4222 *Organometallics* **1999,** *18,* 4222−4225

Notes

Synthesis of 1-(9-Anthracene)phosphirane and Novel Intramolecular π-Stacking of 1-(9-Anthracene)phosphirane Ligands in a *cis*-Platinum(II) Complex

Fan Yang, Philip E. Fanwick,[†] and Clifford P. Kubiak*[,‡]

Department of Chemistry, 1393 Brown Laboratories, Purdue University,
West Lafayette, Indiana 47907-1393

Received January 6, 1999

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Published on September 27, 1999 on http://pubs.acs.org | doi: 10.1021/om990008l

Summary: 1-(9-Anthracene)phosphirane was prepared in two steps starting from anthryldichlorophosphine. 1-(9-Anthracene)phosphirane is found to be quite stable, resisting attempts at thermal, free radical, cationic, or anionic polymerizations. The reaction of 1-(9-anthracene)phosphirane with $PtCl_2$(1,5-cyclooctadiene) produces cis-$PtCl_2[(\overline{PCH_2C}H_2(C_{14}H_9)]_2$, which was characterized by X-ray crystallography. The molecular structure of cis-$PtCl_2[(\overline{PCH_2C}H_2(C_{14}H_9)]_2$ reveals novel intramolecular π-stacking that produces a "tweezer-like" assembly involving the two anthracene phosphirane ligands and the platinum atom.

Introduction

The chemistry of phosphorus-containing small ring compounds has not been studied as extensively as their oxygen, nitrogen, or purely carbocyclic counterparts.[1] Since the original synthesis and earliest studies of phosphiranes by Wagner[2] and Chan,[3] several synthetic approaches to them have been developed. Because of their intrinsic instability, phosphiranes were not studied in detail until Mathey and co-workers developed methods to synthesize phosphiranes within the coordination sphere of group 6 transition metal complexes.[4−6] Uncomplexed phosphiranes, however, are usually not accessible by this method. Recently, we and Wild et al. reported a general synthetic approach to alkyl and aryl phosphiranes via addition of dilithioalkyl phosphides or dilithioaryl phosphides to 1,2-dichloroethanes.[7,8] Here, we extend the method to the synthesis of 1-(9-anthracene)phosphirane. We also report the preparation of the *cis*-bis(phosphirane)platinum complex $PtCl_2$(1-(9-anthacene)phosphirane)$_2$, which was found to display novel intramolecular π-stacking interactions between the anthracene ring systems.

Results and Discussion

Synthesis of 1-(9-Anthracene)phosphirane (3). Dichloroanthrylphosphine (**1**) was synthesized from trichlorophosphine and freshly prepared anthrylmagnesium bromide Grignard reagent. Instead of the expected singlet for **1** in the $^{31}P\{^1H\}$ NMR, three singlets were observed (δ 159.5, δ 152.6, δ 143.3). Similarly, the mass spectra of **1** give three sets of signals, which correspond to the dichloro-, chlorobromo-, and dibromoanthrylphosphines. A control reaction was performed using PBr_3 instead of PCl_3 under the same conditions as employed above. Only a singlet at 143.3 ppm appeared in the $^{31}P\{^1H\}$ NMR, corresponding to dibromoanthrylphosphine. The mass spectra give rise to one set of peaks at *m*/*e* 366, 368, 370, which is a normal distribution for a bromine-containing species. Halogen exchange is quite typical of the alkyl- and arylhalophosphines. Subsequent use of the mixture of chloro- and bromophosphines does not adversely affect their conversion together to anthrylphosphine.

The mixture of dichloroanthrylphosphine (**1**) and the bromo derivatives can be cleanly converted to anthrylphosphine (**2**) at −77 °C by lithium aluminum hydride reduction in ether. Anthrylphosphine (**2**) is an air-sensitive light yellow solid which was purified by flash chromatography under nitrogen. Changing the other substituents on the anthryl phosphines from halogens (**1**) to hydrogens (**2**) shifts the $^{31}P\{^1H\}$ NMR signal upfield by 300 ppm and results in a simple triplet, $^1J_{(P-H)} = 206.4$ Hz. Anthryl phosphine (**2**) was then treated with 2 equiv of MeLi to generate dilithium

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[†] To whom correspondence pertaining to the structural study should be addressed.

[‡] Present address: Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Dr., Dept. 0358, La Jolla, CA 92093-0358.

(1) For reviews on three-membered organophosphorus heterocycles, see: (a) Mathey, F. *Chem. Rev.* **1990**, *90*, 997. (b) Golobov, Y. G.; Gusar, N. I.; Tarasevich, A. S. *Russ. Chem. Rev.* **1983**, *52* (5), 446.

(2) Wagner, R. I.; Freeman, L. V. D.; Goldwhite, H.; Rowsell, D. G. *J. Am. Chem. Soc.* **1967**, *89*, 1102.

(3) Chan, S.; Goldwhite, H.; Keyzer, H.; Rowsell, D. G.; Tang, R. *Tetrahedron* **1969**, *91*, 17.

(4) Marinette, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667.

(5) Marinette, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

(6) Marinette, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

(7) Mézailles, N.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1997**, *16* (6), 1526.

(8) Hockless, D. C. R.; Kang, Y. B.; McDonald, M. A.; Pabel, M.; Willis, A. C.; Wild, B. S. *Organometallics* **1996**, *15*, 1301.

10.1021/om990008l CCC: $15.00 © 1999 American Chemical Society
Publication on Web 09/27/1999

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Published on September 27, 1999 on http://pubs.acs.org | doi: 10.1021/om990008l

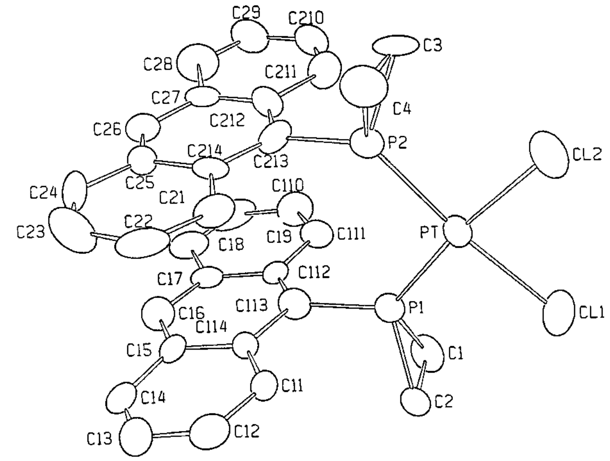
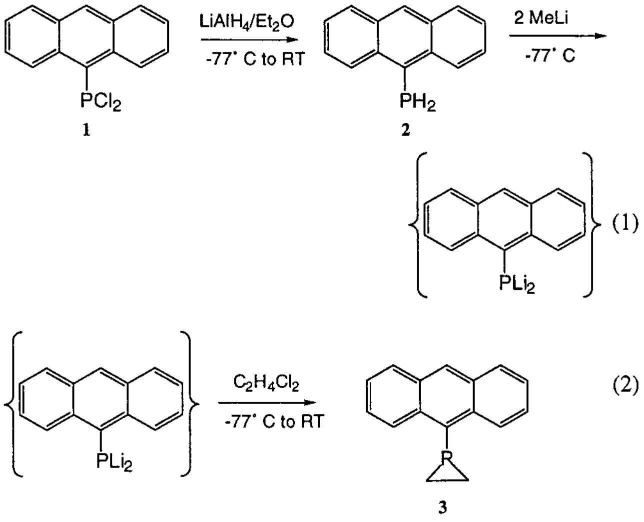


Figure 1. ORTEP drawing of *cis*-dichlorobis[1-(9-anthracene)phosphirane]platinum(II) (**4**). Hydrogen atoms are not shown.

anthrylphosphide *in situ*. This was reacted with 1,2-dichloroethane to afford the phosphirane (**3**). The synthesis of 1-(9-anthracene)phosphirane is summarized in eqs 1 and 2. 1-(9-Anthracene)phosphirane (**3**) is an air-sensitive light yellow solid but is otherwise quite stable. Attempted use of cationic, anionic, or free radical initiators or heating **3** at 110 °C for 3 days under N_2 all failed to polymerize (or decompose) this material.



Preparation and Characterization of *cis*-Dichlorobis[1-(9-anthracene)phosphirane]platinum(II) (4). To further characterize the new phosphirane **3**, it was reacted with $PtCl_2$(1,5-cyclooctadiene). The reaction of phosphirane **3** with *cis*-dichloro(1, 5-cyclooctadienyl)-platinum(II) affords *cis*-dichlorobis[1-(9-anthracene)-phosphirane]platinum(II) (**4**) in excellent yield. The platinum phosphirane complex **4** has been characterized by $^{31}P\{^1H\}$ and ^1H NMR, elemental analysis, plasma desorption mass spectrometry, and X-ray crystallography. The ORTEP drawing of **4** is shown in Figure 1, and data collection and refinement parameters are summarized in Table 1. Selected bond distances and angles are given in Table 2. Complex **4** shows the expected square planar Pt(II) coordination geometry.

Table 1. Crystal Data and Data Collection Parameters for Bis[1-(9-anthracene)phosphirane]platinum(II) (4)

formula	$PtCl_2(PC_{16}H_{13})_2$
fw	738.51
space group	$P2_1/c$ (No. 14)
a, Å	9.996(2)
b, Å	29.644(5)
c, Å	9.6911(13)
β, deg	110.078(15)
V, Å^3	2697.2(17)
Z	4
d_{calc}, g cm^{-1}	31.819
crystal dimens, mm	0.19 × 0.17 × 0.10
temperature, K	295
radiation (wavelength)	Cu Kα (1.5418 Å)
μ	130.10 cm^{-1}
h, k, l range	−11 to 10, −34 to 0, 0 to 21
no. of data collected	4643
no. of unique data	4259
R_{int}	0.047
no. of data used in refinement	4259
refined extinction coeff	0.0004
no. of variables	325
transmission coeff	0.249−0.093
$R(F_o)$, $R_w(F_o^2)$	0.050, 0.099
goodness of fit	1.073

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Bis[1-(9-anthracene)phosphirane]platinum(II) (4)[a]

Bond Distances

atom 1	atom 2	distance	atom 1	atom 2	distance
Pt	P(1)	2.235(4)	P(1)	C(113)	1.81(2)
Pt	P(2)	2.256(4)	P(2)	C(3)	1.79(2)
Pt	Cl(1)	2.332(4)	P(2)	C(4)	1.79(2)
Pt	Cl(2)	2.340(4)	P(2)	C(213)	1.82(2)
P(1)	C(1)	1.80(2)	C(1)	C(2)	1.52(2)
P(1)	C(2)	1.81(2)	C(3)	C(4)	1.50(2)

Bond Angles

atom 1−atom 2−atom 3	angle	atom 1−atom 2−atom 3	angle
P(1)−Pt−P(2)	99.62(14)	C(3)−P(2)−C(213)	106.6(8)
P(1)−Pt−Cl(1)	86.22(2)	C(4)−P(2)−C(213)	106.3(8)
P(2)−Pt−Cl(1)	174.2(2)	C(3)−P(2)−Pt	118.9(6)
P(1)−Pt−Cl(2)	172.62(2)	C(4)−P(2)−Pt	119.0(7)
P(2)−Pt−Cl(2)	87.5(2)	C(213)−P(2)−Pt	129.6(5)
Cl(1)−Pt−Cl(2)	86.7(2)	C(2)−C(1)−P(1)	65.3(8)
C(1)−P(1)−C(2)	49.8(7)	C(1)−C(2)−P(1)	64.9(8)
C(1)−P(1)−C(113)	106.7(7)	C(4)−C(3)−P(2)	65.4(9)
C(2)−P(1)−C(113)	106.2(7)	C(3)−C(4)−P(2)	64.9(9)
C(1)−P(1)−Pt	121.8(6)	C(112)−C(113)−P(1)	118.3(11)
C(2)−P(1)−Pt	120.7(6)	C(114)−C(113)−P(1)	118.0(11)
C(113)−P(1)−Pt	126.9(5)	C(212)−C(213)−P(2)	120.2(12)
C(3)−P(2)−C(4)	49.7(8)	C(214)−C(213)−P(2)	120.0(11)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The bond lengths and angles about the platinum atom are typical of a *cis*-$PtCl_2(PR_3)_2$ complex. Compared to the closely related complex *cis*-dichlorobis(3-*tert*-butyl-1-phenylphosphetane)platinum(II),[9] complex **4** exhibits a P−Pt−P angle of 99.62(14)°, wider by approximately 6°, and in compensation an approximately 4° narrower Cl−Pt−Cl angle. The Pt−P bond lengths of the bis(phosphirane) **4** are also slightly longer than those of the bis(phosphetane) complex. The coordinated phosphirane rings are notable. The C−C−P angles, 64.9(8)−65.4(9)°, together with the C−P−C angles, 49.7(8)° and 49.8(8)°, attest to the high degree of strain in the phosphirane ring. The effects of the strained ring geometry on the hybridization of the phosphorus atom

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are also evident in the $^{31}P\{^1H\}$ NMR. The $^1J(Pt-P)$ value of 4133 Hz is significantly higher than the typical range of 3500−3700 Hz for *cis*-$PtCl_2(PR_3)_2$ complexes.[10] This is ascribed to the high degree of s-character of the electron pair available for coordination to platinum.[7] The most unexpected and notable feature of the complex is that the two anthracene rings of the pair of *cis* anthracene phosphirane ligands lie parallel to each other with an inter-ring separation of 3.4 Å. This π-stacking interaction creates an extensive cleft between the anthracene rings. The 3.4 Å "tweezer-like" arrangement of the two anthracene phosphirane ligands combined with the strongly emitting character of anthracene lumophores raises a number of interesting possibilities for probing intercalated host/guest interactions. Our ongoing studies are being directed along these lines.

Experimental Section

K_2PtCl_4 was obtained on loan from Johnson-Matthey. 9-Bromoanthracene was purchased from Tokyo Chemical Inc. and purified by recrystallization from ethanol−water. Magnesium ribbon, lithium aluminum hydride, methyllithium, and 1,2-dichloroethane were purchased from Aldrich Chemical Co. Phosphorus trichloride was purchased from Strem Chemical Inc. These were used without further purification.

Anhydrous diethyl ether was purchased from Mallinckrodt. Other solvents were degassed and purified by distillation under nitrogen from the appropriate drying agents (sodium/benzophenone for THF, calcium hydride for methylene chloride). Deuterated NMR solvents were purchased from Cambridge Isotope Labs. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a QE-300 spectrometer at 300.6, 75.2, or 121.4 MHz, respectively. Chemical shifts are reported in ppm. ^1H NMR were referenced to external TMS via residual solvent peaks. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Plasma desorption mass spectra (PDMS) were obtained using a Bioion 20R plasma desorption mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrophotometer. All reactions and manipulations were carried out under a nitrogen atmosphere using a nitrogen-filled glovebox or standard Schlenk line techniques. 9-Anthrylmagnesium bromide[11] and $Pt(cod)Cl_2$ (cod = 1,5-cyclooctadiene)[12] were prepared by published literature procedures.

Dichloroanthrylphosphine (1). 9-Anthrylmagnesium bromide (20 mmol) was freshly prepared from 9-bromoanthracene by a literature procedure.[11] To a flask containing diethyl ether (20 mL) and trichlorophosphine (5.5 mL, 60.0 mmol) cooled in an ice bath was slowly added the Grignard reagent via cannula. The reaction mixture turned orange-yellow. The orange suspension was stirred at 0 °C for 2 h and then stirred at room temperature overnight to complete the reaction. Excess trichlorophosphine and diethyl ether were removed *in vacuo* to give an orange solid. Dichloroanthrylphosphine (**1**) was extracted from the residue with diethyl ether, leaving behind the insoluble magnesium salt. After removal of the ether, the yellow product dichloroanthrylphosphine (**1**) was obtained as a mixture with the dibromo and chlorobromo derivatives (4.4 g, 80%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 159.5, δ 152.6, δ 143.3. EI MS (*m*/*e*): 278, 280, 282; 322, 324, 326; 366, 368, 370.

Anthrylphosphine (2). Lithium aluminum hydride (1.0 M) in diethyl ether solution (31.5 mL, 31.5 mmol) was added to 30 mL of diethyl ether and cooled to −77 °C using a 2-propanol/dry ice bath. Dichloroanthrylphosphine (**1**) as a mixture with the dibromo and chlorobromo derivatives (4.0 g, 14.3 mmol based on **1**) in 30 mL of diethyl ether solution was then added dropwise over the course of 3 h. The reaction was stirred in the cold bath for 1 h and allowed to slowly return to room temperature (about 4 h). The reaction mixture was gently refluxed for an hour and then cooled in an ice bath. To the lemon yellow suspension was added a degassed, saturated solution of NH_4Cl-H_2O to neutralize the excess hydride. After the solution was stirred for 10 min, the organic layer was separated, dried over magnesium sulfate, and dried *in vacuo* to give a yellow powder as the crude product. This product was purified by flash chromatography (hexane) under nitrogen to yield 2.5 g (83%) of anthrylphosphine (**2**). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −157.7 (t, $^1J_{(P-H)} = 206.4$ Hz). ^1H NMR ($CDCl_3$): δ 4.21 (d, 2H, PH_2, $^1J_{(P-H)} = 206.4$ Hz), 7.35 (m, 4H), 7.81 (d, 2H), 8.22 (s, 1H), 8.35 (d, 2H). EI MS (*m*/*e*): 210. CI MS (M + H): 211.

1-(9-Anthracene)phosphirane (3). Two equivalents of methyllithium (1.4 M diethyl ether solution, 13.6 mL, 19 mmol) was introduced at −77 °C via syringe to a THF solution of anthrylphosphine (**2**) (2.0 g, 9.5 mmol).

The reaction solution turned purple after adding the first drop of MeLi, and then the color changed to dark green. The green solution was cooled in a 2-propanol/dry ice bath and stirred for 1 h. Degassed 1,2-dichloroethane (0.75 mL, 9.5 mmol) was syringed into the mixture, and the reaction was allowed to return to room temperature gradually. THF and ether were removed *in vacuo*, and the residue was quenched with H_2O. Diethyl ether was then added. The organic phase was separated, dried over $MgSO_4$, filtered, and dried *in vacuo* to give a yellow powder. The product was purified by flash chromatography (hexane) under nitrogen to yield 1.7 g (77%) of light yellow 1-(9-anthracene)phosphirane (**3**). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −246.7 (s). ^1H NMR ($CDCl_3$): δ 1.26 (m, AB, 4H), 7.51−9.0 (m, 9H, $C_{14}H_9$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.4 (d, $P(CH_2)_2$, $^1J_{(P-C)} = 50$ Hz), 126−136 (14 C, $C_{14}H_9$). EI MS (*m*/*e*): 236. CI MS (M + H): 237.

***cis*-Dichlorobis[1-(9-anthracene)phosphirane]platinum(II) (4).** 1-(9-Anthracene)phosphirane (**3**) (22 mg, 0.095 mmol) in 5 mL of methylene chloride was added to a stirred methylene chloride solution of *cis*-dichloro-(1,5-cyclooctadienyl)platinum(II) (16 mg, 0.043 mmol). A yellow precipitate started to form after 20 min. The reaction was stirred at ambient temperature overnight. Solvent was removed *in vacuo*. The remaining solid was washed with hexane and diethyl ether and dried *in vacuo* to give a yellow solid (**4**). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −180.6 (d, $^1J_{(Pt-P)} = 4133$ Hz). ^1H NMR (CD_2Cl_2): δ 1.26 (m, 2H, $P(CH_2)$), 2.20 (td, 2H, $P(CH_2)$), 7.09 (t, 4H), 7.25 (t, 4H), 7.44 (d, 4H), 7.61 (s, 2H), 8.20 (d, 4H). IR (KBr): ν(small ring C−H) 3045 (m). PDMS (*m*/*z*): 738. Anal. Calcd for $C_{32}H_{26}Cl_2P_2Pt$: C, 52.04; H, 3.55. Found: C, 52.09, H, 3.41.

Collection and Refinement of X-ray Diffraction Data for *cis*-Dichlorobis[1-(9-anthracene)phosphirane]platinum(II) (4). Crystals suitable for a single-crystal X-ray diffraction study were grown by placing a concentrated methylene chloride solution of *cis*-dichlorobis[1-(9-anthracene)-phosphirane]platinum(II) (**4**) into a small test tube. The solution was carefully layered with dry heptane, and then the tube was placed inside a freezer. A yellow plate crystal of $C_{32}H_{26}Cl_2P_2Pt$ having approximate dimensions of 0.19 × 0.17 × 0.10 mm was mounted on a glass capillary in a random orientation. Data collection was performed on an Enraf-Nonius CAD_4 computer-controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. The structure was solved using the Patterson heavy-atom method, which revealed the position of the Pt atom. The remaining

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(9) Tumas, W.; Huang, J. C.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1992**, *11*, 1944.

(10) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Complexes*; Springer-Verlag: Berlin, 1979.

(11) Bachmann, W. E.; Kloetzel, M. C. *J. Org. Chem.* **1939**, *3*, 55.

(12) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but constrained to ride on the atom to which they are bonded. The final cycle of refinement converged with $R = 0.050$ and $R_w = 0.099$. The crystallographic and metrical data are summarized in Tables 1 and 2. An ORTEP drawing of **4** is presented in Figure 1.

Acknowledgment. We thank the National Science Foundation (CHE-9615886) for support. F.Y. gratefully acknowledges the Purdue Cancer Center for support through an Indiana Elks Research Fellowship.

Supporting Information Available: A description of experimental procedures, tables of crystal data, atomic positional and thermal parameters, bond distances and angles, and torsional angles for *cis*-$PtCl_2[(PCH_2CH_2(C_{14}H_9)]_2$ (**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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