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Comparison of the neutral benzyldiphenylphosphine complexes $C_6H_6Cr(CO)_2PPh_2Bz$ and $C_5H_5Mn(CO)_2PPh_2Bz$ with the isoelectronic manganiobenzyldiphenylphosphonium salts $[C_5R_5Mn(CO)(NO)PPh_2Bz]BF_4$ [1]

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Abstract

The photolytically or thermally induced substitution reactions of $C_6H_6Cr(CO)_3$, $C_5H_5Mn(CO)_3$ or $[C_5R_5Mn(CO)_2(NO)]BF_4$ (R = H, CH_3) with PPh_2Bz led to isoelectronic benzyldiphenylphosphine complexes of half sandwich type $C_6H_6Cr(CO)_2PPh_2Bz$ (**1**), $C_5H_5Mn(CO)_2PPh_2Bz$ (**2**), $[C_5H_5Mn(CO)(NO)(PPh_2Bz)]BF_4$ (**3a**) and $[C_5Me_5Mn(CO)(NO)(PPh_2Bz)]BF_4$ (**3b**). In contrast to the neutral compounds **1** and **2**, the phosphonium salts **3a**, **3b** can be deprotonated at the α-methylene group by bases such as DBU and LDA to give the neutral manganiodiphenylalkylidenephosphoranes $C_5R_5Mn(CO)(NO)(PPh_2{=}CHPh)$ (**4a**, **4b**). ^1H-, ^{13}C-, $^{31}P\{^1H\}$-NMR, IR and mass spectra of **1**–**4** are given. Crystals of **1** are orthorhombic, space group *Pbca*, with $a = 19.960(3)$, $b = 16.599(3)$ and $c = 14.573(3)$ Å, $Z = 8$ and $R = 0.0521$ for 2433 observed reflections. Crystals of **2** and **3a** are monoclinic, space group $P2_1/c$, with $a = 9.730(3)$, $b = 23.123(6)$ and $c = 9.784(3)$ Å, $Z = 4$ and $R = 0.0430$ for 2512 observed reflections for **2**, and $a = 12.457(3)$, $b = 10.597(3)$ and $c = 18.764(5)$ Å, $Z = 4$ and $R = 0.0477$ for 2765 observed reflections for **3a**.

Keywords: Crystal structures; Chromium complexes; Manganese complexes; Alkylidenephosphorane complexes

1. Introduction

Phosphines, because of their electronic and steric diversity, play an important role as ligands in organometallic chemistry, especially in the study of kinetic and thermodynamic effects, the tailoring of catalysts and the synthesis of clusters and colloids. Phosphine complexes are known of all transition metals in low and high oxidation states [1]. Most of the known examples are with a symmetric tertiary PR_3 ligand (R = alkyl, aryl) and/or a secondary phosphine PR_2H. Complexes with mixed ligands of the type $aryl_2Palkyl$ are less well investigated. We are interested in such complexes in connection with our investigations of organometallated phosphorus compounds which obey the isolobal concept. Using the complex fragment $CpFe(CO)_2$ (ferrio substituent Fp) we have synthesized the mono- and bis-metallated phosphonium salts $[FpPPh_2CH_2R]X$ [2] and $[Fp_2P(Ph)CH_2R]X$ [3], which were then deprotonated in the α-position of the alkyl substituent. Thus we expected to obtain mono- and bis-organometallated alkylidenephosphoranes, a new type of Wittig analogous phosphorus ylide.

The diferriophosphonium salts $[Fp_2P(Ph)CH_2R]X$ (R = Ph, COOEt, Me) can be deprotonated by KOtBu to give $Fp_2P(Ph){=}CHR$. Because of the two ferriosubstituents at the phosphorus atom they do not behave like Wittig analogous phosphorus ylides [4]. Instead, they behave like μ_2-bridged phosphaalkenes and preferentially cleave off the dimer Fp_2. Thus, the unstable phosphaalkenes PhP=CHR result, which in turn dimerize rapidly to give the corresponding 1,3-diphosphetanes [5].

The monoferriophosphonium salt $[FpPPh_2CH_2R]X$ (R = Ph) also reacts with KOtBu, which, however, attacks at the electrophilic carbonyl C-atom. Analogous to Hieber's base reaction [6] we observe elimination of CO_2 and 1 mol phosphine, as well as the formation of the corresponding metallate, which reacts with excess starting material to give the dimeric phosphine substituted complex $[CpFe(CO)$-

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[1] Dedicated to Professor Ivano Bertini, University of Florence, Italy.

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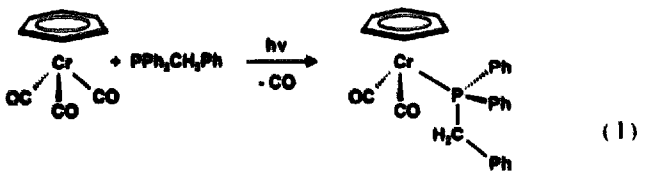
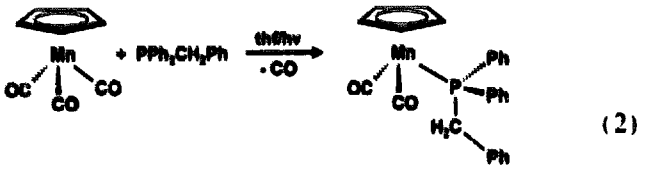
$(\mu\text{-CO})_2Fe(PPh_2Bz)Cp$ [7,8]. In the case of the ferriomethylphosphonium salt $[FpPPh_2Me]X$, the directed α-deprotonation reaction leads to the ferriosubstituted methylidenephosphorane $FpPPh_2{=}CH_2$, which could not be isolated, but which was spectroscopically characterized [2].

We were interested in extending our investigations by varying the organometallic complex fragment. Therefore, we wanted to synthesize the manganese salts $[C_5R_5Mn(NO)(CO)PPh_2CH_2Ph]X$, these being analogous to the iron salts $[CpFe(CO)_2PPh_2CH_2R]X$ [3,4,7] mentioned above, as well as the isoelectronic neutral complexes $C_6H_6Cr(CO)_2PPh_2Bz$ and $C_5H_5Mn(CO)_2PPh_2Bz$. The syntheses, properties and molecular structures (**1**, **2** and **3a**) of the new complexes are described as follows.



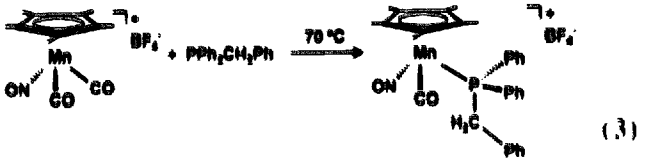
(1)

1



(2)

2



(3)

3a: C_5H_5, 3b: C_5Me_5

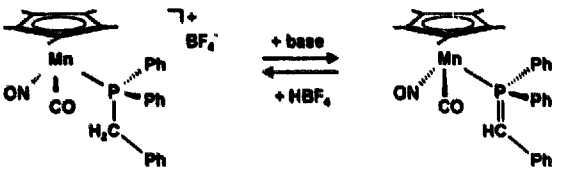
2. Results and discussion

2.1. Synthesis, spectra and properties

Benzyldiphenylphosphine reacts easily with the neutral and cationic half sandwich complexes $C_6H_6Cr(CO)_3$, $CpMn(CO)_3$ and $[C_5R_5Mn(CO)_2(NO)]BF_4$ (R = H, Me) to give the isoelectronic complexes $C_6H_6Cr(CO)_2PPh_2Bz$ (**1**) [9,11], $CpMn(CO)_2PPh_2Bz$ (**2**) [10] and $[C_5R_5Mn(CO)(NO)(PPh_2Bz)]BF_4$ (**3a**, **3b**) [11] in reasonable yields. The substitution reaction is induced by photolysis in the case of $C_6H_6Cr(CO)_3$ and $CpMn(CO)_3$ (Eqs. (1) and (2)) or by thermolysis in the case of the manganese salts $[C_5R_5Mn(CO)_2(NO)]BF_4$ (Eq. (3)).

The resulting yellow (**1**), orange–yellow (**2**) and red solids (**3a**, **3b**) are atmospherically stable. The neutral complexes **1** and **2** are soluble in THF, $CHCl_3$ and toluene, but insoluble in acetone and other polar solvents. On the other hand, the salts **3a**, **3b** are soluble in acetone and acetonitrile, but insoluble in toluene or other non-polar solvents.

Whereas the neutral benzylphosphine complexes of chromium and manganese **1** and **2** are highly stable against nucleophilic attack, the manganese salts **3a**, **3b** react with strong bases such as BuLi under decomposition. With weak nucleophiles like DABCO no reaction was observed. With bases like LDA or DBU, however, the directed α-deprotonation of **3a**, **3b** is observed at low temperatures (Eq. (4)), and the resulting neutral manganioalkylidenephosphoranes $C_5R_5Mn(CO)(NO)PPh_2{=}CHPh$ (**4a**, **4b**) are stable enough for spectroscopic investigations.



(4)

The IR, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR spectra and mass spectra of the compounds **1–3** were recorded (for details see Section 3). The spectra for both neutral compounds **1** and **2** are very similar, but both differ significantly from those of the cationic complexes **3a**, **3b**.

The IR spectra of **1** and **2** show two strong absorptions for $\nu(CO)$ between 1828 and 1931 cm^{-1}, that of **3a**, however, has a single absorption for $\nu(CO)$ at 2037 cm^{-1} and a single absorption for $\nu(NO)$ at 1801 cm^{-1}, the corresponding absorptions of **3b** are at 2011 and 1772 cm^{-1}.

The $^{31}P\{^1H\}$ NMR spectra of all four complexes **1–3a**, **3b** show only singlet signals. For the neutral compounds **1** and **2** they lie between 90 and 92 ppm; those of the salts **3a**, **3b** are found at higher field between 60.8 and 69.4 ppm, the same region as was found for the cation $[CpFe(CO)_2PPh_2Bz]^+$ (66.0 ppm) [7].

The data from the $^{13}C\{^1H\}$ NMR spectra of the comparable compounds **1–3a** are summarized in Table 1 and Fig. 1 together with those from the free PPh_2Bz ligand.

The CO ligands yield doublets at 240.0 ppm ($^1J_{PC}$ = 28.18 Hz) for **1** and at 232.2 ppm ($^1J_{PC}$ = 25.59 Hz) for **2**. **3a** is not stable enough in solution to detect any CO signal. The signals for all phenyl C-atoms of **1** and **2** show values of chemical shifts similar to the free benzyldiphenylphosphine ligand. Only the ipso-C atoms are significantly influenced by coordination, especially their $^1J_{PC(Ph)}$ coupling constants (**1** 139.4, 28.44 Hz; **2** 138.2, 35.07 Hz; **3a** 132.4, 14.21 Hz). The smaller values observed for **3a** result from the positive charge of the phosphonium cation. The corresponding $^2J_{PC(Bz)}$ values of the ipso-C atom of the benzyl substituent are smaller (**1** 135.3, 4.74 Hz; **2** 134.5, 3.79 Hz; **3a** 132.4, 2.84 Hz). The singlets for the C-atoms of the M-bonded aromatic ring ligands are detected at 89.7 ppm (C_6H_6) for **1**, 82.5 ppm (C_5H_5) for **2**, and more downfield at 96.5 ppm (C_5H_5) for **3a** because of its cationic character. The doublet signals for the methylene group lie consistently in the same

Table 1
$^{13}C\{^1H\}$ NMR data (δ (ppm), J (Hz) in parentheses)

PPh_2Bz	1	2	3a
	240.0 d, CO, (28.18)	232.2 d, CO, (25.59)	[a]
138.0 d, i-C_{Ph}, (15.48)	139.4 d, i-C_{Ph}, (28.44)	138.2 d, i-C_{Ph}, (35.07)	133.6 d, o-C_{Ph}, (9.48)
137.3 d, i-C_{Bz}, (8.11)	135.3 d, i-C_{Bz}, (4.74)	134.5 d, i-C_{Bz}, (3.79)	133.0 s, p-C_{Ph}
132.9 d, o-C_{Ph}, (18.43)	132.5 d, o-C_{Ph}, (10.43)	132.5 d, o-C_{Ph}, (9.48)	132.8 d, i-C_{Bz}, (2.84)
129.3 d, o-C_{Bz}, (6.63)	130.2 d, o-C_{Bz}, (3.79)	130.2 d, o-C_{Bz}, (4.74)	132.4 d, i-C_{Ph}, (14.21)
128.7 s, p-C_{Ph}	129.0 s, p-C_{Ph}	129.5 s, p-C_{Ph}	131.1 d, o-C_{Bz}, (4.74)
128.3 d, m-C_{Ph}, (6.64)	127.8 d, m-C_{Ph}, (8.53)	128.1 d, m-C_{Ph}, (8.53)	130.4 dd, m-C_{Ph}, (7.95)
128.2 d, p-C_{Bz}, (1.48)	127.7 s, p-C_{Bz}	127.9 s, p-C_{Bz}, (1.00)	129.6 d, p-C_{Bz}, (2.85)
125.8 d, m-C_{Bz}, (2.21)	126.0 s, m-C_{Bz}	126.4 s, m-C_{Bz}	128.6 d, m-C_{Bz}, (3.79)
	89.7 s, C_6H_6	82.5 s, C_5H_5	96.5 s, C_5H_5
35.9 d, CH_2, (14.74)	41.5 d, CH_2, (8.95)	41.3 d, CH_2, (22.75)	39.1 d, CH_2, (24.64)

[a] CO ligand not detectable.

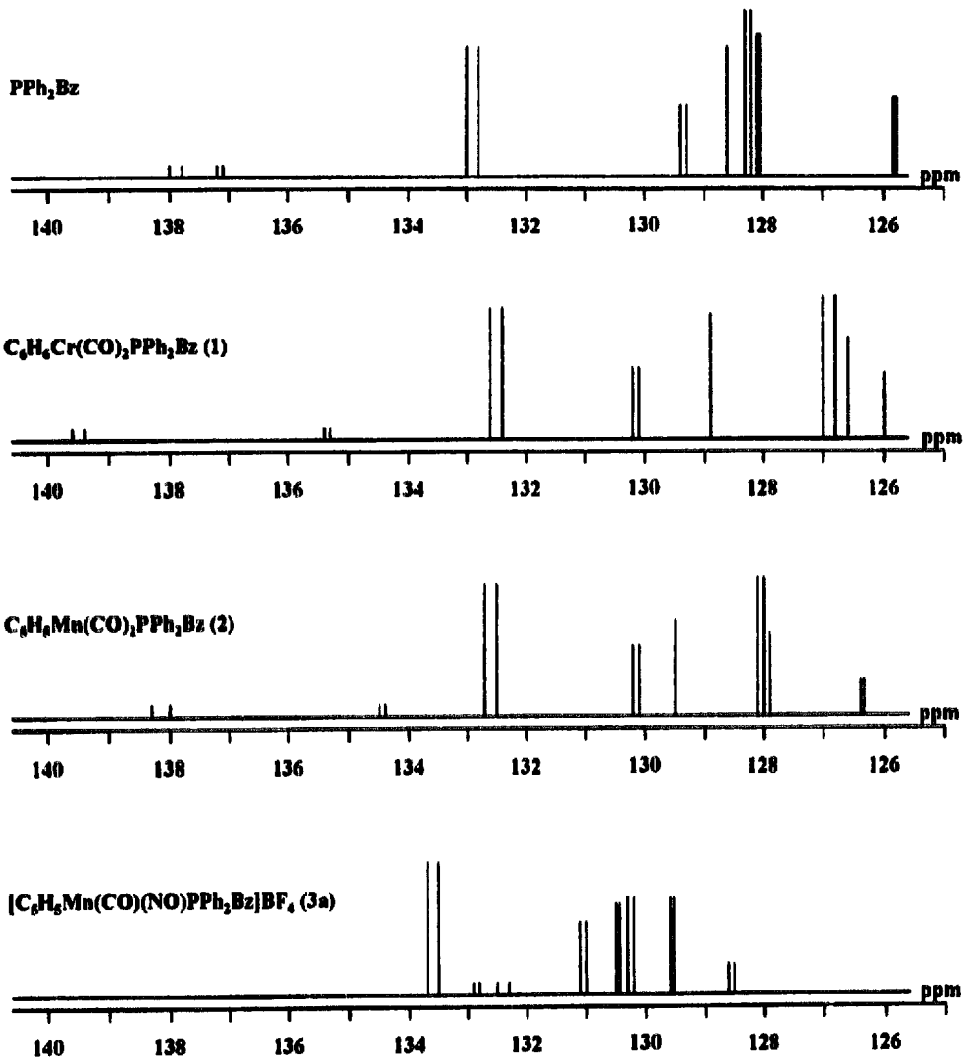


Fig. 1. $^{13}C\{^1H\}$ NMR signals of the phenyl groups in PPh_2Bz, free and coordinate in **1**, **2** and **3a**.

region, but show quite different $^1J_{PC}$ coupling constants (**1** 41.5, 8.98 Hz; **2** 41.3, 22.75 Hz; **3a** 39.1, 24.64 Hz).

The ^1H NMR spectra of **1–3** show an analogous pattern of signals. The phenyl protons are consistently found as broad multiplets within 6.49 and 7.70 ppm. Whereas the protons of the C_6H_6 and C_5H_5 ligands in **1** and **2** are detected at 4.57 or 4.17 ppm, the signal of the C_5H_5 protons in **3a** is shifted to 5.60 ppm; **3b** exhibits a signal for the methyl protons at 1.63 ppm. The protons of the methylene group give singlets at 3.63 (**1**) or 3.69 (**2**) ppm for the neutral derivatives, those of cationic **3a**, **3b** are again found significantly downfield at 4.34 and 3.86 ppm.

The mass spectra of **2**, **3a** and **3b** show the molecular peaks with 452 (M^+) for **2**, 454 (M^+) for **3a** and 524 (M^+) for **3b**. The further fragments in the spectra of the phosphonium salts **3a**, **3b** show clearly that CO is cleaved off before NO.

The $^{31}P\{^1H\}$ NMR spectra of the non-isolable neutral α-deprotonation products **4a**, **4b** show strong singlets at 82.4 and 78.5 ppm as well as a weak singlet at −8.4 ppm for the free PPh_2Bz ligand (in acetone-d6 or $CDCl_3$). No more signal from the starting materials **3a**, **3b** was observed. The addition of HBF_4 shows the reaction according to Eq. (4) is reversible.

In comparison with the corresponding phosphonium salts **3a**, **3b**, the new signals observed for the manganioalkylidenephosphoranes **4a**, **4b** are shifted 11–13 ppm downfield. This contrasts with our results obtained from the ferrio analogues where a similar high field shift is found [7]. This may be due to the different oxidation states of the metals in both complex fragments CpMn(CO)(NO) and $CpFe(CO)_2$.

The purely organic derivatives of P-ylides also show a downfield shift of their $^{31}P\{^1H\}$ NMR signals in comparison with the corresponding phosphonium salts [3].

2.2. *X-ray structure analyses of 1, 2 and 3a*

Suitable single crystals of the three compounds were obtained as follows: by dissolving the yellow residue of **1** in hot ethanol followed by addition of *n*-heptane, by dissolving the orange oil in *n*-hexane (for **2**), and by dissolving the red solid in dichloromethane followed by gradual addition of *n*-hexane (for **3a**).

The measuring and crystal data for the isoelectronic complexes **1**, **2** and **3a** are summarized in Table 2 and their atomic positional parameters in Tables 3–5; the BF_4^- anion of **3a** is disordered. Table 6 contains the most important bond lengths and angles. Figs. 2–4 show the molecular structures of the compounds **1**, **2** and **3a**.

In all three compounds the central metal atoms as well as the phosphine ligands have distorted tetrahedral configurations. The cyclic ligands C_6H_6 and C_5H_5 show an average M–C distance of 2.2148 Å for **1**, 2.1334 for **2**, and 2.1314 Å for **3a**. All carbonyl ligands and the nitrosyl ligand are linear (M–C–O or M–N–O ≈ 177.35°), the corresponding bond lengths M–C vary between 1.835(6) in **1**, 1.755(5) in **2**, and 1.719(4) Å in **3a**, whereas Mn1–N1 is 1.750(5) Å in **3a**. The metal–phosphorus distances vary from 2.4015(14) in the chromium(0) compound **1** to 2.2198(12) Å in the manganese(I) compound **2**, which is comparable with that of $CpMn(CO)PPh_3$ (2.236(3) Å) [12]. In **3a** the oxidation state of manganese is formally zero, so that the Mn1–P1 distance increases slightly to 2.2949(14) Å.

Table 2
Parameters used for the X-ray data collection

Identification code	1	2	3a
Empirical formula	$C_{23}H_{21}CrO_2P$	$C_{26}H_{22}MnO_2P$	$C_{25}H_{23}BF_4MnNO_3P$
Formula weight	462.42	452.35	541.15
Diffractometer	Enraf-Nonius-CAD4	Enraf-Nonius-CAD4	Enraf-Nonius-CAD4
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	*P21/c*	*P21/c*
Unit cell dimensions			
a (Å)	19.960(3)	9.730(3)	12.457(3)
b (Å)	16.599(3)	23.123(6)	10.597(2)
c (Å)	14.573(3)	9.784(3)	18.764(5)
α (°)	90.00(2)	90.00(2)	90.00(2)
β (°)	90.00(2)	94.82(2)	101.92(2)
γ (°)	90.00(2)	90.00(2)	90.00(2)
Volume (Å^3)	4828.6(14)	2193.6(12)	2423.5(10)
Z	8	4	4
Density (calculated) (Mg m^{-3})	1.272	1.370	1.483
Absorption coefficient (mm^{-1})	0.560	0.694	0.640
F(000)	1920	936	1104
Crystal size (mm)	0.07×0.50×0.53	0.13×0.33×0.53	0.13×0.46×0.53
θ range (°)	2.04–22.96	2.10–22.97	2.22–23.00
Index ranges	$0 \le h \le 20, 0 \le k \le 18, 0 \le l \le 16$	$0 \le h \le 10, 0 \le k \le 25, -10 \le l \le 10$	$0 \le h \le 13, 0 \le k \le 11, -20 \le l \le 20$
Reflections collected	3184	3250	3368
Independent reflections	3184 (R_{int} = 0.0000)	3046 (R_{int} = 0.0566)	3368 (R_{int} = 0.0000)
Absorption correction	Semi-empirical from psi-scans	Semi-empirical from psi-scans	Semi-empirical from psi-scans
Max. and min. transmission	0.9987 and 0.9462	0.9954 and 0.8548	0.9999 and 0.7911
Data/restraints/parameters	3184/0/280	3046/0/271	3368/55/345
Gof	1.155	1.127	0.671
Final *R* indices ($I > 2\sigma(I)$)	$R1 = 0.0521$, $wR2 = 0.1224$	$R1 = 0.0430$, $wR2 = 0.1149$	$R1 = 0.0477$, $wR2 = 0.1454$
R indices (all data)	$R1 = 0.0761$, $wR2 = 0.1324$	$R1 = 0.0557$, $wR2 = 0.1338$	$R1 = 0.0591$, $wR2 = 0.1570$
Largest diff. peak/hole (e Å^{-3})	0.262/−0.273	0.322/−0.265	0.358/−0.328

Table 3
Final atomic coordinates ($\times 10^4$) and displacement parameters (in $Å^2 \times 10^3$) of **1**

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr(1)	912(1)	1999(1)	7311(1)	47(1)	55(1)	47(1)	−12(1)	−2(1)	6(1)
P(1)	−236(1)	2323(1)	6979(1)	44(1)	45(1)	38(1)	−5(1)	1(1)	1(1)
O(1)	928(2)	1199(2)	5483(2)	103(3)	70(2)	47(2)	−16(2)	13(2)	12(2)
O(2)	1404(2)	3463(3)	6306(3)	87(3)	81(3)	115(3)	5(3)	3(3)	−26(2)
C(1)	926(2)	1513(3)	6200(3)	52(3)	50(3)	57(3)	1(2)	6(2)	3(2)
C(2)	1208(3)	2903(3)	6711(4)	51(3)	71(4)	72(4)	−18(3)	0(3)	−5(3)
C(3)	749(4)	988(4)	8246(5)	119(6)	94(5)	72(4)	30(4)	−37(4)	−18(5)
C(4)	1431(4)	943(4)	7866(4)	127(6)	74(4)	77(4)	−16(3)	−35(4)	47(4)
C(5)	1893(3)	1565(5)	7948(4)	65(4)	123(6)	83(4)	−14(4)	−23(3)	32(4)
C(6)	1681(4)	2255(4)	8384(5)	97(5)	99(5)	90(5)	−15(4)	−51(4)	−4(4)
C(7)	1023(4)	2306(5)	8772(4)	119(6)	111(5)	56(4)	−28(4)	−27(4)	49(5)
C(8)	555(4)	1684(6)	8688(4)	81(5)	161(7)	46(3)	15(4)	−9(3)	28(5)
C(9)	−344(2)	2752(3)	5809(3)	55(3)	54(3)	43(3)	−1(2)	5(2)	−4(2)
C(10)	−1032(2)	3128(3)	5544(3)	62(3)	54(3)	33(2)	2(2)	−2(2)	−2(3)
C(11)	−1139(3)	3946(3)	5660(4)	89(4)	58(3)	78(4)	−5(3)	−28(3)	0(3)
C(12)	−1774(4)	4297(4)	5424(4)	125(6)	65(4)	88(4)	−7(3)	−28(4)	33(4)
C(13)	−2294(3)	3845(4)	5051(4)	78(4)	112(5)	61(3)	2(3)	−11(3)	36(4)
C(14)	−2196(3)	3045(4)	4923(3)	64(4)	98(4)	62(3)	8(3)	−6(3)	−6(3)
C(15)	−1573(2)	2689(3)	5170(3)	68(3)	63(3)	48(3)	0(2)	−5(3)	−3(3)
C(16)	−814(2)	1439(2)	6997(3)	45(3)	46(2)	41(2)	−2(2)	−2(2)	7(2)
C(17)	−847(2)	933(3)	6238(3)	68(3)	52(3)	43(3)	−6(2)	3(2)	−5(3)
C(18)	−1202(3)	212(3)	6275(4)	86(4)	52(3)	67(3)	−12(3)	−11(3)	−5(3)
C(19)	−1524(3)	−31(3)	7066(4)	90(4)	50(3)	80(4)	3(3)	−7(3)	−16(3)
C(20)	−1489(3)	450(3)	7828(4)	82(4)	61(3)	61(3)	10(3)	10(3)	−10(3)
C(21)	−1141(2)	1179(3)	7796(3)	73(3)	51(3)	46(3)	−5(2)	1(2)	2(3)
C(22)	−708(2)	3069(2)	7679(3)	51(3)	40(2)	40(2)	2(2)	0(2)	2(2)
C(23)	−325(2)	3661(3)	8124(3)	55(3)	48(3)	61(3)	−8(2)	−1(2)	2(2)
C(24)	−657(3)	4251(3)	8629(4)	87(4)	47(3)	67(3)	−17(3)	−4(3)	1(3)
C(25)	−1378(3)	4253(3)	8695(3)	90(4)	52(3)	56(3)	−7(2)	17(3)	17(3)
C(26)	−1765(3)	3686(3)	8252(3)	56(3)	62(3)	66(3)	5(3)	16(3)	9(3)
C(27)	−1435(2)	3092(3)	7742(3)	51(3)	51(3)	55(3)	−3(2)	3(2)	−1(2)

The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}]$.

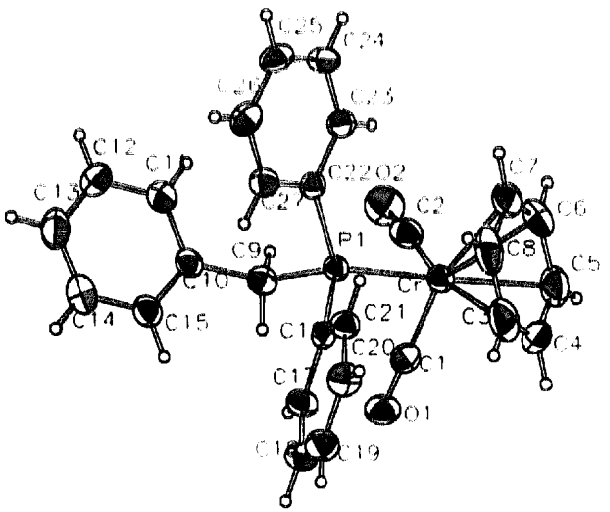


Fig. 2. Molecular structure of **1**.

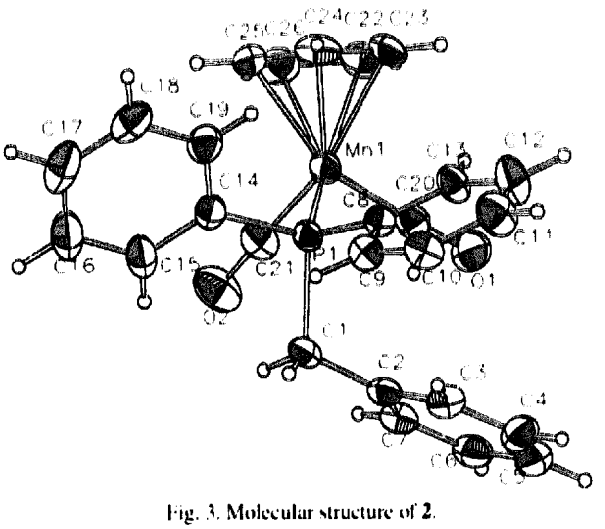


Fig. 3. Molecular structure of **2**.

Because of the steric influence of the benzyl substituent on the phosphorus atom, the corresponding angles C(N)–M–P at the central metal atoms are quite different (**1**, C1–Cr1–P1 86.3(2), C2–Cr1–P1 91.6(6)°; **2**, C21–Mn1–P1 88.88(14), C20–Mn1–P1 96.30(4)°; **3a**, N1–Mn1–P1 88.91(14), C6–Mn1–P1 98.1(2)°).

Looking at the methylene group of the benzyl substituent, the corresponding P–CH_2 distances of **1** (1.860(4) Å) and **2** (1.859(4) Å) are almost identical, whereas that of **3a** is somewhat shorter owing to the positive charge at the phosphorus atom. One should not forget that **3a** is a manganiophosphonium cation and is thus comparable with ferrio-

Table 4
Final atomic coordinates ($\times 10^4$) and displacement parameters (in $Å^2 \times 10^3$) of **2**

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn(1)	7981(1)	521(1)	1630(1)	48(1)	36(1)	52(1)	−4(1)	2(1)	2(1)
P(1)	6995(1)	1242(1)	2683(1)	43(1)	35(1)	45(1)	−4(1)	3(1)	−1(1)
O(1)	6130(5)	484(1)	−873(4)	136(4)	57(2)	86(3)	−17(2)	−46(3)	2(2)
O(2)	9832(4)	1357(2)	507(4)	82(2)	75(2)	120(3)	1(2)	48(2)	−7(2)
C(1)	6711(4)	1935(2)	1740(4)	50(2)	35(2)	59(2)	2(2)	10(2)	−3(2)
C(2)	5672(4)	1894(2)	523(4)	57(2)	30(2)	50(2)	3(2)	4(2)	3(2)
C(3)	4259(5)	1912(2)	670(5)	66(3)	57(3)	54(3)	8(2)	9(2)	9(2)
C(4)	3304(5)	1852(2)	−436(5)	56(3)	71(3)	73(3)	11(3)	−3(2)	8(2)
C(5)	3729(5)	1782(2)	−1720(5)	77(3)	57(3)	64(3)	4(2)	−9(3)	−3(2)
C(6)	5105(5)	1774(2)	−1904(5)	94(4)	48(2)	51(3)	7(2)	7(3)	−4(2)
C(7)	6073(5)	1832(2)	−782(4)	68(3)	41(2)	56(3)	4(2)	13(2)	3(2)
C(8)	5288(4)	1143(2)	3281(4)	45(2)	42(2)	43(2)	3(2)	4(2)	−1(2)
C(9)	4711(4)	1552(2)	4115(4)	57(3)	55(2)	47(2)	−4(2)	10(2)	0(2)
C(10)	3367(5)	1515(2)	4434(4)	68(3)	56(3)	61(3)	−3(2)	24(2)	4(2)
C(11)	2569(5)	1055(2)	3948(6)	57(3)	75(3)	104(4)	−4(3)	31(3)	−4(3)
C(12)	3114(5)	641(2)	3147(6)	60(3)	76(3)	105(4)	−20(3)	16(3)	−22(3)
C(13)	4468(4)	686(2)	2823(5)	54(3)	43(2)	74(3)	−10(2)	13(2)	−4(2)
C(14)	8014(4)	1485(2)	4254(4)	47(2)	43(2)	55(2)	−12(2)	−1(2)	8(2)
C(15)	9023(4)	1899(2)	4211(5)	53(3)	64(3)	78(3)	−16(2)	−3(2)	−11(2)
C(16)	9835(5)	2055(3)	5383(7)	60(3)	81(4)	110(5)	−29(3)	−13(3)	−9(3)
C(17)	9652(6)	1783(3)	6602(6)	66(3)	101(4)	83(4)	−36(3)	−22(3)	22(3)
C(18)	8664(6)	1370(2)	6660(5)	81(3)	79(3)	55(3)	−7(2)	−10(2)	24(3)
C(19)	7827(5)	1221(2)	5514(4)	69(3)	61(3)	53(3)	−4(2)	−5(2)	1(2)
C(20)	6838(5)	527(2)	143(5)	72(3)	39(2)	61(3)	−9(2)	1(2)	2(2)
C(21)	9097(5)	1025(2)	957(5)	57(3)	49(3)	71(3)	−9(2)	22(2)	5(2)
C(22)	8386(5)	−377(2)	1355(6)	80(4)	38(2)	90(4)	−9(2)	4(3)	13(2)
C(23)	7337(5)	−322(2)	2243(6)	65(3)	33(2)	110(4)	13(3)	−1(3)	−4(2)
C(24)	7894(6)	−17(2)	3397(5)	101(4)	44(3)	69(3)	13(2)	15(3)	13(3)
C(25)	9279(5)	115(2)	3201(6)	76(3)	48(3)	90(4)	16(3)	−28(3)	−1(2)
C(26)	9554(5)	−114(2)	1936(6)	62(3)	60(3)	103(4)	9(3)	9(3)	16(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

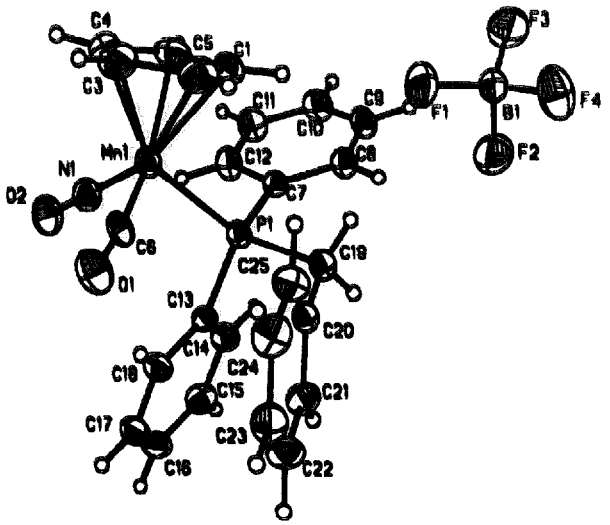


Fig. 4. Molecular structure of **3a**.

phosphonium salts, which we have already discussed [7]. It is remarkable that all P–C distances in **1** are of identical length (within the range 1.860(4) and 1.867(4) Å). In **2** and **3a** the corresponding P–C_{Ph} bonds (**2** 1.847(4) and 1.820(4) Å; **3a** 1.816(4) and 1.818(4) Å) differ from the P–CH_2 bonds (**2** 1.859 Å; **3a** 1.839(4) Å). The difference between **1** and **2**, **3a** is also observed for the CH_2–C_{ipso} distances (**1** 1.558(6), in comparison with **2** 1.499(5), and **3a** 1.511(5) Å).

3. Experimental

All operations were carried out under Ar atmosphere and all solvents were dried according to known methods. PPh_2Bz [11,13], $C_6H_6Cr(CO)_3$ [14], $[C_5H_5Mn(CO)_2(NO)]BF_4$ [15] and $[C_5Me_5Mn(CO)_2(NO)]BF_4$ [11] were synthesized as published and $CpMn(CO)_3$ was purchased from Strem. $C_5Me_5Mn(CO)_3$ was a gift of Professor Dr E. Lindner, University of Tübingen. A 150 W Hg high pressure lamp (Original Quarzlampen GmbH, Hanau) was used for the photolytic reactions. $^{31}P\{^1H\}$ (109.36 MHz), $^{13}C\{^1H\}$ (100.53 MHz) and ^1H (270.16 MHz) NMR spectra were recorded on a Jeol GSX270 spectrometer at 21°C. IR spectra were recorded on a Nicolet 520FT-IR (Nicolet Instrument GmbH) and mass spectra on a MAT 711A (Varian).

3.1. Synthesis of η^6-$C_6H_6Cr(CO)_2PPh_2Bz$ (1)

1.00 g (4.67 mmol) $C_6H_6Cr(CO)_3$ and 1.28 g (4.67 mmol) PPh_2Bz in 120 ml benzene were rapidly stirred and

Table 5
Final atomic coordinates ($\times 10^4$) and displacement parameters (in $Å^2 \times 10^3$) of **3a**

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn(1)	2971(1)	893(1)	6452(1)	55(1)	50(1)	58(1)	−2(1)	13(1)	7(1)
P(1)	2209(1)	2373(1)	5604(1)	39(1)	43(1)	57(1)	−5(1)	16(1)	−1(1)
O(1)	4865(3)	178(4)	5904(2)	64(2)	92(3)	128(3)	−19(2)	26(2)	16(2)
O(2)	1576(3)	−1027(3)	5640(2)	83(2)	67(2)	109(3)	−16(2)	11(2)	−23(2)
N(1)	2124(3)	−265(4)	5963(2)	70(3)	63(3)	81(3)	1(2)	25(2)	2(2)
C(1)	2818(5)	2248(5)	7278(3)	117(5)	65(3)	53(3)	−10(3)	11(3)	14(3)
C(2)	2118(5)	1256(6)	7299(3)	87(4)	105(5)	62(3)	−8(3)	27(3)	11(3)
C(3)	2758(6)	156(6)	7458(3)	145(6)	71(4)	69(3)	9(3)	42(4)	1(4)
C(4)	3840(6)	497(7)	7531(3)	107(5)	114(5)	67(3)	13(3)	2(3)	37(4)
C(5)	3874(5)	1798(7)	7414(3)	94(4)	111(5)	58(3)	−4(3)	−4(3)	−19(4)
C(6)	4094(3)	519(4)	6095(2)	38(2)	50(2)	72(3)	−14(2)	10(2)	10(2)
C(7)	941(3)	2978(4)	5809(2)	40(2)	47(2)	55(2)	−1(2)	15(2)	5(2)
C(8)	821(3)	4212(4)	5990(2)	49(2)	54(3)	70(3)	−4(2)	17(2)	2(2)
C(9)	−130(4)	4603(5)	6205(3)	68(3)	57(3)	93(3)	−10(3)	29(3)	17(2)
C(10)	−959(4)	3767(5)	6217(3)	50(3)	84(4)	97(4)	−8(3)	32(2)	14(2)
C(11)	−846(4)	2547(5)	6041(3)	48(3)	76(3)	112(4)	−9(3)	33(3)	−9(2)
C(12)	91(3)	2135(4)	5831(3)	41(2)	56(3)	95(3)	−7(2)	22(2)	−3(2)
C(13)	1823(3)	1753(4)	4684(2)	48(2)	50(2)	53(2)	0(2)	18(2)	−7(2)
C(14)	834(4)	2069(4)	4234(2)	58(3)	66(3)	60(3)	1(2)	14(2)	1(2)
C(15)	573(4)	1610(5)	3526(3)	68(3)	86(3)	58(3)	1(3)	1(2)	−13(3)
C(16)	1288(5)	830(5)	3271(3)	96(4)	79(3)	58(3)	−13(2)	29(3)	−21(3)
C(17)	2273(4)	526(5)	3712(3)	77(3)	70(3)	67(3)	−13(2)	30(3)	−2(2)
C(18)	2538(4)	971(4)	4412(2)	61(65(3)	65(3)	60(3)	−5(2)	20(2)	5(2)
C(19)	3022(3)	3789(4)	5510(3)	50(2)	52(2)	75(3)	−7(2)	23(2)	−6(2)
C(20)	4108(3)	3491(4)	5308(2)	45(2)	46(2)	70(3)	−5(2)	22(2)	−8(2)
C(21)	4203(4)	3448(5)	4597(3)	53(3)	77(3)	71(3)	9(2)	19(2)	−6(2)
C(22)	5202(4)	3168(5)	4419(3)	67(3)	95(4)	84(3)	−2(3)	40(3)	−8(3)
C(23)	6099(4)	2931(5)	4948(3)	56(3)	80(3)	115(4)	1(3)	44(3)	−3(2)
C(24)	6016(4)	2969(5)	5660(3)	42(2)	94(4)	107(4)	8(3)	15(3)	−6(2)
C(25)	5027(4)	3261(5)	5843(3)	52(3)	85(3)	71(3)	−12(3)	12(2)	−16(2)
F(1)	3236(3)	5394(3)	7207(2)	144(3)	71(2)	135(3)	8(2)	43(2)	22(2)
F(2)	2390(8)	6685(7)	6404(3)	177(8)	115(5)	89(4)	9(3)	−2(5)	−31(5)
F(3)	2167(8)	6912(8)	7530(5)	156(9)	114(5)	152(7)	7(5)	111(7)	17(5)
F(4)	3697(5)	7474(6)	7219(6)	78(4)	96(4)	188(10)	−35(6)	29(5)	−20(3)
F(2A)	3374(13)	7050(13)	7819(7)	129(11)	139(10)	94(9)	−38(8)	−2(8)	−26(8)
F(3A)	3193(17)	7251(15)	6660(10)	203(19)	136(14)	139(13)	78(12)	131(13)	55(13)
F(4A)	1794(8)	6620(16)	7105(12)	53(6)	145(12)	211(19)	−44(12)	23(9)	5(6)
B(1)	2881(4)	6599(5)	7134(3)	73(4)	53(3)	69(4)	−2(3)	18(3)	−2(3)

The unisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Table 6
Selected bond lengths (Å) and angles (°)

1		**2**		**3a**	
Cr(1)–C(1)	1.809(5)	Mn(1)–C(20)	1.755(5)	Mn(1)–C(6)	1.719(4)
Cr(1)–C(2)	1.835(6)	Mn(1)–C(21)	1.759(5)	Mn(1)–N(1)	1.750(5)
Cr(1)–P(1)	2.4015(14)	Mn(1)–P(1)	2.2198(12)	Mn(1)–P(1)	2.2949(14)
P(1)–C(9)	1.860(4)	P(1)–C(1)	1.859(4)	P(1)–C(19)	1.839(4)
P(1)–C(22)	1.860(4)	P(1)–C(8)	1.820(4)	P(1)–C(13)	1.816(4)
P(1)–C(16)	1.867(4)	P(1)–C(14)	1.847(4)	P(1)–C(7)	1.818(4)
C(9)–C(10)	1.558(6)	C(1)–C(2)	1.499(5)	C(19)–C(20)	1.511(5)
Cr(1)–C(1)–O(1)	179.3(4)	Mn(1)–C(21)–O(2)	179.7(5)	Mn(1)–N(1)–O(2)	179.4(4)
Cr(1)–C(2)–O(2)	177.8(5)	Mn(1)–C(20)–O(1)	173.9(4)	Mn(1)–C(6)–O(1)	173.5(4)
C(1)–Cr(1)–C(2)	86.2(2)	C(20)–Mn(1)–C(21)	93.0(2)	C(6)–Mn(1)–N(1)	94.8(2)
C(1)–Cr(1)–P(1)	86.3(2)	C(21)–Mn(1)–P(1)	88.88(14)	N(1)–Mn(1)–P(1)	88.91(14)
C(2)–Cr(1)–P(1)	91.6(6)	C(20)–Mn(1)–P(1)	96.30(14)	C(6)–Mn(1)–P(1)	98.1(2)
C(9)–P(1)–Cr(1)	112.4(2)	C(1)–P(1)–Mn(1)	118.00(14)	C(19)–P(1)–Mn(1)	117.8(2)

photolysed for 3 h. A yellow oil formed, was separated, washed with 140 ml benzene and taken up in 50 ml hot ethanol. After filtration and addition of *n*-heptane to the ethanol solution, yellow crystals were obtained in 42% yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 3.63 (s, CH_2), 4.57 (s, C_6H_6), 6.58–7.52 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 90.05 (s). IR (KBr): ν 1887 (sst, CO), 1828 (sst, CO). *Anal.* Calc. for $C_{27}H_{23}CrO_2P$: C, 70.58; H, 5.05. Found: C, 69.19; H 5.11%.

3.2. Synthesis of η^5-$C_5H_5Mn(CO)_2PPh_2Bz$ (2)

A solution of 0.61 g (3.00 mmol) $C_5H_5Mn(CO)_3$ in 320 ml THF was photolysed for 3 h, then 0.83 g (3.00 mmol) PPh_2Bz was added to the red solution under rapid stirring. The resulting yellow–brown solution was reduced after 1 h by evaporation to obtain a brown solid, which was filtered off. The solvent of the now red solution was removed in vacuo to give an orange oil, which crystallized from 30 ml *n*-hexane as an orange solid. Yield: 63.1%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 3.69 (s, CH_2), 4.17 (s, Cp), 6.63–7.52 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 92.21 (s). IR (KBr): ν 1931 (sst, CO), 1863 (sst, CO). MS (FAB): m/z = 452 (M^+). *Anal.* Calc. for $C_{26}H_{22}MnO_2P$: C, 69.03; H, 4.90. Found: C, 68.70; H 4.98%.

3.3. Synthesis of $[\eta^5$-$C_5H_5Mn(CO)(NO)(PPh_2Bz)]^+ BF_4^-$ (3a)

A solution of 0.52 g (1.80 mmol) $[C_5H_5Mn(CO)_2(NO)]BF_4$ and 0.70 g (2.50 mmol) PPh_2Bz in 25 ml methanol was refluxed for 2 h after which the originally light brown solution turned red. The solvent was removed in vacuo at room temperature to give an orange oil which was dissolved in CH_2Cl_2. Addition of hexane precipitated red crystals. Yield: 73%. ^{1}H NMR (acetone-d6, Me_4Si): δ 4.34 (m, CH_2), 5.60 (s, Cp), 6.81–7.70 (m, Ph). $^{31}P\{^1H\}$ NMR (acetone/CD_3CN): δ 69.40 (s). IR (KBr): ν 2037 (sst, CO), 1801 (sst, NO). MS (FAB): m/z = 454 (M^+), 426 (M^+-CO), 396 (M^+-CO-NO). *Anal.* Calc. for $C_{25}H_{22}BF_4MnNO_2P$: C, 55.49; H, 4.09; N, 2.59. Found: C, 54.96; H 3.99; N, 2.54%.

3.4. Synthesis of $[\eta^5$-$C_5Me_5Mn(CO)(NO)(PPh_2Bz)]^+ BF_4^-$ (3b)

The preparation was as described in Section 3.3; an orange solid formed. Yield: 75%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.63 (s, CH_3), 3.86 (m, CH_2), 6.81–7.70 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.80 (s). IR (KBr): ν 2011 (sst, CO), 1772 (sst, NO). MS (FAB): m/z = 524 (M^+), 496 (M^+-CO), 466 (M^+-CO-NO). *Anal.* Calc. for $C_{30}H_{32}BF_4MnNO_2P$: C, 58.94; H, 5.27; N, 2.29. Found: C, 57.61; H 5.42; N, 2.21%.

3.5. Synthesis of η^5-$C_5H_5Mn(CO)(NO)PPh_2CHPh$ (4a)

One drop of DBU added to the orange–red solution of 0.02 g (0.006 mmol) **3a** in 0.4 ml acetone-d6 at −50°C immediately changed the colour to deep red. $^{31}P\{^1H\}$ NMR δ 82.4 (s); no isolation and no further characterization.

3.6. Synthesis of $\eta^5C_5Me_5Mn(CO)(NO)PPh_2CHPh$ (4b)

The same procedure was used as described in Section 3.5; again a deep red solution formed. $^{31}P\{^1H\}$ NMR δ 78.5 (s); no isolation and no further characterization

4. Supplementary material

Further details of the three crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information, D-76344 Eggenstein-Leopoldshafen on quoting the depository number CSD 406719, CSD 406720 and CSD 406721 the names of the authors, and the journal citation.

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