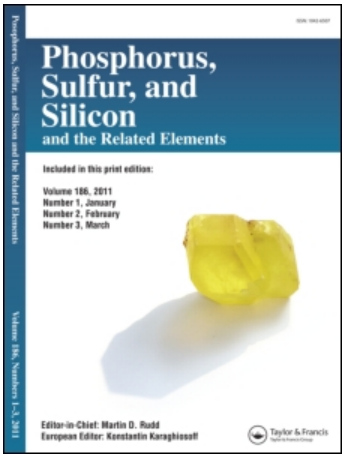

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ON SOME CHEMICAL PROPERTIES OF 1-PHENYLPHOSPHINDOLE

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ON SOME CHEMICAL PROPERTIES OF 1-PHENYLPHOSPHINDOLE

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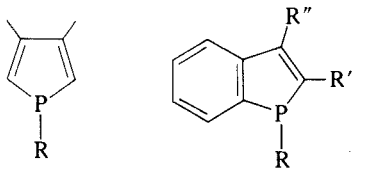
The title compound **5** can be easily synthesized by combination of two published procedures. It undergoes quantitative lithium cleavage of the exocyclic P—Ph bond, and phosphorus substituent exchange by reaction with *t*-butyllithium. The phosphindolyl anion displays a ^{31}P NMR signal at higher field than the corresponding phospholyl anion, and is also more reactive towards ethanol. This indicates a higher basicity and a lower aromaticity of the phosphindolyl anion *vs.* the phospholyl anion. Bromo derivatives in α- as well as β-position to phosphorus were also prepared. Reaction of **5** with $Mn_2(CO)_{10}$ afforded a π-phosphindolyl complex whereas reaction of *t*-butylphosphindole with $Mn_2(CO)_{10}$ only gave a σ-complex. Phosphindolyl anion with $BrMn(CO)_5$ gave μ-phosphido complexes but did not give any ferrocene analogue by reaction with $FeCl_2$, indicating a lowering of the stability of the phosphametallocenes upon benzoannelation.

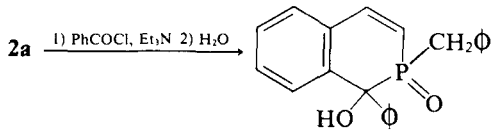
INTRODUCTION

The chemistry of fully unsaturated five-membered phosphorus heterocycles has been up to now largely restricted to phospholes **1** because of the easy access of these molecules. One of us has recently put forward an easy, one-pot synthesis of phospholes.[1] On the other hand, little attention has been paid to phosphindoles **2** because of their relative inaccessibility.



1 **2a:** R = CH_2Ph, R′ = R″ = H
2b: R = R′ = Ph, R″ = *n*-Bu

Chemical studies on **2** have so far been restricted to cleavage of the exocyclic P—C bond[2] and to ring-extension reactions.[3,4] Almost all of this preliminary work has been made with the heavily substituted phosphindole **2b**, which is probably not representative of the phosphindole class: indeed we have shown that cyclic extension with acid chlorides on **2a** gave products of the isophosphinoline type **3** in fair yields,[3] whereas under the same conditions cyclic extension of **2b** gave products of the phosphinoline type **4** in low yields.[4]



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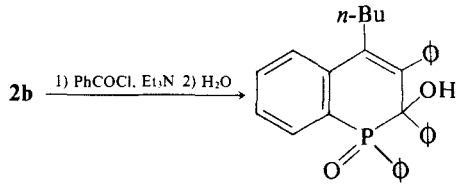
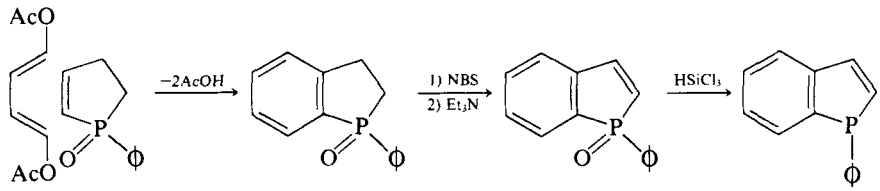


4

From a more general point of view, it is clearly interesting to check the influence of the benzo-annelation on the properties of the phosphole nucleus. Preliminary studies by Mislow showed that the inversion barrier of the pyramidal phosphorus is higher in phosphindoles than in phospholes[2] and that retrocyanoethylation rates of β-cyanoethyl phospholium salts are lower in the phosphindole than in the phosphole case.[5] Both indications point to a less aromatic phosphindole nucleus as anticipated.

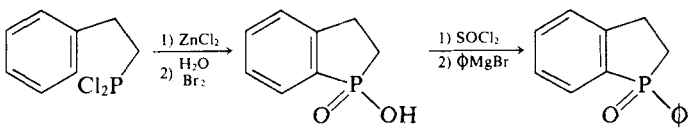
RESULTS AND DISCUSSION

The first synthesis of 1-phenyl-phosphindole **5** involved an initial Diels–Alder reaction between 1,4-diacetoxybutadiene and 1-phenyl-2-phospholene oxide to give the intermediate 1-phenylphosphindoline oxide **6** which was submitted to NBS bromination followed by dehydrobromination and finally reduction by trichlorosilane to **5**.[6]



6 7 5

In view of both the relative unavailability of 2-phospholene oxide and sluggishness of the Diels–Alder reaction (15 days), we chose another published method for the synthesis of **6**, which involves cyclization under Friedel–Crafts conditions of phenyl-2-ethyl-dichlorophosphine **8** followed by hydrolysis and oxidation to give the phosphinic acid **9**, which can be converted into its acid chloride by $SOCl_2$ and reacts with phenyl magnesium bromide to give **6**.[7]

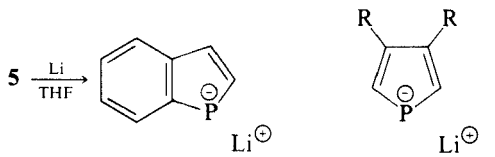


8 9 6

Since the starting dichlorophosphine is available in large quantities, we found this method of preparing **6** superior to the previous one. We found that the following steps leading to **5** were convenient.

One of the most important reactions of phospholes is their ability to give phospholyl anions by cleavage of the exocyclic P—C bond with an alkali metal. The driving force for this selective cleavage is undoubtedly the aromaticity of the phospholyl anions. Superficially, it can be suspected that they are stabilized by a strong cyclic delocalization since they are strictly isoelectronic with thiophenes. Two theoretical studies[8,9] support this view. Furthermore, Quin[10] has shown that phospholyl anions display signals at unusually low field in ^{31}P NMR, and that they do not react with ethanol in contrast to ordinary metal phosphides. Finally, Mislow[2] has found that the same type of exocyclic cleavage took place with the heavily substituted phosphindole **2b**.

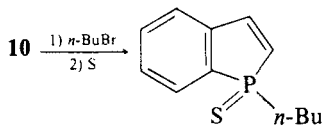
Thus, we decided to allow **5** to react with lithium in THF. A red color, characteristic of a phosphinyl anion, developed instantly. A ^{31}P NMR spectrum of the crude reaction mixture revealed a single, sharp peak at 40 ppm, indicating that the cleavage reaction was quantitative. To this value was assigned the signal of phosphindolyl anion **10**.



10 **11a**: R = H
11b: R = Ph

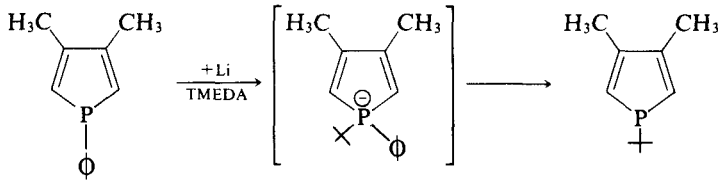
Since the NMR signal of **10** is *ca* 35 ppm upfield from that of **11a** and *ca* 14 ppm upfield from that of **11b**,[11] we suspected a lowering of the cyclic delocalization in **10** due to benzoannelation. Indeed, when **10** reacted with ethanol, a complete discoloration of the reaction mixture occured, due to the disappearance of **10** whereas, under the same conditions, **11b** is not attacked.[10,11]

On the other hand, reaction of **10** with *n*-butyl bromide followed by addition of sulfur, afforded 1-butylphosphindole sulfide **12** in fair yield.



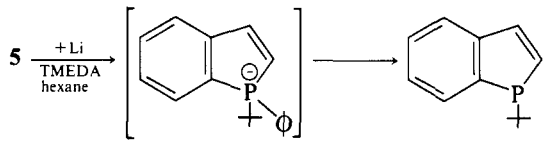
12

The next reaction that we wanted to check was the possibility of phosphorus substituent exchange by reaction of **5** with an alkyl lithium. Over one night, reaction of 1-phenyl-3,4-dimethylphosphole **13** with *t*-butyllithium yields 1-*t*-butyl-3,4-dimethylphosphole **14** probably through a phosphoranyl anion **15** which would be stabilized by eventual relief of the phosphole ring strain, as well as some delocalization of the negative charge.[12]



13 14 15

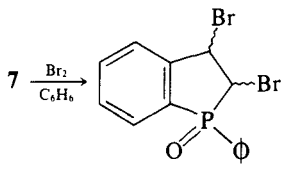
When **5** reacts with *t*-butyllithium in the presence of TMEDA over 10 mn., 1-*t*-butylphosphindole **16** was obtained in fair yield.



17 16

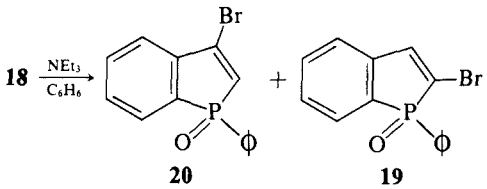
At present, it is not quite clear whether phosphoranyl anions are transition states or true intermediates.[13] If **15** and **17** are transition states, then **17** would probably be more stable than **15** because the negative charge in **17** is stabilized by the benzo electron-withdrawing substituent. This could explain why the exchange is more rapid with the phosphindoles than with the phospholes.

An important difference between phosphindoles and phospholes is that phosphole-P-oxides are Diels–Alder dimers whereas phosphindole-P-oxides are monomers. Thus, it is not possible to obtain functional phosphole monomers from phosphole oxides. As addition of bromine on the double bond of vinylphosphine oxide is known to occur,[14] we decided to allow bromine to react with the oxide **7** and obtained the dibromo derivative **18** in good yield.



18

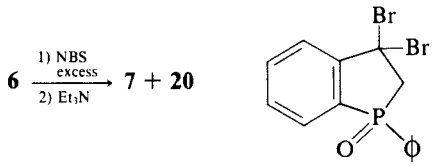
Apparently only one diastereoisomer was obtained. Subsequent treatment of **18** with triethylamine afforded the isomeric α- and β-bromophosphindole oxides **19** and **20**, easily separated by column chromatography, in approximative ratio of 5:1 and in fair overall yield.



20 19

The proton NMR of **19** shows a doublet at 7.35 ppm with $J_{PH} = 30$ Hz superimposed on the aromatic multiplet whereas **20** displays a doublet at 6.65 ppm with $J_{PH} = 20$ Hz.

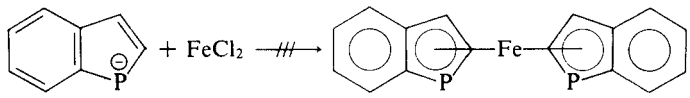
20 Could be obtained in another way: when **6** reacted with an excess of NBS followed by triethylamine dehydrobromination, **7** was obtained as the main product, but **20** was also obtained with a 20% yield, presumably through intermediate **21**.



21

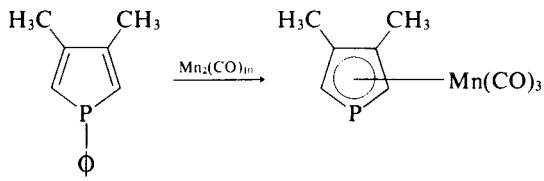
One can see that, by such a simple method as bromination-dehydrobromination of **7**, the phosphindole nucleus can be substituted, thus opening a way to α- as well as β-substituted phosphindoles.[15]

As we had seen earlier that phosphindole **5** could be totally converted into anion **10**, we decided to attempt a reaction between **10** and ferrous chloride in order eventually to obtain a bis(phosphindolyl)iron, which would be a phosphindole analogue of the diphosphaferrocenes.[16]



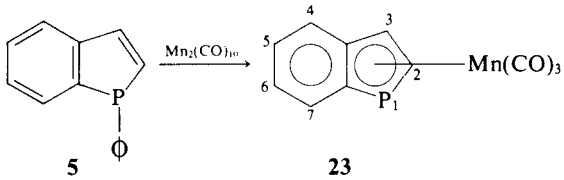
However, in all experimental conditions used by us, we never obtained a trace of the expected complex, but only black intractable tars. Thus, we wanted to know if this failure was due to the inability of **10** to act as 5 π-electron ligand.

The synthesis of phosphacymantrenes involves direct reaction between phospholes and manganese carbonyl. In refluxing xylene, the P—Ph bond of **13** is also cleaved and complex **22** is obtained in good yield.[17]



13 **22**

When we carried out the reaction of **5** with $Mn_2(CO)_{10}$, we did obtain a product **23** in low yield for which all the data indicated that it was a complex of the 5 π-electron phosphindolyl with manganese tricarbonyl.



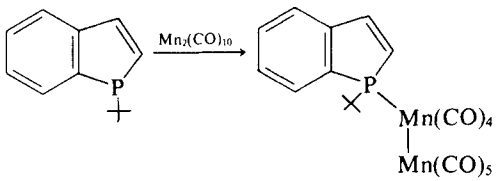
5 **23**

^{1}H NMR data of **23** show that the α- and β-protons of the phosphindolyl ring have respectively $^2J_{PH}$ and $^3J_{PH}$ values of 35.9 and 4.2 Hz, which are very similar to the values obtained for phosphacymantrenes. ^{31}P NMR shows that the signal of **23**

(−54.7 ppm) is slightly upfield from that of **22**. I.R. spectrum of **23** does not show significant differences from the spectra of other phosphacymantrenes.[17]

Attempted Friedel–Crafts acetylation of **23** with CH_3COCl and $AlCl_3$ in either CS_2 or CH_2Cl_2 as solvents did not yield the expected acetylated derivatives, unlike **22**. This reduced reactivity of **23** is no doubt due to the electron-withdrawing effect of the benzo group.

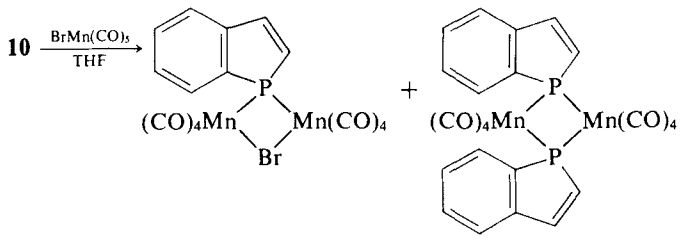
As *t*-butyl-P bonds have been shown to be thermally labile in some cases,[18] we tried to obtain **23** in higher yield than previously by reacting 1-*t*-butylphosphindole **16** with manganese carbonyl. But in this case, we only obtained a simple σ-P complex (**24**) in good yield.



16 **24**

24 Was fully characterized and does not display particular features when compared to other phosphole $Mn_2(CO)_9$ species.[19]

When anion **10** reacted with bromomanganese pentacarbonyl, we did not obtain π-complex **23**, but two complexes which were assigned the classical μ-phosphido structures **25** and **26** on the basis of their physical data. In particular, the I.R. of **25** is similar to other related species of like structure.[20]



25 **26**

The ligand properties of the phosphindolyl anion **10** are more closely related to that of the pyrrolyl anion than that of phospholyl anions: bis(pyrrolyl)iron has never been prepared[21] nor can (pyrrolyl)tricarbonylmanganese be acetylated under Friedel–Crafts conditions.[22] This is probably due to higher basicity and lower aromaticity of the phosphindolyl *vs.* phospholyl anion.

EXPERIMENTAL

Proton NMR spectra were taken at 60 MHz with a Perkin–Elmer R24A or at 80 MHz on a Bruker WP80 spectrometer. Phosphorus NMR was measured at 32.44 MHz on the Bruker instrument. Chemical shifts are expressed with positive sign downfield from internal TMS for proton and from external 85% H_3PO_4 for phosphorus. I.R. spectra were recorded with a Perkin–Elmer model 297 spectrometer. Mass spectra were obtained at 70 eV with an AEI-MS 30 spectrometer. Elemental microanalysis were obtained from the Service Central d'Analyses du CNRS. Separations by column chromatography were made with silica-gel. All manipulations involving air and moisture sensitive compounds were performed under argon.

Phenyl-2-ethyldichlorophosphine **8**, hydroxy-1-phenyl-1-phosphindoline **9** and phenyl-1-phosphindoline oxide **6** were obtained essentially as described in the literature[7] with respective yields of 66, 75 and

95%. Physical data of **6**, **8** and **9** are similar to those published except that **8** did not contain a reported impurity at 4.4 ppm in its proton NMR spectrum.[7]

1-Phenylphosphindole 1-oxide **7**

22.8 g (0.1 mole) of **6**, 19 g (0.105 mole) of NBS and *ca* 0.1 g of dibenzoyl peroxide were refluxed together in 500 ml benzene for 3 hours. The reaction mixture was then cooled to room temperature, filtered, washed with water and dried. 15 ml (0.107 mole) of triethylamine were then added to the reaction mixture which was progressively heated to reflux. After 30 min, the reaction mixture was cooled to room temperature, filtered, washed with water, dried and evaporated to dryness; the resulting oil was column chromatographed (chloroform-acetone 7/3). 16g (0.07 mole, 70%) of product was crystallized in ether.

M.p.:92°C (lit[5] 88) NMR^{1}H (60 MHz. $CDCl_3$) d at 6.06; 6.47, 6.96 ppm (J = 9 Hz, olefinic protons) 7.2 ppm (aromatic). The product we obtained did not have the hygroscopic properties mentioned in the literature.[5]

1-phenylphosphindole **5**

2.26 g (10^{-2} mole) of **7** was refluxed in 200 ml of dry benzene together with 2 ml (2×10^{-2} mole) of trichlorosilane for 1 hour. The cooled solution was hydrolyzed with a degassed solution of NaOH(2M), the organic phase was decanted and evaporated to dryness. 2.0 g (9.5×10^{-3} mole, 95%) of crystalline **5** was obtained.

M.p.:66°C (lit:[5] 66–68). NMR^{1}H ($CDCl_3$, 60 MHz) 6.35 ppm (d, 7.5 Hz, olefinic). ^{31}P: −2 ppm

THF solution of anion **10**

To a solution of 420 mg (2×10^{-3} mole) of **5** in 5 ml THF was added 50 mg (7.1×10^{-3} mole) of clean lithium foil. The solution progressively became deep-red colored. After 16 hours at room temperature, the ^{31}P NMR spectrum of this solution showed a single sharp peak at 40 ppm.

1-n-butylphosphindole sulfide **11**

To a solution of anion **10** prepared as described above were added 90 mg (6.6×10^{-4} mole) of $AlCl_3$, and, at 30 min intervals, successively 0.22 ml (0.23 g, 2×10^{-3} mole) of *n*-butyl bromide and 64 mg (2×10^{-3} mole) of sulfur. After 15 min of stirring, the crude reaction mixture was rapidly filtered through a short column of silica gel, and then evaporated to dryness and chromatographed (toluene). The resulting colorless oil was Kugelrohr-distilled at 125–130°/0.1 mm (0.3 g, 1.3×10^{-3} mole, 67%).

Anal. (calcd) found % C (64.9) 66.0% H (6.8) 6.9. NMR^{1}H (60 MHz, $CDCl_3$) m at 0.9, 1.4, 1.0 ppm (butyl) d at 6.05, 6.55, 6.88 ppm (J = 8 Hz, olefinic) 7.3 ppm (aromatic). ^{31}P: 51 ppm mass spec.: M/e 222 (M^+, 100%) I.R. (neat oil) νP = S 645 cm^{-1}

1-t-butylphosphindole **16**

To a solution of 2.1 g (10^{-2} mole) of 5 in 100 ml of *n*-hexane was added 1.6 ml of TMEDA (10^{-2} mole) followed by 7.5 ml of an 1.46 M solution of *t*-butyllithium in hexane (1.1×10^{-2} mole). After 10 min stirring, the solution was hydrolyzed with water and neutralized with a 2N HCl solution. The organic phase was decanted, dried and chromatographed (benzene/hexane 10/90) 1.2 g (6.3×10^{-3} mole, 63%) of **16** were obtained as volatile white crystals which were purified by vacuum sublimation at 0.1 mm and at room temperature.

M.p.: 29–30°C Anal (calcd) found % C (75.8) 75.9% H (7.9) 7.9% P (16.3) 16.3 NMR^{1}H ($CDCl_3$) 1.07 ppm (d, J = 13 Hz, $(CH_3)C$) d at 6.48, 7.11 ppm (J = 8 Hz, olefinic) 7.5 (m, aromatic) ^{31}P: 23.5 ppm mass spec.: M/e 190 (M^+, 30%) 134 (100%)

2-3 dihydro-1-phenyl-2,3-dibromophosphindole oxide **18**

To a solution of 1.88 g (8.3×10^{-3} mole) of oxide **7** in 20 ml of benzene was added dropwise a solution of 0.5 ml of bromine (excess) in 20 ml of benzene. After 1 hr of stirring, the benzene phase was washed with sodium metabisulfite solution until colorless, then with water and finally with dilute $KMnO_4$ solu-

tion. The benzene phase was dried and evaporated to dryness. 3.01 g (7.8×10^{-3} mole, 94%) of **18** was obtained as white crystals which were recrystallized in toluene.

M.p. 185°C dec. NMR^{1}H 4.55 ppm (dd, $J_{HP} = 1$ Hz, $J_{HH} = 6$ Hz) 5.84 ppm (*t*, $J_{HH} = J_{HP} = 6$ Hz) 7.3 (m, aromatic) ^{31}P: 34.7 ppm mass spec.: M/e 384, 386, 388 (1/2/1, M^+, 100%) IR: $\nu P = O$ 1205 cm^{-1} (KBr)

1-phenyl-2-bromophosphindole oxide **19** *and 1-phenyl-3-bromophosphindole oxide* **20**

To a solution of 2.58 g (6.7×10^{-3} mole) of **18** in 70 ml of benzene was added 10 ml (excess) of triethylamine and the solution was refluxed for 8 hours. The reaction mixture was then cooled to room temperature, filtered, and evaporated to dryness. The residue was chromatographed (toluene/ethyl acetate 80/20). The first eluted fraction afforded **19** (1.30 g, 4.3×10^{-3} mole, 64%).

M.p. 153°C (C_6H_{12}/toluene) Anal (calcd) found % (55.1) 55.2% H (3.3) 3.3% P (10.2) 9.7% Br (26.2) 25.9. NMR^{1}H ($CDCl_3$) 7.3 (m, aromatic) 7.35 (d, $J_{HP} = 35$ Hz) ^{31}P: 31.5 ppm mass spec.: M/e 304, 306 (1/1, M^+, 100%)

The second eluted fraction was **20** (0.26 g, 8.5×10^{-4} mole, 13%) M.p.: 132°C (C_6H_{12}/toluene) Anal (calcd) found % C (55.1) 54.7% H (3.3) 3.6% P (10.2) 9.8% Br (26.2) 26.8. NMR^{1}H 7.4 (m, aromatic) 6.65 (*d*, J = 20 Hz) ^{31}P: 32.3 ppm (broad peak) mass spec.: M/e 304, 306 (1/1, M^+, 100%) IR: $\nu P = O$ 1200 cm^{-1} (KBr)

Reaction of phosphindoline oxide **6** *with an excess of NBS*

To a solution of 0.57 g (2.5×10^{-3} mole) of oxide **6** in 50 ml of benzene was added 2.0 g (1.1×10^{-2} mole) of NBS together with 0.1 g of benzoyl peroxide. This solution was refluxed for 16 hours. After cooling at room temperature, 5 ml (excess) of triethylamine was added and the solution refluxed for another hour. After cooling at room temperature, the solution was filtered, washed with water, and chromatographed (toluene/ethyl acetate 80/20) 0.16 g (5.2×10^{-4} mole, 21%) of **20** was first obtained, followed by 0.23 g (10^{-3} mole, 41%) of **7**, which were identical with **20** and **7** previously obtained.

Reaction of anion **10** *with ferrous chloride*

To a filtered solution of anion **10** prepared as described above with 2.10 g (10^{-2} mole) **5** in 35 ml of THF, was added 3×10^{-3} mole (400 mg) of aluminum chloride, followed by 650 mg (5.1×10^{-3} mole) of ferrous chloride. A black tar, insoluble in all organic solvents and in water, immediately precipitated. The supernatant colorless solution when applied on a TLC plate showed a faint spot that did not migrate in ethyl acetate/methanol 80/20.

(η-*1,2,3,3a,7a phosphindolyl*)*tricarbonylmanganese* **23**

A solution of 1.05 g (5×10^{-3} mole) of **5** and of 1.95 g (5×10^{-3} mole) of dimanganese decacarbonyl in xylene (50 ml) was refluxed for 16 hours. The reaction mixture was then filtered, evaporated to dryness and chromatographed (hexane). The resulting yellow oil crystallized upon scratching (0.25 g, 9×10^{-4} mole, 18%). The crystals were sublimed under vacuum (0.1 mm) at room temperature.

M.p.: 45°C Anal (calcd) found % C (48.5) 48.7% H (2.2) 2.1% P (11.4) 11.8% Mn (20.2) 19.9. NMR^{1}H (C_6D_6, 80 MHz) 4.99 ppm (dd, $J_{HH} = 4.9$ Hz, $J_{HP} = 35.9$ Hz, H_2) 6.19 ppm (ddd, $J_{HH} = 4.9$ Hz, $J_{HP} = 4.2$ Hz, $J_{HH} = 0.7$ Hz, H_3) m at 7.79, 7.55, 7.10 (4H arom.) ^{31}P (C_6D_6): −54.7 ppm mass spect.: M/e 272 (M^+, 12%) 244 (M-CO, 14%) 216 (M-2CO, 25%) 188 (M-3CO, 100%) 133 (L, 20%) IR: $\nu C = O$ 2020, 1960, 1959 cm^{-1} (nujol)

(η-*1,1*-t-*butyl-1-phosphindole*)*nonacarbonyldimanganese* **24**

480 mg (2.5×10^{-3} mole) of phosphindole **16** and 980 mg (2.5×10^{-3} mole) of dimanganese decacarbonyl were refluxed together in 30 ml of xylene for 3 hours. The reaction mixture was chromatographed (hexane/benzene 80/20). 1.05 g (1.9×10^{-3} mole, 78%) of orange crystals of **23** were recrystallized in benzene.

M.p.: 150°C dec. Anal (calcd) found % C (45.6) 45.7% H (2.7) 2.7% P (5.6) 5.6% Mn (19.9) 20.0. NMR^{1}H (80 MHz) 1.19 (d, J = 16 Hz, $(CH_3)_3$) d at 6.43, 6.95, 7.13 (olefinic, J = 8 Hz) 7.50 (m aromatic) ^{31}P: 92.5 ppm (broad) mass spec.: M/e 552 (M^+, 3%) 440 (M-4CO, 20%) 412 (M-5CO, 30%) 357 (M-Mn(CO)$_5$ =

M', 72%) 329 (M'-CO, 30%) 300 (M'-$(CH_3)_3C$ = M", 24%) 273 (M'-2CO, 18%) 245 (M'-3CO, 244 (M"-2CO, 42%) 188 (M"-3CO, 60%) 133 (M"-3CO-Mn, 100%) IR: νC = O 2005 (m) 1995 (vs) 1965 (m) 1935 (m) cm^{-1} (nujol).

Prolonged heating did not yield to **22** and decreased the yield of **23**.

μ_3-(phosphindolyl)-μ_3-bromooctacarbonyldimanganese **25** *and bis-(μ_3 phosphindolyl)octacarbonyldimanganese* **26**

To a solution of anion **10** prepared as described above were added 90 mg (6.6×10^{-3} mole) of $AlCl_3$ and 440 mg of bromomanganese pentacarbonyl (1.6×10^{-1} mole). After 1 hour's stirring, the reaction mixture was evaporated to dryness and quickly chromatographed (hexane/benzene 80/20). A mixture of **25** and **26** (120 mg) was obtained. This mixture was digested with pentane and decanted (twice). The pentane was evaporated to dryness and the residue again digested with fresh pentane and decanted. The pentane solution was filtered, concentrated under a steam of argon, and then cooled at −78°C. Red crystals of **24** were obtained, collected and dried.

M.p.: 146°C dec. Anal % calcd: % C 35.1, % H 1.1, % P 5.7, % Mn 20.1. Calcd with 0.25 pentane per mole of **24**: % C 36.6, % H 1.6, % P 5.5, % Mn 19.5. Found: % C 36.3, % H 1.7, % P 5.5, % Mn 19.7. NMR^1H: d at 7.10, 8.05 ppm (J = 7 Hz, olefinic) 7.52 (m, 4H, aromatic + olefinic) 8.70 (m, 1H aromatic) ^{31}P: −36 ppm (very broad) Mass spec.: M/e 546/548 (M^+, 3%) 518/520 (M-CO, 1%) 462/464 (M-3CO, 12%) 434/436 (M-4CO, 48%) 406/408 (M-5CO, 5%) 378/380 (M-6CO, 9%) 350/352 (M-7CO, 13%) 322/324 (M-8CO, 70%) 272 (LMn(CO_3) M', 8%) 267/269 (M-8CO-Mn, 13%) 244 (M'-CO, 8%) 216 (M'-2CO, 15%) 188 (M'-3CO, 100%) 133 (L, 41%) IR: νC = O 1985 (s) 2005 (s) 2095 (m) ($CHCl_3$)

The pentane residues were washed with fresh pentane and dried: yellow crystals of **26** were obtained.

M.p. 250°C dec. Anal (calcd) found: % C (48.0) 48.0, % H (2.2) 2.2, % P (10.3) 9.9. NMR^1H: d at 7.30, 8.09 ppm (J = 7Hz, olefinic) 7.5 (m, aromatic) 8.56 (m, aromatic) ill-resolved. ^{31}P: no signal, probably due to quadrupole relaxation of Mn and to low solubility of product. Mass spec.: M/e 600 (M^+, 10%) 572 (M-CO, 28%) 488 (M-4CO, 22%) 460 (M-5CO, 22%) 432 (M-6CO, 3%) 376 (M-8CO, 100%) 321 (M-8CO-Mn, 67%) 272 (LMn$(CO)_3$ = M', 2%) 244 (M'-CO, 4%) 216 (M'-3CO, 3%) 188 (LMn, 89%) 133 (L, 28%). IR: νC = O 1980 (s) 1995 (sh) 2050 (s) ($CHCl_3$)

REFERENCES

1. A. Breque, F. Mathey and P. Savignac, *Synthesis*, 983 (1981).
2. W. Egan, R. Tang, G. Zon and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 6205 (1971).
3. F. Nief, C. Charrier, F. Mathey and M. Simalty, *Nouv. Journ. Chim.*, **5**, 187 (1981).
4. A. N. Hughes, K. Amornraksa, S. Phisithkul and V. Reutrakul, *J. Heterocyclic. Chem.*, **13**, 937 (1976).
5. W. B. Farnham and K. Mislow, *J. Chem. Soc. Chem. Commun.*, 496 (1972).
6. T. H. Chan and L. T. L. Wong, *Canad. J. Chem.*, **49**, 530 (1971).
7. D. J. Collins, L. E. Rawley and J. M. Swann, *Austr. J. Chem.*, **27**, 831 (1974).
8. G. Kaufman and F. Mathey, *Phosphorus*, **4**, 231 (1974).
9. C. Guimon, G. Pfister-Guillouzo and F. Mathey, *Nouv. Journ. Chim.*, **3**, 725 (1979).
10. L. D. Quin and W. L. Orton, *J. Chem. Soc. Chem. Commun.*, 401 (1979).
11. J. M. Alcaraz and G. de Lauzon, unpublished results.
12. F. Mathey, *Tetrahedron*, **28**, 4171 (1972).
13. E. P. Kyba, *J. Amer. Chem. Soc.* **97**, 2554 (1975).
14. M. I. Kabachnik, T. Y. Medved, Y. M. Poliakov and K. S. Yudina, *Isv. Akad. Nauk. SSSR, otd. Khim. Nauk.*, 1584 (1962); **CA 58**, 5720c (1963).
15. The only known functional phosphindoles have been reported very recently: T. M. Balthazor, *J. Org. Chem.*, **45**, 2519 (1980).
16. G. de Lauzon, B. Deschamps, J. Fisher, F. Mathey and A. Mitschler, *J. Amer. Chem. Soc.*, **102**, 994 (1980).
17. F. Mathey, *Tetrahedron Lett.*, 4155 (1976).
18. G. Märkl and D. Matthes, *Tetrahedron Lett.*, 4381 (1974).
19. F. Mathey, *J. Organometal. Chem.*, **93**, 377 (1975).
20. H. J. Emeleus and J. Grobe, *Angew. Chem. Int. Ed. Engl.*, **1**, 400 (1962).
21. F. Seel and V. Sperber, *J. Organometal. Chem.*, **14**, 405 (1968).
22. N. I. Pyshnograeva, V. N. Sethkina, V. G. Andrianov, V. T. Strutchkov and D. N. Kursanov, *J. Organometal. Chem.*, **128**, 381 (1977).