^{31}P Chemical Shifts and ^{31}P–^{13}C Coupling Effects in the Stereochemical Analysis of Benzo-7-phosphanorbornene Derivatives

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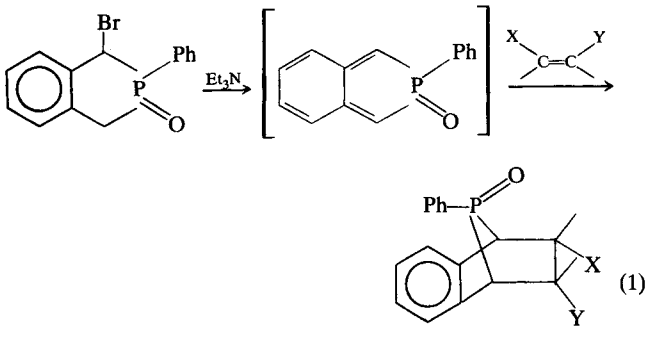
The first phosphines based on the benzo-7-phosphanorbornene system have been prepared and found to have extremely deshielded ^{31}P nuclei. The phosphine with a P-*tert*-butyl group gives the most downfield value (δ +152.5) ever recorded for a tertiary phosphine. The lone-pair orientation in phosphines controls the magnitude of ^{2}J(PC) and ^{3}J(PC), and these effects were used to determine stereochemical features of the phosphines. These compounds were formed by $HSiCl_3$–pyridine reduction of the Diels–Alder adducts of isophosphindole oxides with norbornadiene. ^{13}C NMR was also used to confirm the assignment of these phosphine oxides.

INTRODUCTION

Compounds with the benzo-7-phosphanorbornene moiety are formed when the highly reactive 2-phenylisophosphindole oxide is generated as in Eqn (1) in the presence of a dienophile or is allowed to dimerize.[1] Only one isomer is reported to be formed in the cycloadditions.



(1)

Little is known about this ring system[2] and it has not previously been characterized by ^{31}P or ^{13}C NMR spectroscopy. These spectra could, however, contain the special ^{31}P shift effects and stereospecificity of some ^{31}P–^{13}C couplings that are of great importance in 7-phosphanorbornene (7-PNB) derivatives.[3–5] Thus, 7-PNB phosphines with *syn* substitution have the most downfield ^{31}P shifts ever recorded for tertiary phosphines; values beyond δ +100 are common, whereas tri-*tert*-butylphosphine had previously set the extreme at δ +63.8.[6] The *anti* isomers are not as strongly deshielded and have signals about 50–70 ppm upfield of the *syn* forms. Deshielding is also noted for P(IV) derivatives, but is less dramatic. Significant deshielding occurs for ^{13}C at the 7-position of norbornene[7] and for ^{17}O[8] and ^{29}Si derivatives,[9] and has been attributed to a hyperconjugative type of interaction, involving the sigma bond to the atom at the 7-position and an antibonding π-orbital.

Stereochemical features of 7-PNB phosphines can be determined with the aid of two- and three-bond coupling constants,[4] since both are large only when ^{13}C is close to the phosphorus lone pair, and are small or negligible when remote. In phosphine oxides[10] and other P(IV) derivatives, dihedral angle control of ^{3}J(PC) is present and, therefore, this coupling can also be useful for stereochemical analysis. Consequently, the structure and stereochemistry previously assigned to the Diels–Alder adducts of isophosphindole oxides by ^{1}H NMR can be confirmed by ^{13}C NMR spectroscopy, further demonstrating the power of this technique for stereochemical analysis of heterocyclic phosphorus compounds.

We employed the reported[1] method for the synthesis of two benzo-7-phosphanorbornene oxides, and prepared the first known phosphines in this series by reducing the oxides with the $HSiCl_3$–pyridine system found[4] to be effective with 7-PNB oxides. Our spectral examination of the phosphines was particularly rewarding in that one of them has set a new record for deshielding of ^{31}P in a tertiary phosphine. The expected ^{31}P–^{13}C coupling effects were also present, and the stereochemistry of the phosphines and their oxides is firmly established.

RESULTS

Synthesis of benzo-7-phosphanorbornene derivatives

Chan and Nwe[1] showed that dehydrobromination of 1-bromo-2-phenylisophosphindole oxide (**1**) by triethylamine in the presence of norbornadiene as a dienophile resulted in the formation of the benzo-7-phosphanorbornene derivative **2** (Fig. 1). We repeated this reaction successfully (65% yield), and

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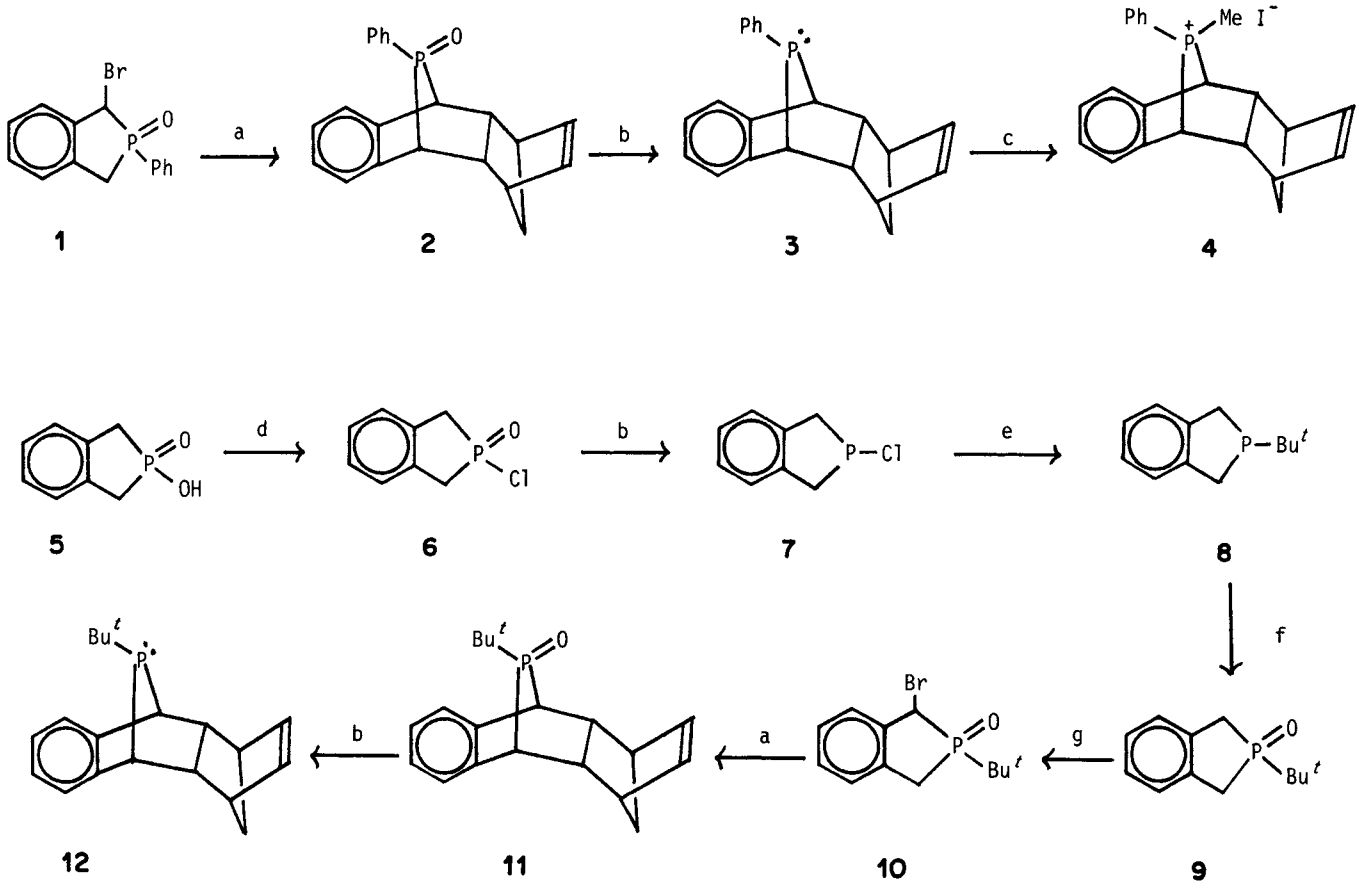
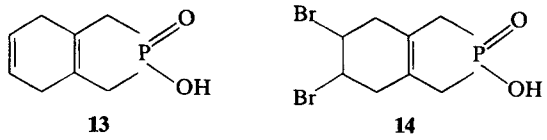


Figure 1. Synthesis of benzo-7-phosphanorbornenes: a = Et_3N, norbornadiene; b = $HSiCl_3$, pyridine; c = MeI; d = $SOCl_2$; e = *t*-BuMgCl; f = H_2O_2; g = *N*-bromosuccinimide.

then applied the trichlorosilane–pyridine reagent, the use of which was suggested by its success with phosphole oxide dimers,[4] for the deoxygenation to the phosphine **3**. The yield was 62%; the product was very sensitive to air oxidation, and was analysed by high-resolution mass spectrometry. The phosphine was also oxidized with H_2O_2 (retention) to reform the phosphine oxide, and quaternized to salt **4**. Oxidation accompanied the formation of **4**, and a pure sample could not be obtained.

The same approach was used for the synthesis of the P-*tert*-butyl derivatives, oxide **11** and phosphine **12**. A number of steps starting with the phosphinic acid **5** were required to prepare the necessary 1-bromoisophosphindoline **10**. From **5** was prepared the phosphinic chloride **6**; direct reaction with *tert*-butylmagnesium chloride gave only a trace of the desired phosphine oxide **9**, but the longer route involving reduction of the phosphinic chloride to the phosphinous chloride (**7**, 63%) with the $HSiCl_3$–pyridine reagent recently demonstrated to be useful for such conversions,[11] followed by *tert*-butylation, was successful for generating the phosphine **8**. Oxidation and bromination by *N*-bromosuccinimide proceeded smoothly, but conversion by the Chan and Nwe method[1] to the 7-phosphanorbornene oxide **11** occurred in only 27.8% yield. Reduction of the oxide provided the phosphine (73%). This compound was rapidly oxidized and a pure methiodide could not be obtained. The phosphine was characterized by its high-resolution mass spectrum, which contained the expected *m/z* for the molecular ion of the phosphine.

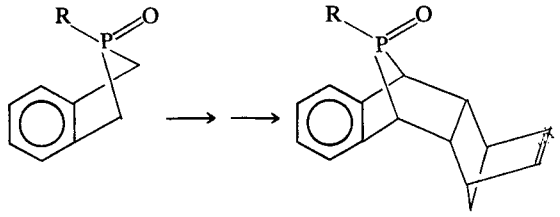
Phosphinic acid **5** was prepared by a new method for this work. Previously we had reported[12] a synthesis based on dehydrogenation of the dihydro derivative **13**, approached by a McCormack cycloaddition of dimethylenecyclohexene with PBr_3. We have now found that a more convenient synthesis for large quantities consists of the conversion of **13** to its dibromo derivative **14**,[13] followed by dehydrohalogenation with triethylamine. The overall yield for the two steps is approximately 80%.



13 **14**

^{31}P NMR spectra

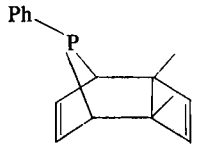
The benzo-7-PNB oxides can be considered as 1,3-bridged isophosphindoline oxides, and therefore any exaltation of ^{31}P NMR shifts can be recognized by comparing the spectra for the two series of compounds.



R	δ ^{31}P	δ ^{31}P
C_6H_5	+54.4	**2**, +75.7
$C(CH_3)_3$	+78.6	**11**, +97.8

The expected deshielding is obvious, and is of similar magnitude to that found among 7-phosphanorbornenes (as incorporated in the dimers of phosphole oxides) when compared to 3-phospholenes.[3] The deshielding is of comparable size for both *syn*- and *anti*-7-PNB isomers, and is not indicative of stereochemistry.

The phosphines derived from the two oxides **2** and **11** had ^{31}P shifts of +133.7 (**3**) and +152.5 (**12**). The latter value is the most downfield ever observed for a tertiary phosphine (cf., δ +147 for **15**[4]).



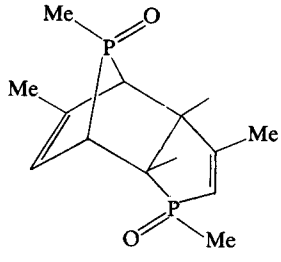
15

The benzene ring of the benzo-7-PNB series is therefore established as participating in the same orbital interaction as seen for the 7-PNB series, both for P(III) and P(IV) derivatives. In the P-*tert*-butyl derivatives, the deshielding[14] β-effects of the three methyls also contribute to the downfield shift.

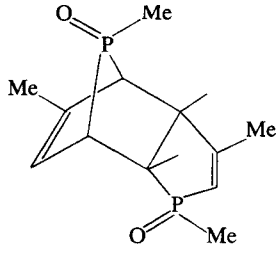
The ^{31}P values for the phosphines leave no doubt that the P-substituents occupy the *syn* position. Since these phosphines are formed from the oxides with retention,[4] and are converted to the same oxides on peroxide oxidation (also retention), the configuration at P of the initial Diels–Alder adducts is firmly established as that proposed by Chan and Nwe.[1]

^{13}C NMR spectra

Oxides. The assignment of signals was made without difficulty (Table 1) and requires no comment except for the distinction of C-1,4 from C-4a,9a. Their chemical shifts differ by less than 1 ppm in both **2** and **11**, but one signal has a significantly smaller J(PC) value (3–4 Hz) than the other (9–12 Hz). Since the ring fusion at C-4a, 9a is known to be *endo* (as will be proved in the phosphines), the larger J(PC) is appropriate for C-1,4 since it has a large dihedral angle (*ca* 150°) with respect to ^{31}P. Giving ^{2}J(PC) a magnitude of 3–4 Hz is acceptable, as such small values are frequently observed.[15] Whereas a larger ^{2}J(PC) value is found for phosphole oxide dimers[5] with *syn*-methyl (e.g. **16a**, 12.3 Hz), an *anti* compound (e.g. **16b**) has a greatly exalted value (20.1 Hz) and

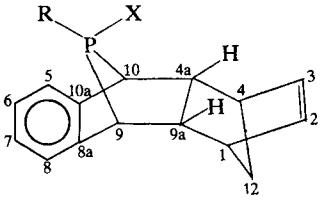


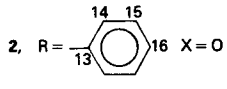
16a



16b

Table 1. ^{31}P and ^{13}C NMR data for benzo-7-phosphanorbornene derivatives





2, R = , X = O

3, R = Ph, X = l.p.[a]

11, R = $C(CH_3)_3$, X = O

12, R = $C(CH_3)_3$, X = l.p.[a]

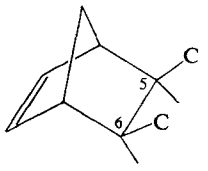
	^{31}P NMR			
	+75.7	+133.7	+97.8	+152.5
	^{13}C NMR[b]			
C-9, 10	46.1 (60.4)	50.0 (12.0)	44.0 (51.6)	48.3 (17.6)
C-4a, 9a	43.7 (4.4)	45.5 (24.2)	43.4 (3.3)	45.8 (24.2)
C-1, 4	44.4 (12.1)	45.1 (12.1)	44.0 (9.9)	45.6 (12.1)
C-12	41.3	40.2	40.9	41.1
C-2, 3	140.1	140.5	139.9	140.7
C-8a, 10a	137.0 (6.6)	144.8 (3.3)	137.4 (7.7)	146.0 (3.3)
C-5, 8	124.8 (9.0)	123.3	124.3 (8.8)	123.0
C-6, 7	127.8	125.4	127.7	125.9
C-13	128.4 (83.5)	137.5 (29.7)	33.1 (49.4)	30.4 (34.3)
C-14	131.6 (7.7)	131.1 (13.2)	26.9	29.6 (16.5)
C-15	127.8 (11.0)	127.6 (4.4)		
C-16	131.2 (3.3)	127.2		

[a] l.p. = lone pair.
[b] J(PC) values in parentheses.

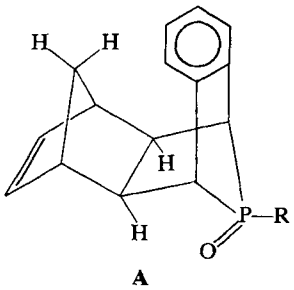
these relationships can be taken to mean that the small ^2J(PC) values found in **2** and **11** are indicative of *syn* substitution.

Elucidation of the sp^2 ^{13}C signals of the fused benzo and the double bond was straightforward for the P-*tert*-butyl derivative **11**, and this allowed their distinction from the sp^2 carbons of the P-phenyl substituent in **2**.

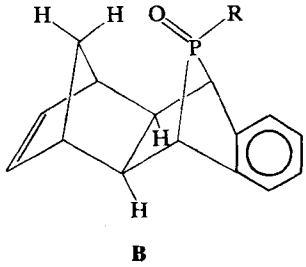
A chemical shift effect is present that is useful in proving the *endo* ring fusion. This section of the molecule can be viewed as a norbornene with 5,6-substituents.



In norbornene,[16] the chemical shift of C-7 is δ 48.5. When two methyl substituents are *endo* on norbornenes, little perturbation of the C-7 shift occurs (δ 49.3). When two methyls are *exo*, however, their *γ-gauche* relationship to C-7 causes a pronounced upfield shift to δ 41.8. The shifts found for C-12 (corresponding to C-7 of norbornene) of **2** and **11** of about δ 41 are, therefore, appropriate for sterically crowded norbornenes, as represented by **A** or **B**.



A



B

A distinction between these isomers cannot be made by ^{13}C NMR but, fortunately, a ^1H NMR effect pointed out by Chan and Nwe[1] makes this possible; shielding of one proton on C-12 (δ 0.3 in **2**) by the benzo group is present, which can only arise from orientation **A**.

Phosphines. The magnitude of the two-bond coupling to C-4a, 9a (24.2 Hz in both **3** and **12**) confirms the *syn* configurational assignment at P, since this places the lone pair close to the coupled carbons and allows large coupling. The values resemble those in *syn*-7-PNB phosphines.[4] This orientation should lead to small two-bond coupling to aromatic carbons C-8a, 10a, and in fact only 3.3 Hz is observed for both phosphines. Similar effects operate on the two ^3J(PC) values; those carbons (C-1, 4) on the same face as the lone pair have sizeable values (12.1 Hz for both), whereas the remote carbons (C-5, 8) show no coupling. The coupling to C-1, 4 is that expected for *endo* fusion, since this gives a dihedral angle of about 150° to ^{31}P. Were the fusion *exo*, an angle of about 80° would result, and there should be negligible coupling regardless of the orientation of the lone pair.[17]

The phosphines also illustrate the sensitivity of ^1J(PC) to the bond angle contraction at P and to the diversion of s-character into the exocyclic bond. Thus, the ring carbons (9 and 10) have relatively small ^1J(PC) values (**3**, 12.0 Hz; **12**, 17.6) whereas the exocyclic carbons have large values (**3**, 29.7 Hz; **12**, 34.3). The oxides do not show this sensitivity. Similar ^1J(PC) effects have been observed in the 7-PNB series.[4,5]

EXPERIMENTAL

General

Proton NMR spectra were obtained with a Bruker NR-80 spectrometer; carbon and phosphorus FT NMR spectra were recorded on a JEOL FX-90Q spectrometer at 22.5 and 36.2 MHz, respectively. Both were noise-decoupled, with signals downfield of the references (tetramethylsilane and 85% H_3PO_4, respectively) given positive signs. Mass spectral analysis was performed by the Research Triangle Mass Spectrometry Center, and elemental analyses by MHW Laboratories, Phoenix, AZ. Melting points are corrected; boiling points are uncorrected. Phosphines were handled in a nitrogen atmosphere.

1-Bromo-2-phenylisophosphindoline 2-oxide (1)

2-Phenylisophosphindoline 2-oxide, prepared by a reported method,[12] was brominated with *N*-bromosuccinimide (25% excess) according to Chan and Nwe.[1] The product was purified by silica gel chromatography, using 1:1 ethyl acetate–methylene chloride as eluant. The ^1H NMR spectrum agreed with that reported[1]; $^{31}P(CDCl_3)$, δ +46.7.

1,4,4a,9,9a,10-Hexahydro-11-phenyl-1,4-methano-9,10-phosphinideneanthracene 11-oxide (2)

Bromide **1** (6.50 mmol) was subjected to reaction with triethylamine and norbornadiene as reported,[1] giving **2** in 65% yield, m.p. 162–164 °C (lit.[1] m.p., 156–158 °C). The ^1H NMR spectrum matched that reported; for ^{31}P and ^{13}C NMR, see Table 1.

1,4,4a,9,9a,10-Hexahydro-11-phenyl-1,4-methano-9,10-phosphinideneanthracene (3)

To 50 ml of dry benzene were added pyridine (0.70 g, 88 mmol) and trichlorosilane (0.40 g, 30 mmol) under N_2 at 0 °C. After 10 min, phosphine oxide **2** (0.188 g, 0.59 mmol) was added to the mixture. The mixture was refluxed for 1 h under N_2, then cooled in an ice–water bath while being hydrolysed with 30 ml of 30% NaOH solution. The aqueous layer was separated and extracted with benzene (2 × 20 ml). The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum to give 0.110 g (62%) of **3**

(b.p. 120 °C, 0.1 mmHg); for ^{31}P and ^{13}C NMR, see Table 1. Mass spectrum: calculated for M^+ ($C_{21}H_{19}P$), 302.1225; found, *m/z* 302.1227.

The phosphine formed a methiodide **4**, ^{31}P NMR ($CDCl_3$) δ +83.7, on treatment in benzene with methyl iodide. The product was contaminated with oxide **2**.

2-Hydroxyisophosphindoline 2-oxide (5)

To a suspension of the dibromide **14**[13] (21.1 g, 0.0641 mol) in acetone (200 ml) was added dropwise a solution of triethylamine (22.4 g, 0.0221 mol) in acetone (30 ml). The reaction mixture was refluxed for 10 days and the solvent was then removed under vacuum. The resulting solid was dissolved in water (100 ml); acidification with 10% HCl to pH 1 gave a tan precipitate of **5**. Recrystallization from water gave 9.7 g (90%) of slightly tan needles; m.p. 152–154 °C (lit.[12] m.p., 156–158 °C); ^{31}P NMR($CDCl_3$), δ +72.0.

2-Chloroisophosphindoline 2-oxide (6)

A mixture of the phosphinic acid **5** (3.00 g, 0.0178 mol) and thionyl chloride (2.55 g, 0.0214 mol) was stirred at room temperature for 18 h under N_2. The excess of thionyl chloride was then removed by adding benzene (6 ml) and vacuum evaporation. The process was repeated, and left **6** as a light tan solid in quantitative yield: ^{31}P NMR ($CDCl_3$), δ +80.4. The product was used immediately in the synthesis of **7**.

2-Chloroisophosphindoline (7)

To 50 ml of dry benzene were added pyridine (5.08 g, 0.0642 mol) and trichlorosilane (2.98 g, 0.0214 mol) under N_2 at 0 °C. After 10 min the acid chloride **6** (3.33 g, 0.0178 mol) was added and the mixture was refluxed for 3 h and then allowed to stand at room temperature for 18 h. The resulting heavy precipitate was filtered off and the filtrate was concentrated under vacuum to give 1.93 g (63%) of **7**,[18] b.p. 60 °C (0.02 mmHg); ^{31}P NMR ($CDCl_3$), δ +125.0, which was used without further purification in the synthesis of phosphine **8**.

2-*tert*-Butylisophosphindoline 2-oxide (9)

To anhydrous diethyl ether (5 ml) were added Mg turnings (1.37 g, 0.0566 mol), *tert*-butyl chloride (1.26 g, 0.0136 mol) and a single, small crystal of iodine to initiate the reaction. A solution of *tert*-butyl chloride (4.81 g, 0.0519 mol) in 25 ml of anhydrous diethyl ether was added dropwise to maintain reflux. After the reaction mixture had been stirred for 0.5 h at room temperature, it was cooled in an ice–water bath and a solution of the phosphinous chloride (1.93 g, 0.0113 mol) in 25 ml of dry tetrahydrofuran was added dropwise. The reaction mixture was stirred for 18 h at room temperature. Saturated NH_4Cl solution (30 ml) was added slowly to hydrolyse excess of the Grignard reagent. The organic layer was separated and the aqueous layer was filtered to remove the white precipitate. The precipitate was washed with benzene (50 ml) and the aqueous layer was extracted with benzene (2 × 25 ml). All organic layers were combined, dried over $MgSO_4$ and concentrated under vacuum. The ^{31}P NMR spectrum showed the presence of both the desired phosphine **8**, and the corresponding oxide **9** formed by air oxidation during the work-up procedure. A solution of this mixture in $CHCl_3$ (50 ml) was washed with 5% H_2O_2 (2 × 25 ml), effecting complete oxidation of **8** to **9**. Recrystallization from benzene–hexane gave pure **9** (1.7 g, 74%), m.p. 123.5–125.5 °C; ^{31}P NMR ($CDCl_3$), δ +78.6. Analysis: calculated for $C_{12}H_{17}OP$, C 69.21, H 8.22, P 14.87; found, C 69.30, H 8.10, P 14.70%.

1-Bromo-2-*tert*-butylisophosphindoline 2-oxide (10)

To a solution of 0.751 g (3.61 mmol) of **9** in dry carbon tetrachloride (50 ml) were added *N*-bromosuccinimide (0.770 g, 4.33 mmol) and benzoyl peroxide (100 mg). The reaction mixture was refluxed for 13.5 h, cooled to room temperature and washed with water (2 × 20 ml). The organic layer was dried over $MgSO_4$ and concentrated to give 0.7 g (64%) of **10**; ^1H NMR ($CDCl_3$), δ 1.15 [d, $^3J(PH) = 16.6$ Hz, 9H, $C(CH_3)_3$], 3.31 (m, 2H, CH_2), 5.29 (broad d, ^1H, CHBr), 7.2 (m, 4H, Ar*H*); ^{31}P NMR($CDCl_3$), δ +68.0. The crude product was used directly in the synthesis of **11**.

1,4,4a,9,9a,10-Hexahydro-11-*tert*-butyl-1,4-methano-9,10-phosphinideneanthracene 11-oxide (11)

To a solution of **10** (0.52 g, 0.0018 mol) in dry benzene (50 ml) were added norbornadiene (4.40 g, 0.0477 mol) and triethylamine (2.81 g, 0.0278 mol). The mixture was refluxed for 72 h and cooled to room temperature. Triethylammonium bromide was filtered off and the filtrate was concentrated under vacuum to give a yellow oil. After chromatography on silica gel with methanol–chloroform (5:95), **11** was isolated as a slightly hygroscopic solid (0.148 g, 27.8%); ^1H NMR ($CDCl_3$), δ −0.51 [d, $^2J(HH) = 9.8$ Hz, 1H, H of CH_2 *syn* to benzo], 0.62 [d, $^2J(HH) = 9.8$ Hz, 1H, H of CH_2 *syn* to C=C], 0.86 [d, $^3J(PH) = 14.1$ Hz, 9H, $C(CH_3)_3$], 2.53 and 2.88 (both broad d, 2H, bridgehead *H*), 3.45 (m, 2H, C*H*PO) 6.19 (broad d, 2H, C=CH), 7.19 (m, 4H, Ar*H*); for ^{31}P and ^{13}C NMR, see Table 1. Mass spectrum: calculated for M^+ ($C_{19}H_{23}OP$), 298.1487; found, *m/z* 298.1486.

1,4,4a,9,9a,10-Hexahydro-11-*tert*-butyl-1,4-methano-9,10-phosphinideneanthracene (12)

To 50 ml of dry benzene were added pyridine (0.59 g, 0.0075 mol) and trichlorosilane (0.34 g, 0.0025 mol) under N_2 at 0 °C. After 10 min the phosphine oxide **11** (0.148 g, 0.00050 mol) was added to the mixture. The

reaction mixture was refluxed for 1 h under N_2 and then cooled in an ice–water bath while being hydrolysed with 30 ml of 30% NaOH solution. The aqueous layer was separated and extracted with benzene (25 ml). The combined organic layers were dried over $MgSO_4$ and concentrated to give **12** as a yellow oil (0.103 g, 73%); for ^{31}P and ^{13}C NMR, see Table 1. Mass spectrum: calculated for M^+ ($C_{19}H_{23}P$), 282.1538; found, m/z 282.1539.

Acknowledgement

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