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SYNTHESIS AND SOME REACTIONS OF A 2,2′-BIPHOSPHOLYL

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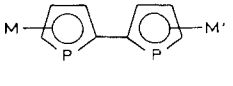
Summary

1,1′-Diphenyl-3,3′,4,4′-tetramethyl-2,2′,5,5′-tetrahydro-2,2′-biphosphole obtained by reductive dimerization of the appropriate phosphole has been converted into the corresponding 2,2′-biphosphole by *P*-bromination followed by dehydrobromination of the resulting *P*,*P*′-tetrabromo compound with α-picoline. This 2,2′-biphosphole gives two isomeric *P*-sulfides upon reaction with sulfur, and a $Mo(CO)_4$ chelate upon reaction with $Mo(CO)_6$. Cleavage of the two *P*-phenyl bonds by lithium in THF yields the corresponding biphospholyl anion, which is converted into a mixture of two isomeric bis(η^5,η^5-2,2′-diphosphafulvalene)diirons by treatment with $FeCl_2$. The reaction of $Mn_2(CO)_{10}$ in boiling xylene affords a mixture of three complexes, including a (η^5,η^5-2,2′-diphosphafulvalene)hexacarbonyldimanganese produced by thermal cleavage of the two P–Ph bonds. Under CO pressure there is a [1,5] P → C shift of the two phenyl groups, leading to formation of (η^5,η^5-3,3′-diphenyl-2,2′-diphosphafulvalene)hexacarbonyldimanganese.

Introduction

In view of the extensive organic [1] and coordination [2] chemistry of phospholes, a convenient route to 2,2′-biphospholes would be of value. For example, such species would provide the coordination chemist with a wide range of new chelating diphosphines and would be the logical starting point for the preparation of interesting diphosphafulvalene π-complexes such as **1**. Up to now, however, only one such synthesis has been reported [3]; this is based on the thermal decomposition



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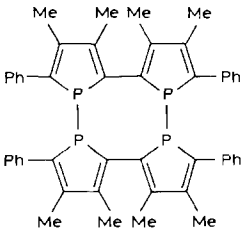

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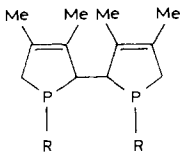

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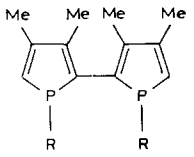

(4)

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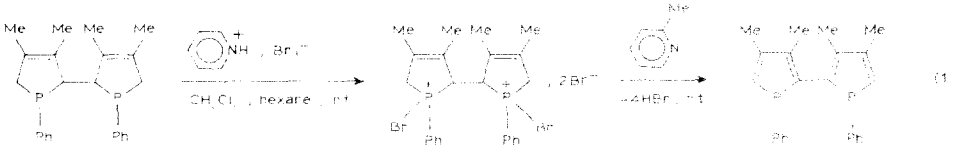
of 1-phenyl-3,4-dimethylphosphole, which yields inter alia the red tetraphosphine **2**. In spite of its simplicity, this approach has one main drawback namely that **2** is fully substituted, and thus the development of a chemistry based on substitution in the phosphole rings is ruled out. In collaboration with Nelson [4], we have demonstrated that it is possible to perform the reductive dimerization of phospholes in the presence of nickel salts and alcohols, to give 2,2′-biphospholenes, **3**. We show here that these products can be readily converted into the corresponding 2,2′-biphospholes **4**, and describe our preliminary studies on the reactions of these species.

Results and discussion

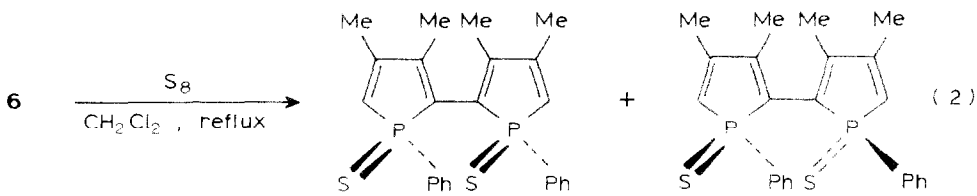
The biphospholene to biphosphole conversion was studied on the readily preparable [4], 1,1′-diphenyl derivative **5**. *P*-Bromination of **5** is easily achieved by use of pyridinium tribromide as the brominating agent. The tetrabromo compound thus obtained is then dehydrobrominated with α-picoline as the base (eq. 1).



(1)

(5) (6)

The overall yield of the 2,2′-biphosphole **6** is ca. 50%. The route is similar to that previously used by Quin [5], to convert monocyclic tervalent phospholenes into the corresponding phospholes. The dehydrobromination step involves an optimized procedure for the synthesis of phospholes devised in our group [6]. The biphosphole **6** is a solid (m.p. 108°C) which is fairly resistant toward oxidation, and can be purified by chromatography on silica gel. Since the pyramidal inversion barrier of phospholes is low (ca. 16 kcal/mol [7]), **6** can be regarded as a mixture of isomers interconverting rapidly on the NMR time scale at room temperature and giving only one sharp ^{31}P resonance ($\delta(^{31}P)$ (**6**) + 12.5 ppm in $CDCl_3$; δ positive for downfield shifts from external 85% H_3PO_4). The pyramidal inversion at phosphorus is, of course, suppressed when the lone pairs react with sulfur and mixture of isomeric *P*-sulfides is obtained (eq. 2).

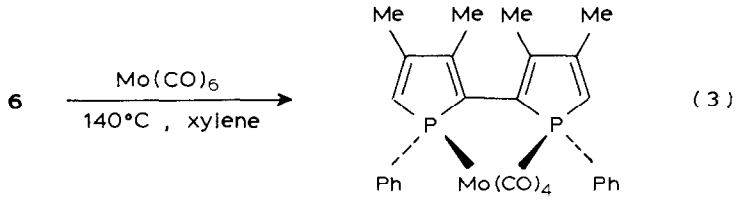


(2)

(**7a**) (**7b**)

The major isomer ($\delta(^{31}P)$ + 47.1 ppm in $CDCl_3$) probably has the less hindered structure **7b**; the minor isomer ($\delta(^{31}P)$ +47.7 ppm in $CDCl_3$) constitutes approximatively one third of the total amount of **7**. In contrast, the reaction of **6** with

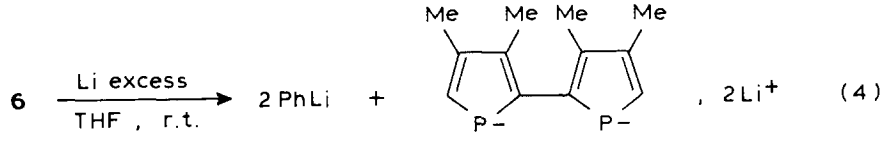
molybdenum hexacarbonyl gives only one isomer of the chelate **8** ($\delta(^{31}P)$ +51.7 ppm in CH_2Cl_2), for obvious geometrical reasons (eq. 3).



(3)

(**8**)

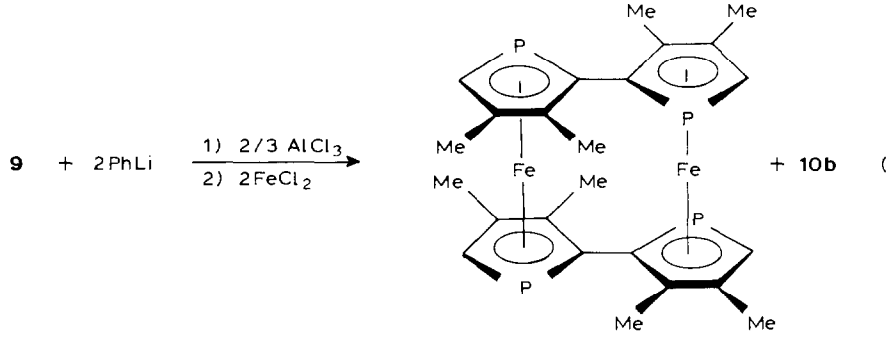
Cleavage of the two exocyclic phosphorus–phenyl bonds is readily achieved by use of lithium in THF (eq. 4).



(4)

(**9**)

This reaction is strictly similar to that in the well-known synthesis of monocyclic phospholyl anions from phospholes [8]. The dianion **9** shows practically the same downfield shift of the ^{31}P resonance as the 3,4-dimethylphospholyl anion ($\delta(^{31}P)$ +56.7 in THF vs. +58.9 ppm for the monocyclic species [9]. The dianion is a valuable precursor for preparation of a series of 2,2′-biphospholes by *P*-alkylation or a series of bimetallic η^5 complexes. For example, the reaction with anhydrous $FeCl_2$ yields a mixture of two isomeric bis(diphosphafulvalene)diirons (eq. 5).



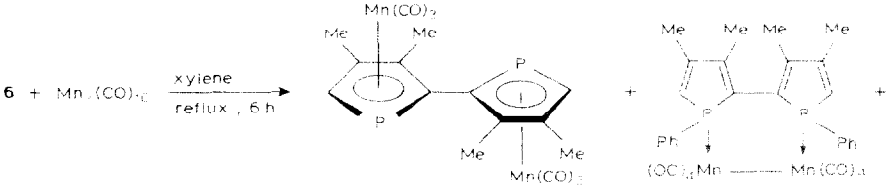
(5)

(**10a**)

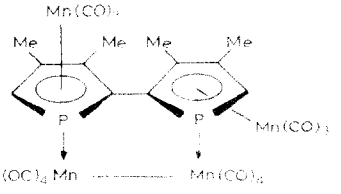
Anhydrous $AlCl_3$ is used to destroy the phenyllithium formed along with **9**, since it has been shown [10] that such an organolithium compound can react with phosphaferrocenes and would thus reduce the yield in their synthesis. By this procedure an inseparable ca. 1/1 mixture of **10a** and **10b** is obtained in ca. 20% yield. The identities of **10a** and **10b** were established by elemental analysis, mass spectrometry [EI, 70 eV: *m/e* 552 (*M*, 100%), 276 (*M*/2, 13%)], and ^1H and ^{31}P NMR spectroscopy ($\delta(^{31}P)$ −64.7 and −46.3 ppm in CD_2Cl_2). The observed upfield shift

of the ^{31}P resonances is characteristic of phosphaferrocenes (for 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene: $\delta(^{31}P)$ −72 ppm in $CDCl_3$ [11]). It is practically impossible to distinguish between the various possible isomeric structures of **10**, but it is highly likely that the least hindered "head to tail" isomer **10a** is one of the two products.

The reaction of **6** with dimanganese decacarbonyl in boiling xylene in a stream of argon at room pressure gives mainly one isomer of the bis-η^5-phospholyl complex, which is suggested to be the less hindered isomer **11a**, together with two other complexes **12** and **13** (eq. 6).



(6)



(13)

Complex **12** is probably an intermediate in the formation of **11a**, since heating of **12** in refluxing xylene for 7 h gives **11a** together with the other possible isomer **11b** in 50% yield. The two isomers **11a** and **11b** can be separated by column chromatography but it is difficult to determine their stereochemistries unambiguously from the spectral data. The overall formulae of **11a** and **11b** were established by elemental analysis, mass spectrometry, and ^{31}P NMR spectroscopy:

11a: first isomer (higher R_f): $\delta(^{31}P)$ −26.2 ppm in $CDCl_3$; mass (EI 70 eV): m/e 498 (M, 15%), 414 (M − 3CO, 30%), 330 (M − 6CO, 100%); IR (decalin): ν(CO) 2020, 2010, 1950, 1942 cm^{-1}.

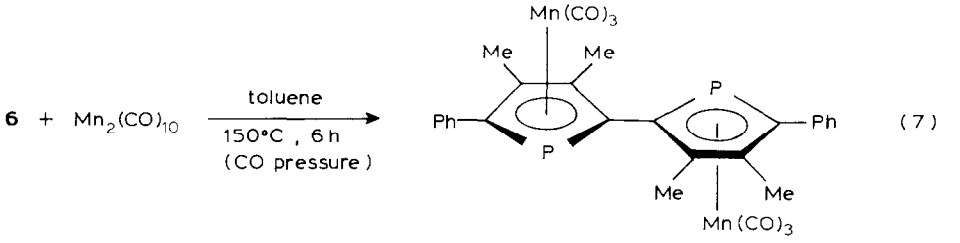
11b: second isomer (lower R_f): $\delta(^{31}P)$ −17.6 ppm in $CDCl_3$; mass (EI, 70 eV): m/e 498 (11%), 414 (37%), 330 (100%); IR (decalin): ν(CO) 2022, 2015, 1948, 1942 cm^{-1}.

Both the reaction and the physical data for the products are similar to those observed with the monocyclic 1-phenyl-3,4-dimethylphosphole [12]. Another major component of the crude product mixture is the biphosphole complex **12**, obtained in 34% yield. The identity of **12** was established by elemental analysis, mass spectrometry ((CI, NH_3): m/e 709 (M + 1, 39%), 437 (100%)), and ^1H and ^{31}P NMR spectroscopy ($\delta(^{31}P)$ +69.5 ppm in $CDCl_3$). The structure of the Mn_2 skeleton is similar to that in the corresponding $Ph_2PCH_2PPh_2$ complex with diequatorial substitution [13]. This similarity was demonstrated by the similarity of the IR spectra of **12** and $(Ph_2PCH_2PPh_2)Mn_2(CO)_8$ [13]: **12** (decalin): ν(CO) 2050s,

2005m, 1990s, 1972vs, 1915m; $(Ph_2PCH_2PPh_2)Mn_2(CO)_8$ (*n*-hexane): ν(CO) 2060s, 2000m, 1997s, 1952m, 1925s.

A small amount of complex **13** is also obtained (in ca. 8% yield). Its identity was mainly established by mass spectrometry (EI, 70 eV): *m/e* 831 (*M*–H, 1.6%), 747 (831–3CO, 2.8%), 719 (831–4CO, 2.4%), 636 (*M*–7CO, 12%), 608 (*M*–8CO, 32%), 552 (*M*–10CO, 26%), 496 (*M*–12CO, 30%), 440 (*M*–14CO, 24%), 330 (*M* – 14CO – 2Mn, 100%).

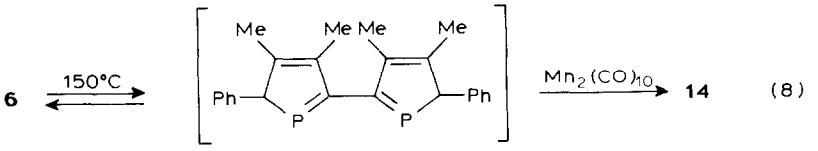
The reaction between **6** and $Mn_2(CO)_{10}$ takes a different course when performed in a closed vessel under autogenous CO pressure at 150°C (eq. 7).



(7)

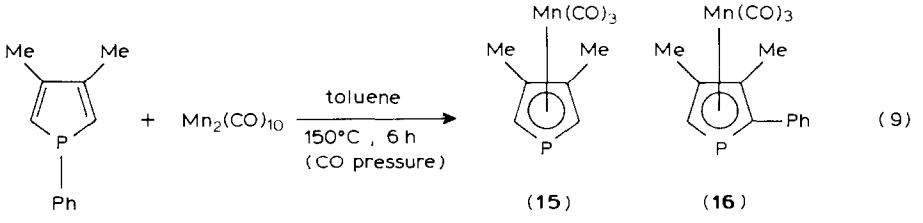
(14)

In this case the major product is the new π-complex **14**, obtained in ca. 40% yield. The nature of **14** was established by elemental analysis, mass spectrometry ((EI, 70 eV): *m/e* 650 (*M*, 14%), 566 (*M* – 3CO, 47%), 482 (*M* – 6CO, 100%)), IR ((decalin): ν(CO) 2015s, 1950vs cm^{-1}), and ^1H, ^{13}C, and ^{31}P NMR spectroscopy ($\delta(^{31}P)$ –14.1 ppm in $CDCl_3$) and we assign to it the less hindered of the isomeric structures. A minor by-product ($\delta(^{31}P)$ –5 ppm) is probably the other isomer, related to **14** as **11b** is to **11a**. The formation of **14** means that under CO pressure the complexation reaction is sufficiently slow so as to be preceded by a [1,5]-sigmatropic shift of the two phenyl groups from phosphorus to carbon within the phosphole rings (eq. 8).



(8)

This type of shift is well known for monocyclic phospholes [14]. It accounts for the formation of 2-phenyl-substituted phosphaferrocenes in the reaction of 1-phenylphospholes with $[CpFe(CO)_2]_2$ [15,16]. However, phenyl-substituted products have never been observed before in the reaction of 1-phenylphospholes with $Mn_2(CO)_{10}$, and so we decided to repeat the reaction of 1-phenyl-3,4-dimethylphosphole with $Mn_2(CO)_{10}$, but instead of working under a stream of argon as before [12], we performed the reaction in a closed vessel under autogenous CO pressure. This gave, in addition to the "normal" 3,4-dimethylphospholyl π-complex **15**, the 2-phenyl-3,4-dimethylphospholyl π-complex **16**, obtained in 13% yield (eq. 9).



(9)

(15) (16)

Complexes **15** and **16** were separated by chromatography on silica gel. The identity of **16** was established by elemental analysis, mass spectrometry [(EI, 70 eV): *m/e* 326 (*M*, 10%), 270 (*M* − 2CO, 23%), 242 (*M* − 3CO, 100%)]. IR [(decalin): *ν*(CO) 2018vs, 1950vs, 1938vs cm^{-1}], and ^1H, ^{13}C, and ^{31}P NMR spectroscopy ($\delta(^{31}P)$ −37.7 ppm in $CDCl_3$).

It seems clear that the chemistry of **6** closely parallels that of the corresponding "monomeric" 1-phenyl-3,4-dimethylphosphole.

Experimental

NMR spectra (δ in ppm from internal Me_4Si for ^1H and ^{13}C and from external H_3PO_4 for ^{31}P, positive for downfield shifts in all cases) were recorded on a Bruker WP 80 instrument at 80.13, 20.15, and 32.44 MHz, respectively. Mass spectra (Electronic Impact Desorption or Chemical Ionization Desorption) were recorded on a Nermag R10-10 spectrometer by Mr Charré (SNPE). All reactions were carried out under argon. Chromatographic separations were performed on deoxygenated silica gel columns (70–230 mesh, Riedel de Haën).

*1,1′-Diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole (**6**)*

To a solution of 2.4 g (6.3×10^{-3} mol) of 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′,5,5′-tetrahydro-2,2′-biphosphole **5** in 40 ml of CH_2Cl_2 and 40 ml of hexane, was added 4.4 g (1.37×10^{-2} mol) of pyridinium tribromide. The mixture was well stirred for 2 h and then 3.1 g (3.33×10^{-2} mol) of α-picoline in 10 ml of hexane was added. After 2 h stirring the solvents were distilled off and the residue was chromatographed on silica gel with a mixture of hexane and CH_2Cl_2 (70/30) as eluant. Evaporation of the solvents led to a slightly yellow oil, which crystallized on standing: yield 1.2 g (51.3%); m.p. 108°C; ^1H NMR ($CDCl_3$): δ 1.79 (pseudo t, 6H, C(3) and C(3′)-Me), 2.08 (pseudo q, 6H, C(4) and C(4′)-Me), 6.43 (m, 2H, =CH), 7.20 (br s, 10H, Ph); ^{31}P NMR $\{^1H\}$ ($CDCl_3$) 12.5; ^{13}C NMR $\{^1H\}$ ($CDCl_3$): δ 15.01 (s, Me), 18.26 (s, Me), 140.59 (pseudo t, C_β), 143.01 (pseudo t, C_β), 150.18 (br s, C(2)C(2′)); mass spectrum (EI, 70 eV, 200°C): *m/e* (relative intensity) 374 (*M*, 100%), 297 (*M* − Ph, 20%), 265 (*M* − PhP − 1, 40%), 187 (*M*/2, 25); Anal. Found: C, 76.97; H, 6.46; P, 16.57. $C_{24}H_{24}P_2$ calcd.: C, 76.98; H, 6.46; P, 16.55%.

*1,1′-Diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole-P,P′-disulfides (**7a** and **7b**)*

To a solution of 0.3 g (8×10^{-4} mol) of biphosphole **6** in 5 ml of CH_2Cl_2 was added 0.1 g (3.1×10^{-3} mol) of sulfur. After 2 h reflux the solvent was distilled off and the residue chromatographed on silica gel with toluene as eluant: yield 0.25 g (71%) of a mixture of **7a** and **7b** as a pale yellow solid; ^1H NMR ($CDCl_3$): δ 1.66 (pseudo t, C(4) and C(4′)-Me of the minor isomer) (the signal at 1.66 ppm corresponding to the C(4),C(4′)-methyls of the minor isomer represents about 16% of the total methyl signals integration); 2.10 (br s, C(3),C(3′),C(4), and C(4′)-Me of the major isomer), 2.14 (partly masked, C(3) and C(3′)-Me of the minor isomer), 6.00 (d, ^2J(H–P) 31.1 Hz, =CH of the major isomer), 6.09 (d, ^2J(H–P) 30.6 Hz, =CH of the minor isomer), 6.8–7.7 (m, 10H, Ph); ^{31}P NMR ($CDCl_3$): δ 47.15 major isomer and 47.75 minor isomer; mass spectrum (EI, 70 eV, 200°C): *m/e* (relative intensity) 438 (*M*, 86%), 405 (*M* − SH, 100%), 219 (*M*/2, 20%); Anal. Found: C, 65.84; H, 5.40; P, 14.18. $C_{24}H_{24}P_2S_2$ calcd.: C, 65.73; H, 5.52; P, 14.12%.

*(η^1-P,η^1-P'-1,1'-Diphenyl-3,3',4,4'-tetramethyl-2,2'-biphosphole)tetracarbonylmolybdenum (**8**)*

A mixture of 0.95 g (2.5×10^{-3} mol) of biphosphole **6** and 0.8 g (3×10^{-3} mol) of $Mo(CO)_6$ in 10 ml of xylene was kept at 120–140°C for 1 h then allowed to cool to room temperature. Complex **8** crystallized out: yield 1.2 g (82.5%), yellow crystals; m.p. 245°C (dec); ^{1}H NMR ($CDCl_3$): δ 1.95 (pseudo q, 6H, C(3) and C(3')-Me), 2.06 (br s, 6H, C(4) and C(4')-Me), 6.50 (br d, ^2J(H–P) 35.4 Hz, 2H, =CH), 7.25–7.55 (m, 10H, Ph); mass spectrum (EI, 70 eV, 250°C): *m/e* (relative intensity) 584 (*M*, 17%), 528 (*M* − 2CO, 33%), 472 (M − 4CO, 95%), 374 (*M* − $Mo(CO)_4$, 25%).

*Bis(η^5,η^5-4,4',5,5'-tetramethyl-2,2'-diphosphafulvalene)diiron (**10**)*

To a solution of 1.4 g (3.7×10^{-3} mol) of biphosphole **6** in 40 ml of dry THF was added an excess of Li. After 4 h stirring the excess of lithium was removed and 0.33 g (2.4×10^{-3} mol) of anhydrous $AlCl_3$ was rapidly added at −10°C. After 0.5 h at room temperature, 0.7 g (5.5×10^{-3} mol) of anhydrous $FeCl_2$ was added in two portions. After 0.5 h stirring the solvent was removed and the residue chromatographed on silica gel with toluene as eluant: yield 0.2 g (20%) of **10a** + **10b**; orange red crystals; ^{1}H NMR (CD_2Cl_2): δ 1.77, 1.93, 2.73 and 3.06 (four singlets, 4 × 6H, C(4), C(4'), C(5), and C(5')-Me), 3.14 and 3.98 (two multiplets, 2 × 2H, C(3), and C(3')-H); Anal. Found: C, 52.20; H, 5.21; Fe, 19.79; P, 22.16. $C_{24}H_{28}Fe_2P_4$ calcd.: C, 51.83; H, 5.80; Fe, 20.09; P, 22.28%.

*(η^5,η^5-4,4',5,5'-Tetramethyl-2,2'-diphosphafulvalene)hexacarbonyldimanganese (**11a**)*

A mixture of biphosphole **6** (1.9 g, 5×10^{-3} mol) and $Mn_2(CO)_{10}$ (3.9 g, 10^{-2} mol) in xylene (30 ml) was heated for 6 h at 150°C with stirring. After cooling and concentration complexes **12** and **13** partly crystallized out (0.9 g). The solution was filtered and evaporated, and the residue was chromatographed on silica gel. The excess of $Mn_2(CO)_{10}$ was removed by elution with hexane, then elution with hexane/toluene (80/20) gave **11a** as a yellow oil which tenaciously retained approximately one molecule of toluene per mole of **11a**: $R_f \sim 0.4$; yield 1 g. Anal. Found: C, 50.43; H, 3.87; Mn, 17.31; P, 9.92. $C_{18}H_{14}Mn_2O_6P_2 + C_7H_8$ calcd.: C, 50.87; H, 3.76; Mn, 18.61; P, 10.49%; ^{1}H NMR ($CDCl_3$): δ 2.14 (s, 6H, Me), 2.21 (s, 6H, Me), 4.48 (pseudo dxt, 2H, =C*H*P); ^{13}C NMR ($CDCl_3$): δ 14.66 (m, CH_3), 16.17 (s, CH_3), 95.54 (dxd, ^1J(C–P) 67.1 Hz, ^4J(C–P) ≃ 4.2 Hz, CH_α), 110.14 (m, C_β), 111.41 (d, C_α), 112.62 (s, C_β), 223.55 (s br, CO). (For mass spectrum see Results and discussion.)

*Isomer **11b***

A solution of 1.2 g of complex **12** in xylene (25 ml) was refluxed for 7 h then cooled and concentrated. The residue was chromatographed with a mixture of hexane and toluene (80/20) as eluant. Isomer **11a** was initially eluted ($R_f \sim 0.4$, yield 0.1 g) then isomer **11b** ($R_f \sim 0.25$, yield 0.3 g, 12% from **6**). Complex **11b** was obtained pure by recrystallization from hexane/toluene (90/10) at 0°C: m.p. ~ 176°C (dec.). Anal. Found: C, 42.39; H, 2.60; Mn, 21.91. $C_{18}H_{14}Mn_2O_6P_2$ calcd.: C, 43.40; H, 2.83; Mn, 22.05%. ^{1}H NMR ($CDCl_3$): δ 1.96 (s, 6H, Me), 2.13 (s, 6H, Me), 4.38 (pseudo dxt, 2H, C*H*P); ^{13}C NMR ($CDCl_3$): δ 12.72 (s, CH_3), 15.99 (s, CH_3), 95.17 (d, ^1J(C–P) = 64.7 Hz, HC–P), 108.86 (dxd, ^1J(C–P) 58.6, ^2J(C–P) 15.9

Hz, C_α), 109.7 (m, C_β), 116.98 (s, C_β), 223 (s br, CO). (For mass spectrum see Results and discussion.)

*(η^1-P,η^1-P'-1,1'-Diphenyl-3,3',4,4'-tetramethyl-2,2'-biphospholeoctacarbonyldimanganese (**12**)*

Complex **12** was obtained in 34% overall yield (1.2 g) from the reaction mixture from which **11a** had been isolated. **12** partly crystallized out along with **13** from the crude reaction mixture. A further quantity was obtained by chromatography of the residual oil. The various products were eluted in the following order: (1) $Mn_2(CO)_{10}$ (hexane), (2) **11a** (hexane/toluene, 80/20), (3) **12** + **13** (toluene). **12** was further purified by crystallization from $CH_2Cl_2/CHCl_3$ (80/20); orange crystals; m.p. ~ 200°C (dec); Anal. Found: C, 54.21; H, 3.44; Mn, 15.51; P, 8.93. $C_{32}H_{24}Mn_2O_8P_2$ calcd.: C, 54.28; H, 3.55; Mn, 15.52; P, 8.75%. ^{1}H NMR ($CDCl_3$): δ 1.86 (s, 6H, Me), 2.18 (s, 6H, Me), 6.92 (d, ^2J(H–P) ~ 35.2 Hz, 2H, C*H*P), 7.30 (m, 10H, Ph).

*[η^1-P,η^1-P'-(η^5,η^5-4,4',5,5'-Tetramethyl-2,2'-biphosphafulvalene)hexacarbonyldimanganese]octacarbonyldimanganese (**13**)*

The residue from the recrystallization of crude complex **12** was chromatographed with toluene/hexane (80/20). The yellow oil obtained, crystallized slowly; m.p. ~ 260°C (dec)($CHCl_3$); yield 0.3 g; Anal. Found: C, 35.23; H, 1.64; Mn, 25.01; P, 7.34; $C_{26}H_{14}Mn_4O_{14}P_2$ calcd.: C, 36.33; H, 1.69; Mn, 26.41; P, 7.44%; ^{1}H NMR ($CDCl_3$): δ 2.08 (s, 6H, Me), 2.19 (s, 6H, Me), 5.03 (pseudo t, 2H, C*H*P); ^{31}P NMR ($CDCl_3$): δ 78.45; IR (decalin) ν(CO), 2065m, 2020vs, 1988vs, 1976s, 1950s cm^{-1}. (For mass spectrum see Results and Discussion.)

*(η^5,η^5-5,5'-Diphenyl-4,4',5,5'-tetramethyl-2,2'-diphosphafulvalene)hexacarbonyldimanganese (**14**)*

A mixture of **6** (1.9) g and $Mn_2(CO)_{10}$ (3.9 g) in toluene (15 ml) was heated at 150°C in a pressure vessel (CO pressure ~ 3 atm.) for 6 h. The solvent was then evaporated off and the residue was chromatographed with hexane/toluene (80/20) as eluant. A yellow oil was obtained, which crystallized slowly from hexane/benzene (90/10); m.p. ~ 200°C (dec.); yield 1.3 g. Anal. Found: C, 53.98; H, 3.43; Mn, 17.40; P, 9.13. $C_{30}H_{22}Mn_2O_6P_2$ calcd.: C, 55.43; H, 3.41; Mn, 16.90; P, 9.53%. ^{1}H NMR ($CDCl_3$): δ 2.21 (s, 6H, Me), 2.41 (s, 6H, Me), 7.20–7.30 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$): δ 14.53 (s, CH_3), 15.99 (m, CH_3), 107.95 (dxd, ^1J(C–P) 64.7, ^2J(C–P) 18.3 Hz, C(2), C(2')), 109.29 (m, C_β), 111.41 (s, Cβ), 118.35 (dxd, ^1J(C–P) 62.26 Hz, *C*-Ph), 223.61 (s, CO).

*2-Phenyl-3,4-dimethylphosphacymantrene (**16**)*

A mixture of 1-phenyl-3,4-dimethylphosphole (3.8 g, 2×10^{-2} mol) and $Mn_2(CO)_{10}$ (2.0 g, ~ 5×10^{-3} mol) in toluene was heated at 150°C in a pressure vessel (CO pressure ~ 3 atm). The residue was chromatographed with hexane. The first, yellow, product (R_f 0.46) was the phosphacymantrene **15** and the second yellow product was the phosphacymantrene **16** (R_f 0.20). Yield of **16** 0.8 g Anal. Found: C, 55.95; H, 3.70; P, 9.18. $C_{15}H_{12}MnO_3P$ calcd.: C, 57.10; H, 3.71; P, 9.43%. ^{1}H NMR ($CDCl_3$): δ 2.12 (s, 3H, Me), 2.17 (s, 3H, Me), 4.51 (d, ^2J(H–P) 34.9 Hz, 1H, C*H*P), 7.22 (s, 5H, Ph); ^{13}C NMR ($CDCl_3$): δ 13.08 (s, Me), 15.75 (s, Me), 94.96 (d, ^1J(C–P) 62.3 Hz, *C*H-P), 109.84 (d, ^2J(C–P) 7.3 Hz, *C*-Me), 111.53 (d, ^2J(C–P) 4.9 Hz, *C*-Me), 119.68 (d, ^1J(C–P) 59.8 Hz, *C*-Ph), 223.79 (s, CO).

References

1 F. Mathey, Top. Phosphorus Chem., 10 (1980) 1; L.D. Quin, The Heterocyclic Chemistry of Phosphorus, Wiley Interscience, New York, 1981.
2 F. Mathey, J. Fischer and J.H. Nelson, Structure and Bonding, 55 (1983) 153.
3 F. Mathey, F. Mercier, F. Nief, J. Fischer and A. Mitschler, J. Am. Chem. Soc., 104 (1982) 2077.
4 F. Mercier, F. Mathey, J. Fischer and J.H. Nelson, J. Am. Chem. Soc., 106 (1984) 425; Inorg. Chem., 24 (1985) 4141.
5 L.D. Quin, S.G. Borleske and J.F. Engel, J. Org. Chem., 38 (1973) 1858.
6 A. Brèque, F. Mathey and P. Savignac, Synthesis (1981) 983.
7 W. Egan, R. Tang, G. Zon and K. Mislow, J. Am. Chem. Soc., 93 (1971) 6205.
8 E.H. Braye, I. Caplier and R. Saussez, Tetrahedron 27 (1971) 5523.
9 C. Charrier, H. Bonnard, G. De Lauzon, and F. Mathey, J. Am. Chem. Soc., 105 (1983) 6871.
10 B. Deschamps, J. Fischer, F. Mathey and A. Mitschler, Inorg. Chem., 20 (1981) 3252.
11 G. De Lauzon, B. Deschamps, J. Fischer, F. Mathey and A. Mitschler, J. Am. Chem. Soc., 102 (1980) 994.
12 F. Mathey, A. Mitschler, and R. Weiss, J. Am. Chem. Soc., 100 (1978) 5748.
13 R. Colton and C.J. Commons, Aust. J. Chem., 28 (1975) 1673.
14 F. Mathey, F. Mercier, C. Charrier, J. Fischer and A. Mitschler, J. Am. Chem. Soc., 103 (1981) 4595.
15 F. Mathey, J. Organomet. Chem., 139 (1977) 77.
16 F. Mercier and F. Mathey, J. Organomet. Chem., 263 (1984) 55.