BORANE ADDUCT

Derek T. Craft^a, Sarah M. Arcella^a, Susan M. McDowell^a, Bruce N. Storhoff^a, Abigail E. Gay^b, Michael A. Deibel^b, Paul J. Ogren^b & Phillip E. Fanwick^c

^a Ball State University, Muncie, Indiana, USA

^b Earlham College, Richmond, Indiana, USA

^c Purdue University, West Lafayette, Indiana, USA

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AN IMPROVED SYNTHETIC METHOD FOR DIPHENYL-1-PYRENYLPHOSPHINE AND THE PROPERTIES AND STRUCTURE OF ITS BORANE ADDUCT

*Derek T. Craft,^a Sarah M. Arcella,^a Susan M. McDowell,^a
Bruce N. Storhoff,^a Abigail E. Gay,^b Michael A. Deibel,^b
Paul J. Ogren,^b and Phillip E. Fanwick^c*
*Ball State University, Muncie, Indiana, USA;^a Earlham College,
Richmond, Indiana, USA;^b and Purdue University,
West Lafayette, Indiana, USA^c*

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An efficient synthetic method for diphenyl-1-pyrenylphosphine, DPPP, has been developed involving a low temperature Li-Br exchange reaction using the commercially available 1-bromopyrene. An estimate of the donor ability of this phosphine has been obtained by measuring the $A_{1\nu}(\text{CO})$ band of the $\text{Ni}(\text{CO})_3\text{L}$ complex which was found to be 0.4 wave numbers lower than that from the PPh_3 complex indicating that DPPP is a slightly better donor than PPh_3 . The BH_3 adduct of DPPP has been prepared and, as the situation for the oxide of DPPP, this adduct is fluorescent. It is estimated that the fluorescence intensity is about half that of DPPP. An x-ray structure of this adduct has been obtained, and the bond lengths and angles appear to be in expected ranges.

Keywords: Borane; diphenyl-1-pyrenylphosphine; DPPP; structure

Detection of lipid oxidation and the presence of oxidizing agents in lipids has attracted considerable recent attention in view of the direct connections with aging, diseases such as atherosclerosis and food quality.¹ One of the fluorometric reagents used to detect the presence of oxidizing agents in lipids is diphenyl-1-pyrenylphosphine, DPPP (Figure 1) which is a commercially available product.^{2–9} DPPP is not fluorescent

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Address correspondence to Bruce N. Storhoff, Department of Chemistry, Ball State University, Muncie, IN 47306-0445, USA. E-mail: bstorhoff@bsu.edu

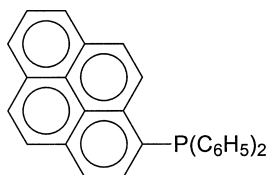


FIGURE 1 Diphenyl-1-pyrenylphosphine.

but the oxide, DPPPO, is, so it provides a method for such detection especially when used in conjunction with HPLC methods.

Recently it came to our attention that an efficient and well described synthetic method for DPPPP had yet to be published,* and that no x-ray structural data for this compound or its derivatives had been reported. As a result, we developed a synthetic method that provides the phosphine in high yield, and we prepared a BH_3 derivative that provided x-ray quality crystals. Herein we report the results from that study.

EXPERIMENTAL

Reagents and Materials

Methyl diphenylphosphinite, 1-bromopyrene, 2.5 M n-butyllithium and 1.0 M borane-tetrahydrofuran complex were purchased from Aldrich Chemical Co. $\text{Ni}(\text{CO})_4$ was purchased from Strem Chemicals, Inc. Ultra low water tetrahydrofuran, THF, was purchased from J. T. Baker. The oxide of DPPPP, DPPPO, was prepared as previously described.⁸

Methods and Instruments

Reactions and purifications were carried out under a blanket of argon. IR and NMR spectra were recorded on Perkin Elmer Spectrum 1000 and JEOL Eclipse instruments, respectively. The ^{11}B and ^{31}P NMR spectra were recorded in CDCl_3 , and they are referenced to BF_3OEt_2 and H_3PO_4 , respectively. The IR instrument was calibrated with solutions of $\text{Ni}(\text{CO})_3\text{PPh}_3$ for which the $\text{A}_1 \nu(\text{CO})$ stretching band has been reported to be 2068.9 cm^{-1} .¹⁰ Elemental analyses were carried out by Midwest Microlab Ltd., Indianapolis, IN. Fluorescence spectra were recorded on an instrument built at Earlham College. The x-ray analysis was carried out on a Nonius KappaCCD at the Purdue Chemistry Crystallography Center, Purdue University, West Lafayette, IN.

*The method described in Akasaka et al.⁹ involves reacting PPh_2^- with 1-bromopyrene providing a 13.6% yield. There is also mention of grignard-based reaction in reference 8.

DPPP

1-Bromopyrene (4.92 g, 1.75×10^{-2} mol) was dissolved in 250 ml of THF and cooled in an ethyl acetate/liquid nitrogen bath. n-Butyllithium (7.0 ml, 1.8×10^{-2} mol) was added via syringe over a period of 15 min resulting in the formation of a yellow precipitate. The mixture was stirred an additional 20 min at this temperature and then methyl diphenylphosphinite (3.5 ml, 1.8×10^{-2} mol) in 5 ml of THF was added over a period of 15 min resulting in a solution. The mixture was stirred and cooled for an additional 15 min and then the cold bath was removed. During the course of the next hour the solution turned very dark, but it slowly changed to a tan color as it neared room temperature. After reaching room temperature 1 ml of triethylamine and 5 ml of 20% aqueous ammonium chloride were added, and the bulk of the solvent was then removed with a rotary evaporator. The resulting solid was dissolved in 75 ml of dichloromethane and extracted with 2×50 ml of water. The nonaqueous phase was collected and the solvent removed providing 6.31 g (93%) of yellow product with physical and spectroscopic properties that matched those reported.⁸ $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3): $\delta - 13.2$.

DPPP·BH₃

Borane-tetrahydrofuran complex (5.2 ml 5.2×10^{-3} mol) was added dropwise to DPPP (2.00 g, 5.18×10^{-3} mol) in 20 ml of THF that was cooled in an ice bath. After the addition, the solution was warmed to room temperature and stirred for an additional 30 min. The solvent was removed and the sample dried under vacuum providing 2.07 g (100%) of yellow solid. A 1.72 g sample of this yellow solid was crystallized from ca. 2 ml each of THF and hexane providing, after cooling slowly to -10°C , 0.93 g of yellow crystals. Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{BP}$: C, 84.02%, H, 5.54%. Found: C, 84.36%, H, 5.65%. IR (KBr) 2384.6 (s), 2349.7 (sh). $^{11}\text{B}\{\text{H}\}$ NMR (CDCl_3) $\delta -35.3$ (br). m.p. = $207.5\text{--}209.0^\circ$.

Ni(CO)₃L IR Studies

The Ni(CO)₃L IR studies were carried out *in situ* in dichloromethane as previously described.^{10,11}

Single-Crystal X-Ray Diffraction Study of DPPP·BH₃

A colorless plate with approximate dimensions of $0.4 \times 0.4 \times 0.3$ mm was mounted on a glass fiber in a random orientation and cooled to

TABLE I Crystallographic Data for DPPPBH₃

Formula	C ₂₈ H ₂₂ BP
Space group	<i>P</i> 1̄ (No. 2)
Cell dimens at 150 K	
a, Å	9.2385 (10)
b, Å	10.6120 (10)
c, Å	12.4365 (13)
α, deg	66.657 (5)
β, deg	74.617 (5)
γ, deg	78.902 (5)
V, Å ³	1074.09 (19)
Z, molecules/cell	2
ρ _{calc} , g cm ⁻³	1.238
Unique data	4991
R	0.047
R _w	0.107
Goodness of fit	1.054

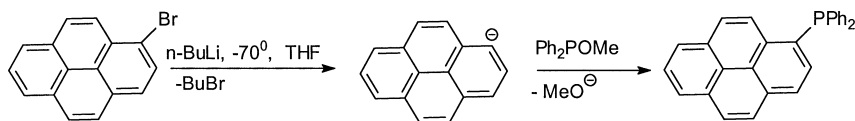
150 K. Preliminary and final data collection were performed with Mo K α radiation, $\lambda = 0.71073$ Å, on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the data. Hydrogen atoms were constrained and included in the refinement. Crystal and collection parameter data are presented in Table I. The data have been deposited with the Cambridge Crystallographic Data Center.

Fluorescence Spectra

Fluorescence spectra of DPPPO and DPPPBH₃ were obtained on solutions prepared by dissolving 3.0 mg of each compound in 10.0 ml of dichloromethane. The entrance and exit slits were set at 10 nm and 5 nm, respectively.

RESULTS AND DISCUSSION

DPPP has been obtained in excellent yield by way of the reaction sequence shown in Scheme 1. The method uses commercially available materials, and it can be carried out in a single flask in about an hour. The crude product is about 95% pure as indicated by NMR. For example, the ³¹P spectrum displays, in addition to the DPPP signal at $\delta - 13.1$, small peaks at $\delta - 15.1$, +22.0 and +33.4 which are in the ranges expected for Ph₂PBu, hydrolyzed Ph₂POMe, and oxidized DPPP. As described previously,⁹ the DPPP can be purified by chromatography,



SCHEME 1 Reaction scheme for DPPP.

and we found that toluene also could be used to recrystallize the material.

Since one of our goals was to characterize the chemical properties of the P(III) center, we elected to study the donor properties of the center by examining the $A_1 \nu(\text{CO})$ stretching frequency of $\text{Ni}(\text{CO})_3\text{DPPP}$ using well established methods that involve using $\text{Ni}(\text{CO})_3\text{PPh}_3$ as the standard.^{10,11} The values obtained for the former and latter were 2068.96 and 2069.35 cm^{-1} respectively. Given the paucity of data to which the DPPP data could be compared, we elected to prepare a small amount of $\text{PhP}(\text{pyrene})_2$ by the method reported for DPPP with $\text{PhP}(\text{OMe})_2$ in place of Ph_2POMe which yielded a compound that provided a ^{31}P signal at $\delta - 21.1$. This molecule also provided a $\nu(\text{CO})$ stretching frequency at 2068.45 cm^{-1} . These results are consistent with the conclusion that each pyrene group, compared to a phenyl ring, slightly increases the donor ability of the P(III) centers.

Despite many attempts with common solvents and solvent mixtures, x-ray quality crystals of DPPP were not, however, obtained. Given the fact that we did not find any x-ray data for DPPP, its oxide or sulfide, we elected to prepare the borane adduct, DPPPBH_3 . The adduct was obtained in excellent yield simply by mixing the phosphine with commercially available 1.0 M solution of BH_3 in THF. It proved to readily crystallize, and the structure was determined as described above. An ORTEP diagram is shown in Figure 2, and selected bond distances and angles are presented in Table II. In regard to bond lengths, the P–C lengths are in the 1.81–1.82 Å range as are six of the nine reported distances for three reported triarylphosphine-borane molecules.^{12,13} In addition all the C–C lengths are unremarkable and range from 1.377 to 1.429 Å, and the P–B length, 1.919 Å, also matches the average reported for other triarylphosphine borane adducts.^{12,13} The C–P–C angles for the aforementioned three adducts are from 104 to 108°, and those for this adduct are clearly in that range. In regard to C–P–B values, those from the three reported examples range from 109.2 to 114.1°, whereas those from the DPPP adduct are, as shown, between 109.2 and 117°. Whether the latter value is out of a normal range is uncertain given the paucity of data for related systems.¹⁴ As evident in the ORTEP diagram, the B–H bonds are “staggered” rather than “eclipsed” with

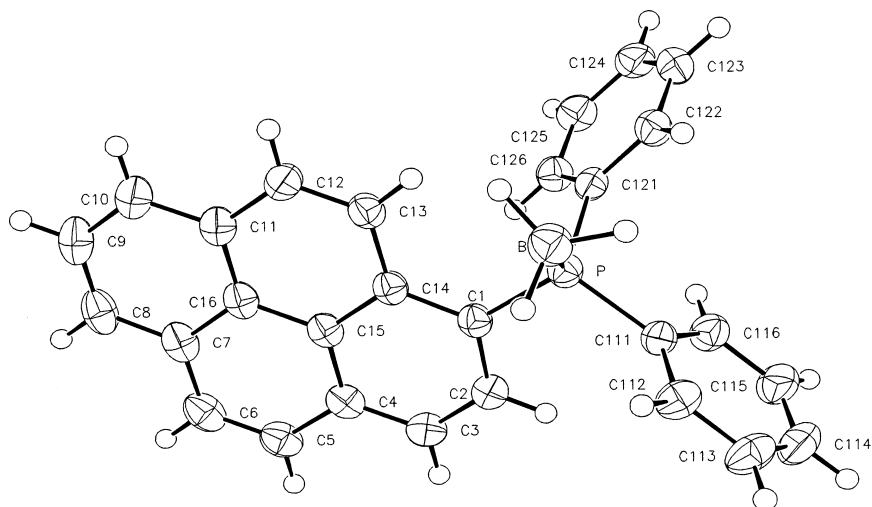


FIGURE 2 ORTEP diagram of DPPPBH₃.

the P–C bonds. The H–B–P–C torsion angles (see Table II) average 48.1 and -72.0° .

One approach to evaluating whether the pyrene group has a steric impact on the overall structure is to examine the torsion angles from the centroid of the ipso carbons through the P atom to the ipso and neighboring carbons as described by Dunitz.¹⁵ With this approach,

TABLE II Selected Bond Lengths (Å) and Angles (deg) for DPPPBH₃

Bond lengths		Bond angles	
P–C1	1.8165 (16)	C1–P–C111	105.00 (7)
P–C111	1.8122 (15)	C1–P–C121	106.31 (7)
P–C121	1.8151 (16)	C111–P–C121	104.52 (7)
P–B	1.919 (2)	C1–P–B	117.00 (9)
B–H (1B)	1.13 (2)	C111–P–B	109.15 (9)
B–H (2B)	1.116 (19)	C121–P–B	113.82 (9)
B–H (3B)	1.16 (2)	P–B–H (1B)	102.8 (10)
		P–B–H (2B)	107.9 (10)
		P–B–H (3B)	106.5 (9)
		H (1B)–B–P–C1	48.8
		H (1B)–B–P–C111	-70.2
		H (1B)–B–P–C121	44.2
		H (1B)–B–P–C1	-72.2
		H (1B)–B–P–C121	51.3
		H (1B)–B–P–C1	-73.5

larger angles correspond to a greater clockwise rotation around the P–C bond. This evaluation of DPPP BH_3 gives rise to values of 53.5° , 48.3° , and 32.2° for the C_1 , C_{121} , and C_{111} rings, respectively, arranged in this order so that the torsion angle from P through these carbons is positive. These in turn provide hexagonal coordinates (X_{H} , Y_{H} and Z_{H}) of 8.8° , 12.5° , and 44.6° which are entirely consistent with those of other reported Ph_3PX fragments.¹⁵

The fluorescence spectra of both BH_3DPPP and DPPPO were obtained on dichloromethane solutions. For both, the positions of maximum excitation and emission were 388 nm and 402 nm respectively. The former was estimated to be about half as fluorescent as the latter. How the fluorescence intensity depends on the nature of the DPPP-X bond has yet to be established, but it is plausible that it is related to the strength of that bond.

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