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FULL PAPER

Synthesis and characterization of pentakis(dimethylphosphanyl)-cymantrene $[Mn\{C_5(PMe_2)_5\}(CO)_3]$, the first cyclopentadienyl complex with five phosphanyl substituents†

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Treatment of the highly reactive $[Mn(C_5Cl_3Li_2)(CO)_3]$ with PPh_2Cl or PEt_2Cl gave the 1,3-bis(phosphanyl)-cymantrenes $[Mn\{C_5Cl_3(PR_2)_2\}(CO)_3]$ (R = Ph, **1** or Et **2**). The stepwise repeated reaction of $[Mn(C_5Br_5)(CO)_3]$ with ^{n}BuLi and PMe_2Cl yielded a 4:1 mixture of $[Mn\{C_5H(PMe_2)_4\}(CO)_3]$ **3** and $[Mn\{C_5(PMe_2)_5\}(CO)_3]$ **4**, from which the latter can be isolated in 10% yield. A structure determination of **4** shows a planar cyclopentadienyl ring with a "paddle wheel" conformation of the five PMe_2 substituents.

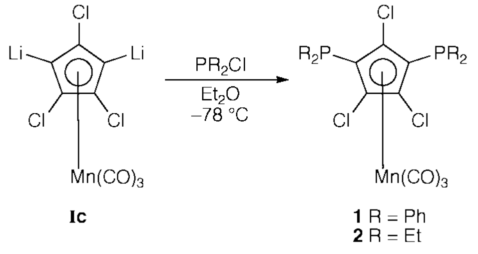
Introduction

The research on metallocenylpolyphosphanes has mainly concentrated on 1,1′-bis(diphenylphosphino)ferrocene and its mono- or bis-ring substituted derivatives. The interest in these compounds comes mainly from Hayashi's discovery that rhodium and palladium complexes of these compounds are highly active catalysts for many organic transformations, and that, in particular, chiral ferrocenylphosphines can successfully be applied in a variety of transition-metal catalysed asymmetric reactions.[2] Another group of ferrocenyl diphosphines has been developed by Togni *et al.*,[3–5] who used 1,2-disubstituted ferrocenes of the type $[FeCp\{C_5H_3(PPh_2)(CHMePRR')\}]$ in asymmetric catalysis. Recent advances in this field have been summarized by Richards and Locke.[6] Since this field of research is only concerned with the formation of P,P′ (or P,N; P,O or P,S) chelate complexes, there was no need to introduce further phosphane substituents into the cyclopentadienyl ring. Thus, it is not surprising that there are only very few examples of cyclopentadienyl complexes with two phosphanyl substituents attached to the same ring,[7–9] and to the best of our knowledge no examples of complexes with three or more phosphanyl substituents are known. Since we have shown that the synthesis of complexes with five methylsulfanyl-[10] or dimethylsilyl[11] substituents is possible starting from pentahalogenocyclopentadienyl complexes, we decided to examine the same synthetic strategy for the synthesis of a cyclopentadienyl-penta(phosphane) complex.

Results and discussion

From mechanistic studies on the lithium–halide exchange reaction of pentahalogenocymantrenes $[Mn(C_5X_4Br)(CO)_3]$ (X = Cl, **Ia** or Br **Ib**) we knew that isolation of the highly reactive $[Mn(C_5Cl_3Li_2\text{-}1,3)(CO)_3]$ **Ic** was possible,[12] and regarded this substance as appropriate to test the viability of this strategy to prepare cyclopentadienyl polyphosphanes.

Treatment of compound **Ic** with PPh_2Cl or PEt_2Cl in Et_2O at −78 °C resulted in the desired bis-phosphanyl compounds $[Mn\{C_5Cl_3(PR_2)_2\}(CO)_3]$ (R = Ph **1** or Et **2**) isolated in approximately 50% yield (Scheme 1). Both compounds contain the monophosphanes $[Mn\{C_5Cl_3H(PR_2)\}(CO)_3]$ (R = Ph **1a** or Et **2a**) and according to the ^{31}P NMR spectra also several other minor (≤5%) unidentified by-products are present, which are most likely to be due to unwanted side reactions with impurities in the starting chlorophosphanes.



Scheme 1

We thought that the chances for the preparation of a cyclopentadienyl pentaphosphane ligand might be higher if steric interactions were minimized. Ideally, this would be achieved with the PH_2 group, but since this would make extreme anaerobic and water-free conditions necessary we decided the second best candidate would be the PMe_2 substituent. Assuming that the phosphorus lone pair is not more sterically demanding than the hydride substituent, the analogy to the $SiMe_2H$ substituent, which could be successfully introduced five times,[11] seemed to justify this approach.

Indeed, when we treated compound **Ib** in a "one pot synthesis" consecutively alternating with ^{n}BuLi and PMe_2Cl in three steps according to Scheme 2 we obtained a product mixture that contained two major components **3** and **4** in an approximate 4:1 ratio together with a couple of minor (≤ 5%) impurities. Compounds **3** and **4** could be separated by column chromatography and identified by multinuclear (^1H, ^{13}C and ^{31}P) NMR spectroscopy and high-resolution mass spectrometry as the tetraphosphane $[Mn\{C_5H(PMe_2)_4\}(CO)_3]$ **3** and the pentaphosphane $[Mn\{C_5(PMe_2)_5\}(CO)_3]$ **4**. The latter could be isolated in approximately 10% yield as off-white microcrystalline material. The ^1H NMR spectrum (270 MHz) shows at room temperature a very broad singlet (half-width 19 Hz), which on cooling to −70 °C splits into two still broad singlets (half-width 11 Hz) with a separation of *ca.* 67 Hz. This behaviour is apparently a consequence of the frozen rotation around the C (ring)–P bond, leaving the distal methyl groups

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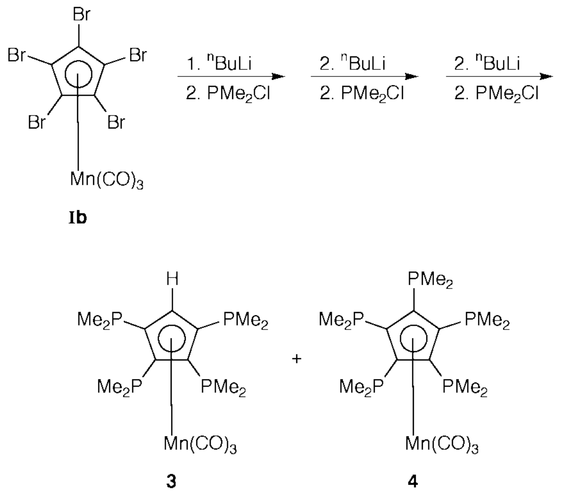
† Coordination chemistry of perhalogenated cyclopentadienes and alkynes. Part 24.[1] *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4299/

Table 1 Comparison of ν(CO) and δ(^{13}CO) data of the cymantrenes [$Mn(C_5X_5)(CO)_3$]

X	$\tilde{\nu}$(CO)/cm^{-1}	δ(^{13}CO)
H	2023, 1939	225.1
Me	2020, 1930	227.2
Br	2044, 1963	220.9
$SiMe_2H$	2017, 1940	225.0
PMe_2	2020, 1947	224.0



Scheme 2

non-equivalent to the proximal ones. A free activation enthalpy of 52 kJ mol^{-1} can be calculated from these data, while for the pentakis(dimethylsilyl) complex [$Mn\{C_5(SiMe_2H)_5\}(CO)_3$] an activation enthalpy of *ca.* 40 kJ mol^{-1} was estimated.[11] Obviously the phosphorus lone pair has a larger steric demand than the hydride substituent. The electronic effect of the five PMe_2 substituents on the $Mn(CO)_3$ fragment, as can be derived from the ν(CO) bands and the δ (Mn–^{13}CO) signals, seems to be similar to the one exerted by five methyl or silyl groups (see Table 1). To get further insight into the sterical consequences of attaching five phosphanyl substituents to a cyclopentadienyl ring, a structure determination of **4** was performed.

Molecular structure of compound 4

The molecular structure of compound **4** (Figs. 1 and 2) is very similar to that of pentakis(dimethylsilyl)cymantrene.[11] Compound **4** crystallizes, however, with two independent molecules in the triclinic space group $P\bar{1}$. The structure solution with SHELXS 97[14] gave the positions of manganese, the five ring carbon atoms and five phosphorus atoms. The next Fourier-difference analysis showed that there were actually two positions for phosphorus atom. Refinement of the site occupation factors resulted in an 80 : 20 preference for one position ("A") in both molecules. The quality of the data set in combination with the much smaller scattering power of carbon compared to phosphorus did not allow the refinement of two positions for the ring or methyl carbons. Therefore no discussion of P–C distances or C–C–P and C–P–C angles is possible. Both molecules of **4** show planar cyclopentadienyl rings (rms deviation from planarity 0.0077 and 0.0093 Å). The phosphorus atoms on the "A" site either lie in the plane (P1, P3 and P12, P15) or on the distal side of the ring (in relation to the $Mn(CO)_3$ moiety). The largest distance from the cyclopentadienyl ring is found for the P atoms between the ones within the plane, *i.e.* P2 (0.36 Å) and P11 (0.41 Å). All PMe_2 groups are oriented in the same way, forming a chiral paddle wheel, as was observed for the $SiMe_2$ groups in [$Mn\{C_5(SiMe_2H)_5\}(CO)_3$].[11] Owing to the missing "B" positions for the carbon atoms, it can only be speculated that these correspond to the enantiomer of "A", but this appears reasonable in the view of similar observations with other pentasubstituted cyclopentadienyl complexes.[15] The C–C bond lengths within the cyclopentadienyl ring average to 1.419 Å with a variation from 1.394(7) to 1.433(7) Å, thus showing no particular influence of the pentasubstitution (in the parent compound [$Mn(C_5H_5)(CO)_3$] the average C–C distance is 1.422 Å with a variation from 1.400 to 1.439 Å[16]). Thus, it is only the substituents that bear the consequences of steric congestion, and not the cyclopentadienyl ring itself.

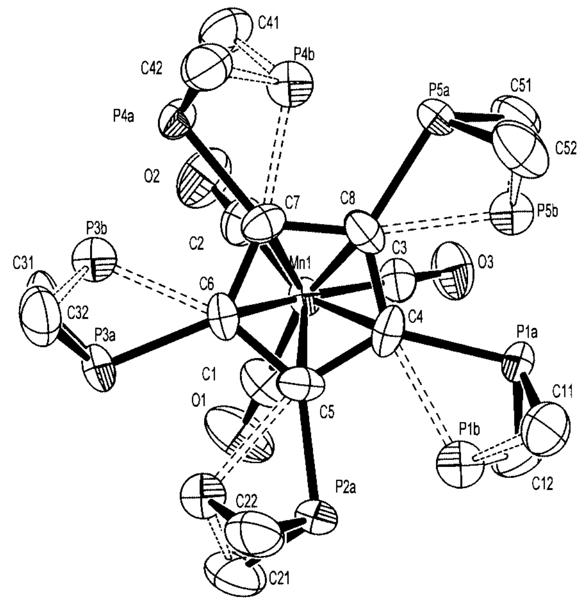


Fig. 1 Top view (ORTEP 3)[13] of molecule 1 of compound **4**, showing the disorder in the phosphorus positions. Averaged distances (in Å, molecules 1/2): Mn–C (cp) 2.150(2)/2.143(2); C–C 1.421(3)/1.417(3); P–C (cp) 1.874(3)/1.880(2).

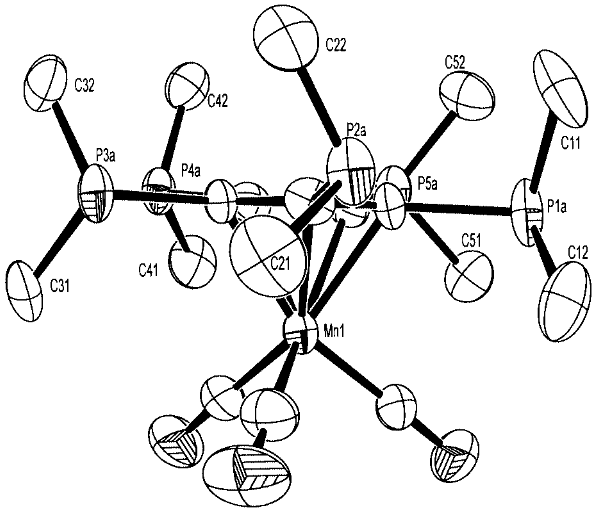


Fig. 2 Side view (ORTEP 3) of molecule 1 of compound **4**.

In conclusion, we could show that our concept of alternating stepwise lithium–halide exchange and electrophilic substitution, starting from pentahalogenocyclopentadienyl complexes, also works for the multiple introduction of phosphanyl substituents. Also with the synthesis of **4**, for the first time a pentaphosphane with local C_{5h}-symmetry could be prepared. Both complexes **3** and **4** may act as bis-chelating ligands and thus allow the synthesis of oligomeric or polymeric multimetallic co-ordination compounds. Preliminary experiments with **4** and complexes of Ni^0 or Pd^{II} resulted in the immediate precipitation of highly insoluble powders, indicating the ready formation of co-ordination polymers.

Table 2 Crystallographic data for compound **4**

Empirical formula	$C_{18}H_{30}MnO_3P_5$
Formula weight	504.21
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.519(2)
b/Å	14.653(3)
c/Å	17.505(4)
α/°	72.72(2)
β/°	89.84(2)
γ/°	79.68(2)
V/Å^3	2531.0(9)
Z	4
μ(Mo-Kα)/mm^{-1}	0.852
Reflections collected	9042
Independent reflections [R_{int}]	7255 [0.0287]
Data/parameters	7255/531
$R1$ [$I > 2\sigma(I)$]	0.0541
$wR2$ (all data)	0.1476

Experimental

The reactions were performed under nitrogen with freshly distilled solvents using standard Schlenk techniques. Compounds [$Mn(C_5Cl_4Br)(CO)_3$] **Ia** and [$Mn(C_5Br_5)(CO)_3$] **Ib** were prepared according to literature procedures,[17] PMe_2Cl was a generous gift from Professor A. Schmidpeter used in the form of an approximately 0.50 M solution prepared by dissolving 1.0 mL PMe_2Cl in 25.0 mL Et_2O. The other reagents were commercially available and used without further purification. The NMR spectra were obtained on a JEOL-GSX-270 spectrometer referenced either to residual solvent peaks (^1H, ^{13}C) or to external 85% H_3PO_4 (δ 0.00). IR spectra on a Nicolet-520-FT-IR spectrometer and mass spectra on a Finnigan MAT 90 spectrometer.

The structure determination was performed on a SYNTEX R3 diffractometer equipped with a Siemens P4 update. Data (Table 2) were collected by ω-scan technique, using Mo-Kα radiation with a graphite monochromator. The structure was refined by full matrix least squares methods using SHELXL 97-II.[18]

CCDC reference number 186/1699.

See http://www.rsc.org/suppdata/dt/1999/4299/ for crystallographic files in .cif format.

Preparations

Tricarbonyl[trichlorobis(diphenylphosphanyl)cyclopentadienyl]manganese, [$Mn(CO)_3\{C_5Cl_3(PPh_2)_2\}$ 1. A solution of 330 mg compound **Ia** (0.78 mmol) in 5 mL THF was treated with 4.87 mL of a 1.6 M ^{n}BuLi solution in hexane (7.8 mmol) at −78 °C. After stirring for five minutes the orange-red solution was treated with 20 mL cold (−78 °C) hexane, which resulted in an off-white precipitate. Stirring was stopped after ten minutes to allow the precipitate to settle. From this solid the supernatant solution was removed *via* a Teflon cannula using positive nitrogen pressure, and the residue washed twice with two *ca.* 25 mL portions of cold hexane, which were again removed *via* cannula. This procedure yields a rather pure sample of the dilithio complex **Ic**.

The (moist) residue of compound **Ic** was dissolved in 10 mL Et_2O and cooled to −78 °C. Addition of 0.28 mL PPh_2Cl (1.56 mmol) to this red solution resulted in a change to dark brown and precipitation of a beige powder. Stirring was continued for two hours at −78 °C, and the temperature then raised to ambient within 30 min. The precipitate formed was removed by centrifugation, and evaporation of the solvent *in vacuo* resulted in a yellow powder: **1** (285 mg, 54%). $C_{32}H_{20}Cl_3MnO_3P_2$ (calc./found): C, 56.9/57.1; H, 2.98/3.29%. ^1H NMR (C_6D_6, 270 MHz): δ 7.55–7.48 (m), 7.12–7.07 (m), 6.99–6.95 (m) (PC_6H_5, **1** + **1a**) and 4.13 (s) ($C_5\mathit{H}Cl_3PPh_2$, **1a**). ^{31}P NMR (C_6D_6, 109 MHz): δ −15.3 (**1a**) and −15.4 (**1**). ^{13}C NMR (C_6D_6, 100 MHz): δ 221.5 (MnCO), 134.3 (m), 129.6 (s), 128.9 (m) (PC_6H_5), 113.5 ("t") (J 5, CCl), 107.0 ("d") (J 22, C_2Cl_2), 87.3 (d) (J 40 Hz, $\mathit{C}PPh_2$) and 78.6 (s) (CH, **1a**).

Tricarbonyl[trichlorobis(diethylphosphanyl)cyclopentadienyl]manganese, [$Mn\{C_5Cl_3(PEt_2)_2\}(CO)_3$] 2. A solution of compound **Ic** in Et_2O was prepared as described above, however using only 250 mg of **Ia** (0.59 mmol) and 3.7 mL of BuLi solution (5.9 mmol); 0.14 mL PEt_2Cl (1.18 mmol) was added at −78 °C and the mixture stirred for 30 min at this temperature. After warming to room temperature, the precipitate formed was removed by filtration and the filtrate evaporated *in vacuo*. The light yellow precipitate was recrystallized several times by dissolving in the minimum amount of pentane and cooling to −18 °C. Compound **2** was isolated as a yellow powder (150 mg, 52%). $C_{16}H_{20}Cl_3MnO_3P_2$ (calc./found): C, 39.7/37.1; H, 4.16/4.31%. IR (ν(CO), pentane): 2037 and 1969 cm^{-1}. ^1H NMR (C_6D_6, 270 MHz): δ 4.17 (s) ($C_5\mathit{H}Cl_3PEt_2$, **2a**), 1.90–1.66 (m) ($PC\mathit{H}_2Me$, **2** + **2a**) and 1.03–0.88 (m) ($PCH_2C\mathit{H}_3$, **2** + **2a**). ^{31}P NMR (C_6D_6, 109 MHz): δ − 19.5 (s) (**2**) and −20.2 (s) (**2a**). ^{13}C NMR (C_6D_6, 100 MHz): δ 222.1 (MnCO), 114.4 ("t") (J 9, CCl, **2**), 107.1 ("d") (J 11, CCl, **2a**), 106.73 ("d") (J 16, C_2Cl_2, **2**), 106.69 ("d") (J 13, CCl, **2a**), 98.4 (s) (CCl, **2a**), 86.5 ("d") (J 46, $\mathit{C}PEt_2$, **2**), 85.2 ("d") (J 45, $\mathit{C}PEt_2$, **2a**), 78.7 (s) (CH, **2a**), 19.6 ("d")/18.7 ("d") (J 11/11, $P(\mathit{C}H_2Me)_2$, **2**), 19.3 ("d")/19.1 ("d") (J 10/10, $P(\mathit{C}H_2Me)_2$, **2a**), 10.9 ("d")/10.7 ("d") (J 19/18, $P(CH_2\mathit{C}H_3)_2$, **2**) and 10.8 ("d") (J 19 Hz, $P(CH_2\mathit{C}H_3)_2$, **2a**).

Tricarbonyl[tetrakis(dimethylphosphanyl)cyclopentadienyl]manganese [$Mn(CO)_3\{C_5H(PMe_2)_4\}$] 3 and tricarbonyl[pentakis(dimethylphosphanyl)cyclopentadienyl]manganese [$Mn\{C_5(PMe_2)_5\}(CO)_3$] 4. A solution of 1.00 g compound **Ib** (1.67 mmol) in 20 mL Et_2O was treated with 1.04 mL ^{n}BuLi solution (1.67 mmol) at −78 °C. After stirring for 30 min 3.63 mL PMe_2Cl solution (1.82 mmol) were added and the mixture was warmed to r.t. within 16 h. The resulting suspension was then cooled to −78 °C and treated with 2.08 mL BuLi solution (3.34 mmol) and 6.95 mL PMe_2Cl solution (3.48 mmol). After continuous stirring and warming to r.t. within 6 h the reaction mixture was again cooled to −78 °C and treated with 2.08 mL BuLi solution and 6.95 mL PMe_2Cl solution and warmed to r.t. within 16 h. Then the solvents were evaporated *in vacuo* and the residue was extracted with three 40 mL portions of pentane. The combined extracts were again evaporated *in vacuo*, and the remaining oil (507 mg) was examined by ^{31}P NMR. The spectrum showed a large number of signals, and therefore the residue was taken up in pentane and chromatographed in two portions (silica gel columns, 2.5 × 30 cm, pentane: Et_2O 20 : 1 as eluent) under nitrogen. The first fractions of each run were combined. Evaporation to dryness left 56 mg of a white microcrystalline solid **4** (7% yield). $C_{18}H_{30}MnO_3P_5$ (calc./found): C, 42.9/43.3; H, 6.00/6.02%. ^1H NMR (C_6D_6, 270 MHz): δ 1.63 (s, PCH_3). ^{31}P NMR (C_6D_6, 109 MHz): δ −49.6 (s, $C_5(PMe_2)_5$). ^{13}C NMR (C_6D_6, 67.9 MHz): δ 224.0 (s) (MnCO), 114.8 (m) ($\mathit{C}_5(PMe_2)_5$) and 14.5 (m) (PCH_3). HRMS: $\{[C_5(PMe_2)_5]Mn(CO)_3 - CH_3\}^+$ (calc./found) m/z 489.0029/489.0032.

Evaporation of the combined second fractions left 268 mg of an orange-yellow oil, which according to its ^{31}P NMR spectrum consisted mainly of compound **3** with 5–10% impurities. Recrystallization of this oil from pentane at −18 °C produced pure (according to ^{31}P NMR) **3** as solvent containing crystals, albeit in low yield. The crystals lose solvent upon removal of the mother liquid. On the other hand, the oily sticky nature of the vacuum dried residue did not allow the determination of the elemental analysis data. ^1H NMR (C_6D_6, 270 MHz): δ 4.99 (s) ($C_5\mathit{H}(PMe_2)_4$), 1.59 ("t") ($J = 4.7$, PCH_3), 1.52 ("t") ($J = 4.6$, PCH_3), 1.11 ("d") ($J = 4.8$, PCH_3) and 0.94 ("d") ($J = 4.5$ Hz, PCH_3). ^{31}P NMR (C_6D_6, 109 MHz): δ −48.4 (m) and −58.1 (m) (AA′XX′ system). HRMS: {[$C_5(PMe_2)_4H$]Mn-$(CO)_3$ − 3CO}$^+$ (calc./found) *m*/*z* 360.0287/360.0248.

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