# 1,3-Distanna-2-phospha-[3]ferrocenophanes - Synthesis, Reactivity and NMR Spectroscopic Properties

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1,1,3,3-Tetramethyl-2-organo(R)-1,3-distanna-2-phospha-[3]ferrocenophanes [R = Me (2a), <sup>*i*</sup>Bu (2b), C<sub>6</sub>H<sub>11</sub> (2c), Ph (2d)] and one arsa-analogue 2d(As) were obtained from the reaction of 1,1'-bis(chlorodimethylstannyl)ferrocene 1 with either bis(trimethylsilyl)methylphosphane or the dilithio derivatives, Li<sub>2</sub>PR and Li<sub>2</sub>AsPh, respectively. All compounds 2 react with chalcogens (oxygen, sulfur, selenium) by cleavage of the Sn-P bonds and formation of the known 1,3-distanna-2-chalcogena-[3]ferrocenophanes. In contrast, 2d traps pentacarbonylmetal fragments [M(CO)<sub>5</sub>] to give the stable phosphane complexes [M = Cr (4d), Mo (5d), W (6d)]. The 1,1'-bis(diorganophosphanostannyl)ferrocenes [R = <sup>*i*</sup>Bu (3b), Ph (3d)] were prepared for comparison of NMR data. The ferrocenophanes 2 are fluxional with respect to fast movement of the cyclopentadienyl rings which induces inversion at the pyramidal phosphorus atom. This dynamic process is slow in the cases of 2d(As) and of the pentacarbonyl complexes 4d - 6d. All new compounds were characterised by <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>119</sup>Sn NMR spectroscopy. Various 2D heteronuclear shift correlations (*e.g.* <sup>31</sup>P/<sup>1</sup>H and <sup>119</sup>Sn/<sup>1</sup>H) were carried out for the compounds 2 and also for non-cyclic derivatives such as bis(trimethylstannyl)phenylphosphane and <sup>2</sup>J(<sup>119</sup>Sn,<sup>117</sup>Sn) < 0]. The NMR data suggest that the molecular frameworks of the ferrocenophanes 2 are not particularly strained.

### 1. Introduction

Ferrocenophanes [1] containing tin atoms in the bridge are of considerable interest owing to both the reactivity of tin-element bonds and the stabilising effect of the rather rigid and bulky 1,1'-ferrocenediyl group. Thus, 1-stanna-[1]ferrocenophane undergoes ring-opening polymerisation [2, 3], and, as a result of the strained structure, transition metal fragments insert into one of the Sn-C(1) bonds [3]. 1,2-Distanna-[2]ferrocenophane [4] reacts with Pt(0) fragments by oxidative addition to give 1,3-distanna-2-platina-[3] ferrocenophanes [5, 6], which can be regarded as model compounds for the catalytic distannation of alkynes [7, 8]. Chalcogens readily insert into the Sn-Sn bonds of both 1,2-distanna-[2] ferrocenophane [9] and 1,2,3-tristanna-[3] ferrocenophane [10]. In the present report we now describe the synthesis and reactivity of the first 1,3distanna-2-phospha-[3]ferrocenophanes and of a 1,3-distanna-2-arsa-[3]ferrocenophane. In addition to their promising ligand properties, the phosphorus compounds, in particular, are of interest with respect to their NMR spectroscopic features considering the presence of several magnetically active nuclei such as <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>117</sup>Sn and <sup>119</sup>Sn.

#### 2. Results and Discussion

2.1. Synthesis and reactivity of 1,3-distanna-2-phospha-[3]ferrocenophanes

The synthetic approach is outlined in Scheme 1 which also reveals information on the reactivity of 1,3-distanna-2-phospha-[3]ferrocenophanes. 1,1'-Bis(chlorodimethylstannyl)ferrocene 1 [11, 12] appears to be a most convenient starting material for the synthesis of various ferrocenophanes containing at least two tin atoms attached to the ferrocene unit [4, 9]. The salt elimination reaction of 1 with various dilithiophosphanes affords the compounds  $2\mathbf{b} \cdot \mathbf{d}$  in moderate to good yields.

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Scheme 1.

The arsenic derivative 2d(As) was prepared in the same way, using dilithio(phenyl)arsane. An alternative route is available via the reaction of 1 with bis(trimethylsilyl)methylphosphane which leads to 2a by cleavage of the P-Si bonds and elimination of two equivalents of Me<sub>3</sub>SiCl. The reactions of 1 with two equivalents of lithio(diorgano)phosphanes afford the open stannylphosphanes 3b,d which were studied by NMR spectroscopy in order to provide a meaningful comparison of NMR data.

Addition of pentacarbonylmetal fragments  $[M(CO)_5]$  (M = Cr, Mo, W) in THF to **2d** leads to the respective phosphane complexes as shown in the cases of **4d** - **6d** which are analogous to known complexes in which bis(trimethylstannyl)-phenylphosphane serves as a ligand [13]. In contrast, all compounds **2** react with chalcogens E = O, S, Se by cleavage of the Sn-P bonds (Sn-As bonds in the case of **2d**(As)) to give the known [9, 10] 1,3-distanna-2-chalcogena-[3]ferrocenophanes and the phosphorus(V) chalcogenides [RP(E)E]<sub>n</sub>.

#### 2.2. NMR spectroscopic results

All NMR spectroscopic data (Tables I - III) are in support of the proposed structures of the new compounds 2 - 6. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the ferrocenophanes 2 indicate fluxional structures, in contrast to the situation in the complexes 4 - 6. Low temperature <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2d prove the presence of a rigid structure ( $\Delta G^{\#}_{(coal.)} =$ 67.7 ± 2 kJ/mol at -10°C). In the case of 2d(As), the dynamic processes are already slow at ambient temperature. For steric reasons, it is assumed that the



Scheme 2.

substituent R occupies the *exo*-position. Since the dynamic processes in 2 lead to averaged resonance signals of the SnMe groups and of the ferrocenediyl units  $[{}^{1}H(2,5)/{}^{13}C(2,5)$  and  ${}^{1}H(3,4)/{}^{13}C(3,4)]$ , the lone pair of electrons at the phosphorus atom and the group R must on average occupy identical positions (Scheme 2; rapid interconversion of A and **B**). This can be explained either by fast inversion at the pyramidal phosphorus atom (which is unlikely because of the rather high activation energy of this process) or by movement of the two cyclopentadienyl rings against each other (Scheme 2: C). The latter dynamic process has been proposed in order to explain the dynamic behaviour of 1,2,3-trichalcogena-[3]ferrocenophanes [14]. In the case of the pentacarbonylmetal complexes 4d - 6d, all dynamic processes are slow at room temperature, as shown by the characteristic patterns of signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra.

The typical magnitude [15] of the coupling constants  ${}^{1}J({}^{119}\text{Sn},{}^{31}\text{P})$ , observed both in the  ${}^{31}\text{P}$  and <sup>119</sup>Sn NMR spectra, indicates the presence of Sn-P bonds. It is important to know the sign of coupling constants  $J({}^{31}P,X)$  in order to use this parameter as a diagnostic criterion. Changes in the magnitude of  $|{}^{1}J({}^{119}Sn, {}^{31}P)|$  in going from the phosphane 2d to the pentacarbonylmetal complexes 4d - 6d have been observed previously for comparable phosphane complexes [13, 16], and there was no change in the sign of this coupling constant. We have confirmed this trend in the case of the ferrocenophanes 2 by determining the absolute positive sign of  ${}^{1}J({}^{119}Sn, {}^{31}P)$ , as expected [13] (the sign of the reduced coupling constant  ${}^{1}K({}^{119}Sn, {}^{31}P)$  is negative because of  $\gamma(^{119}\text{Sn}) < 0$ ). The negative sign of  ${}^{1}K({}^{119}Sn, {}^{31}P)$  can be traced to negative contributions to the Fermi contact term arising from the presence of the lone pair of electrons at the phos-

No.	$\delta^1 H$ H(2,5)	H(3,4)	SnMe <sub>2</sub>	PR	$\frac{\delta^{13}C}{C(1)}$	C(2,5)	C(3,4)	SnMe <sub>2</sub>	PR	$\delta^{31} \mathbf{P}$	$\delta^{119}$ Sn
2a	4.01	4.21	0.36 [50.3] (1.3)	1.34 [56.2] (5.4)	71.5 [n.m.] (< 1)	74.3 [50.1]	70.2 [39.6]	-8.9 [310.8] [8.8] <sup>[b]</sup> (5.8)	-1.8 [19.5] (-31.7)	-211.3 (736.0)	-47.6 [362.3] (736.0)
2b	4.05	4.21	0.49 [51.3] (1.1)	1.33 [4.1] (12.3)	70.0 [n.m.] (< 1)	74.5 [49.6]	70.7 [38.4]	-4.9 [302.3] [8.7] <sup>[b]</sup> (6.2)	31.6, 36.6 [18.5], [25.6] (28.9), (12.1)	-111.8 (793.0)	-5.3 [362.6] (793.0)
2c	4.08	4.22	0.45	2.3 <sup>[c]</sup>	70.5 [n.m.] (< 1)	74.8 [50.2]	70.9 [38.4]	-8.7 [305.6] [8.5] <sup>[b]</sup> (10.2)	31.0, 38.5 <sup>[d]</sup> [16.8], [38.5] (26.6), (11.8)	-155.2 (771.0)	1.4 [367.7] (771.0)
<b>2d</b> [e]	4.02	4.21	0.38 [51.0] (1.9)	7.0-7.7	71.0 [435.6]	74.6 [50.8]	70.7 [39.8]	-7.0 [320.7] [9.0] <sup>[b]</sup> (9.2)	132.5 <sup>[f]</sup> [15.4] (23.9)	-156.1 (735.0)	1.3 [365.4] (735.0)
2d(As)	4.02 4.11	4.23	0.48 [52.8] 0.49 [52.8]	7.0-7.8	72.3 [416.7] [1.8]	74.7 [54.2] 74.7 [53.8]	70.7 [39.9] 70.4 [40.6]	-6.70 [294.6] -6.73 [294.0]	134.8 <sup>[g]</sup> [n.m.]	_	-14.5 [393.7]

Table I. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>119</sup>Sn NMR data<sup>[a]</sup> of the 1,3-distanna-2-phospha-[3] ferrocenophanes **2a** - **d** and of the 2-arsa analogue **2d**(**As**).

<sup>[a]</sup> In C<sub>6</sub>D<sub>6</sub> at room temperature: coupling constants  $J(^{119}Sn,^{1}H)$ ,  $J(^{119}Sn,^{13}C)$  in brackets,  $J(^{31}P,^{1}H)$ ,  $J(^{31}P,^{13}C)$ ,  $J(^{119}Sn,^{31}P)$  in parentheses; <sup>[b] 3</sup> $J(^{119}Sn,P,Sn,^{13}C)$ ; <sup>[c]</sup>  $\delta^{1}H$  (cyclohexyl H(2-6): 1.9, 1.5, 1.1 multiplets without assignment; <sup>[d]</sup>  $\delta^{13}C(3/5)$  (cyclohexyl) = 27.7 (9.5),  $\delta^{13}C(4) = 26.0$ ; <sup>[e]</sup> at -20 °C in [D<sub>8</sub>]toluene:  $\delta^{1}H = 4.05$ , 4.02 (H2/5), 4.21 (broad; H3/4), 0.36 [51.2] (2.4), 0.34 [51.0] (1.4) (SnMe\_2);  $\delta^{13}C(-40 \text{ °C}) = 74.6$  (broad; C(2/5), 70.9, 70.6 (C3/4), -6.8 (7.1), -6.9 (10.6) (SnMe\_2); <sup>[f]</sup>  $\delta^{13}C(ortho) = 135.6 [30.7] (14.4)$ ,  $\delta^{13}C(meta) = 128.6 [2.4] (5.3)$ ,  $\delta^{13}C(para) = 126.7 [6.5]$ ; <sup>[g]</sup>  $\delta^{13}C(ortho) = 136.5 [26.4]$ ,  $\delta^{13}C(meta) = 129.6$ ,  $\delta^{13}C(para) = 126.9$ .

phorus atom [17]. In the complexes **4d** - **6d** this lone pair of electrons is engaged in the coordinative P-M bond, and therefore, negative contributions should be reduced in a similar way as it was found for other stannylphosphane metal complexes [13, 16] or stannylphosphane borane complexes [18]. The signs of other coupling constants involving <sup>31</sup>P are even more difficult to predict and therefore experimental evidence is required.

The determinations of coupling signs are based either on appropriate 1D heteronuclear double experiments [13, 19] or on 2D heteronuclear shift correlations (HETCOR) relating two active nuclei (*e.g.*<sup>31</sup>P and <sup>1</sup>H) and one passive nucleus (*e.g.*<sup>119</sup>Sn or <sup>117</sup>Sn) [18, 20, 21]. These experiments (examples are given in the Figs. 1 and 2) lead to the determination of absolute signs of coupling constants, once a so-called "key coupling constant" is involved for which the absolute sign is known [*e.g.*<sup>1</sup>J(<sup>13</sup>C,<sup>1</sup>H) [22] or <sup>2</sup>J(<sup>119</sup>Sn,<sup>1</sup>H<sub>Me</sub>) [23]]. On the basis of such experiments it proved possible to determine the negative sign of  ${}^{1}J({}^{31}P,{}^{13}C)$ , the positive sign of  ${}^{2}J({}^{31}P, {}^{1}H_{Me})$  and the negative sign of  ${}^{3}J({}^{119}\text{Sn,P,C},{}^{1}\text{H})$  in 2a. Noteworthy in this context is the determination of the negative sign of  ${}^{2}J({}^{119}\text{Sn},{}^{117}\text{Sn})$  in **2a**, since only few examples of signs of geminal Sn-Sn couplings are known [21, 24]. We have also determined the negative sign of  ${}^{2}J({}^{119}Sn, {}^{117}Sn)$  in bis(trimethylstannyl)phenylphosphane and -arsane, (Me<sub>3</sub>Sn)<sub>2</sub>PPh and (Me<sub>3</sub>Sn)<sub>2</sub>AsPh, for comparison. This was achieved by a 2D<sup>119</sup>Sn/<sup>1</sup>H HETCOR experiment, based on long range coupling constants  ${}^{4}J({}^{119}\text{Sn,P,Sn,C,}{}^{1}\text{H}) \text{ and } {}^{4}J({}^{119}\text{Sn,As,Sn,C,}{}^{1}\text{H}) \approx 1$ Hz, which enables one to compare the signs of  ${}^{2}K({}^{117}Sn, {}^{1}H_{SnMe})$  and  ${}^{2}K({}^{119}Sn, {}^{117}Sn)$ , as has been described previously [21].

The chemical shifts of heavy nuclei such as <sup>31</sup>P or <sup>119</sup>Sn and also the coupling constants in which these nuclei are involved should indicate the influence of the ferrrocenophane structure when compared with data for non-cyclic derivatives. The chemi-

No	$\delta^{1}$ H H(2.3.4.5) <sup>[b]</sup>	SnMe <sub>2</sub>	PR	$\delta^{13}C$ C(1)	C(2.5)	C(3.4)	SnMe <sub>2</sub>	PR	$\delta^{31} \mathbf{P}$	$\delta^{119}$ Sn
	(-,-,-,-)	2		-(-)	- (-,- /	-(-,-)	2			
4d	4.25 (2 H) 4.26 (4 H)	0.61 [52.0]	6.7-7.6	70.0 [420.3]	74.7 [54.6]	71.4 [42.8]	-5.5 [331.6] [9.3] <sup>[d]</sup>	$136.5^{[c]}$ [10.1]	-110.3 (235.5)	11.1 [92.8]
	5.65 (2 H),	(5.1) (0.51) (53.3) (2.1)		(2.0)	(0.9) 74.5 [55.5]	71.1 [43.4]	(7.9) -6.4 $[333.9] [6.9] ^{[d]}$ (12.0)	(4.1)		(255.5)
5d	4.14 (2 H) 4.15 (2 H) 4.08 (2 H) 4.04 (2 H)	0.78 [53.5] (2.5) 0.60 [52.9] (2.2)	6.7-7.6	71.7 [441.2] (< 1)	74.7 [53.8]	71.3 [42.8] 70.6 [43.0]	(-4.3) [316.4] [11.1] <sup>[d]</sup> (7.4) -5.7 [319.0] [11.0] <sup>[d]</sup> (11.1)	134.6 <sup>[e]</sup> [8.5] (8.0)	-130.3 (203.0)	11.6 [136.2] (203.0)
6d	4.23 (2 H) 4.24 (2H) 4.25 (2 H) 3.92 (2 H)	0.83 [53.6] (2.5) 0.62 [53.0] (2.3)	6.9-7.5	71.4 [437.3] (< 1)	74.7 [54.8] [74.5 [55.4]	71.1 [42.2] 70.9 [41.6]	-4.1 [317.6] [11.1] <sup>[d]</sup> (7.6) -5.5 [320.4] [11.1] <sup>[d]</sup> (6.8)	134.7 <sup>[f]</sup> [8.3] (7.9)	-152.9 (150.5) [g]	13.4 [108.0] (150.5)

Table II. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>119</sup>Sn NMR data<sup>[a]</sup> of the pentacarbonylmetal phosphane complexes 4d - 6d.

Table III. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>119</sup>Sn NMR data<sup>[a]</sup> of the 1,1'-bis(phosphanyldimethylstannyl)ferrocenes **3b,d**.

No	$\delta^1 H$				$\delta^{13}$ C					$\delta^{31} \mathbf{P}$	$\delta^{119}$ Sn
	H(2,5)	H(3,4)	SnMe <sub>2</sub>	$PR_2$	C(1)	C(2,5)	C(3,4)	SnMe <sub>2</sub>	$PR_2$		
3b	4.05	4.21	0.48 [51.3] (2.0)	1.32 [4.3] (12.0)	69.0 [476.8] (9.2)	74.9 [50.1]	70.8 [39.8]	-8.2 [304.6] (5.8)	32.5, 36.4 [18.0], [25.8] (28.9), (12.5)	-57.8 [702.0]	-47.6 (702.0)
3d	4.01	4.19	0.39 [53.7] (1.6)	7.0-7.6	69.1 [485.2] (9.6)	74.3 [50.5]	71.1 [38.8]	-8.4 [312.2] (6.5)	137.5 C(1) <sup>[b]</sup> [18.2] (25.5)	-54.1 [614.0]	-12.7 (614.0)

<sup>[a]</sup> In C<sub>6</sub>D<sub>6</sub> at room temperature; coupling constants  $J(^{119}\text{Sn},^{1}\text{H})$ ,  $J(^{119}\text{Sn},^{13}\text{C})$  in brackets,  $J(^{31}\text{P},^{1}\text{H})$ ,  $J(^{31}\text{P},^{13}\text{C})$ ,  $J(^{119}\text{Sn},^{31}\text{P})$  in parentheses; <sup>[b]</sup>  $\delta^{13}\text{C}(ortho) = 135.7$  [25.5] (12.0);  $\delta^{13}\text{C}(meta) = 128.6$  (5.0);  $\delta^{13}\text{C}(para) = 126.7$ .

cal shifts  $\delta^{31}P = -329.6$  and  $\delta^{119}Sn = +14.2$  and the coupling constants  ${}^{1}J({}^{119}Sn, {}^{31}P) = +724.0$  Hz and  ${}^{2}J({}^{119}Sn, {}^{119}Sn) = -313.8$  for (Me<sub>3</sub>Sn)<sub>2</sub>PPh and (Me<sub>3</sub>Sn)<sub>2</sub>PPh-M(CO)<sub>5</sub> (M = Cr, W) [13, 25] are very similar to the data obtained here for **2d**. This is also true for  $\delta^{119}Sn = -1.7$  and  ${}^{2}J({}^{119}Sn, {}^{119}Sn) =$ -396.0 observed for (Me<sub>3</sub>Sn)<sub>2</sub>AsPh and **2d**(As). In the cases of  ${}^{1}J({}^{119}Sn, {}^{31}P)$  and  ${}^{2}J({}^{119}Sn, {}^{117}Sn)$ , we have confirmed that the sign of the coupling constants is the same in the ferrocenophanes and in their non-cyclic counterparts. Therefore, it is concluded that there is no particular strain in the structures of the ferrocenophanes 2 and 4d - 6d, and that the bond angles at the phosphorus atoms are comparable to those of non-cyclic compounds. This is also supported by the NMR data (Table III) of the ferrocene derivatives 3b, d.

#### Experimental

All necessary precautions were taken to exclude oxygen and moisture during the synthesis and handling of



Fig. 1. Contour plot of the 101.7 MHz 2D  ${}^{31}P/{}^{1}H$  heteronuclear shift correlation based on  ${}^{2}J({}^{31}P, {}^{1}H_{Me})$  for **2a**. The negative tilt of the cross peaks for tin satellites indicates that the signs of  ${}^{1}J(Sn, {}^{31}P)$  (>0) and  ${}^{3}J({}^{119}SnP, C, {}^{1}H)$  (<0) are opposite.

the compounds. Starting materials such as  $Fe(C_5H_4-SnMe_2Cl)_2 1$  [12],  $MeP(SiMe_3)_2$ [26],  $Li_2PR$ ,  $LiPR_2$  [27] and  $Li_2AsPh$  [28],  $PhPH_2$  [29], and analogously <sup>*t*</sup>BuPH\_2,  $C_6H_{11}PH_2$ ,  $PhAsH_2$  [30] were prepared as described. The phosphanes <sup>*t*</sup>Bu\_2PH and Ph\_2PH and 1.6 M solutions of <sup>*n*</sup>BuLi in hexane were used as commercial samples.

NMR spectra were recorded on Bruker ARX 250, AC 300 or DRX 500 spectrometers, equipped with multinuclear units and accessories for measurements at variable temperatures. Chemical shifts are given with respect to Me<sub>4</sub>Si  $[\delta^{1}H(CHCl_{3}/CDCl_{3}) = 7.24, (C_{6}D_{5}CD_{2}H) = 2.03;$  $\delta^{13}$ C (CDCl<sub>3</sub>) = 77.0, (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>) = 20.4], H<sub>3</sub>PO<sub>4</sub>, 85% aq. for  $\delta^{31}P = 0$ , and Me<sub>4</sub>Sn [ $\delta^{119}Sn = 0$  with X( $^{119}Sn$ ) = 37.290665 MHz]. The assignment of <sup>1</sup>H and <sup>13</sup>C NMR signals was based on the presence  $^{117/119}$ Sn satellites, together with routinely performed 2D <sup>1</sup>H/<sup>1</sup>H COSY and 2D<sup>13</sup>C/<sup>1</sup>H HETCOR experiments. All conditions for 2D HETCOR experiments were optimised by appropriate 1D polarisation transfer experiments [31]. IR Spectra: Perkin Elmer 983 G spectrometer; EI MS spectra (70 eV): Finnigan MAT 8500 spectrometer with direct inlet (the calculated isotope distributions were found to be in agreement with the experimental patterns).



Fig. 2. Contour plot of the 92.1 MHz <sup>119</sup>Sn/<sup>1</sup>H heteronuclear shift correlation of **2a** based on  ${}^{3}J({}^{119}Sn,P,C,{}^{1}H)$ . The negative tilt of the cross peaks for tin satellites indicates that the signs of  ${}^{3}K(Sn,P,C,{}^{1}H)$  (>0) and  ${}^{2}K(Sn,Sn)$  (< 0) [ ${}^{2}J(Sn,Sn)$  also < 0] are opposite.

#### 1,1,2,3,3-Pentamethyl-1,3-distanna-2-phospha-[3]ferrocenophane (**2a**)

A solution of **1** (0.1 g; 0.18 mmol) in toluene (10 ml) is prepared and MeP(SiMe<sub>3</sub>)<sub>2</sub> (0.04 g; 0.18 mmol) is injected. The mixture is stirred for 2 h at room temperature and then the solvent is removed *in vacuo*. The remaining orange oil is identified (<sup>1</sup>H, <sup>31</sup>P NMR) as pure **2a**; C<sub>15</sub>H<sub>23</sub>FePSn<sub>2</sub>, EI MS: *m/e* (%) = 528 (60) [M<sup>+</sup>], 365 (100) [M<sup>+</sup> - SnMe<sub>3</sub>].

#### 1,1,3,3-Tetramethyl-2-organo-1,3-distanna-2-phospha-[3]ferrocenophanes (**2b** - **d**)

*General procedure:* A solution of **1** (0.15 g; 0.27 mmol) in THF (20 ml) is added to a freshly prepared suspension of Li<sub>2</sub>PR in THF (15 ml) at 0 °C. The reaction mixture is stirred at room temperature for 5 h, then the solvent is removed in vacuo and the residue extracted with hexane. After filtering off all insoluble material, the solvent is again removed in vacuo, and the pure products (<sup>1</sup>H, <sup>31</sup>P NMR) are isolated as orange oils (69 -79 % yield). **2b**: C<sub>18</sub>H<sub>29</sub>FePSn<sub>2</sub>, EI MS: m/e (%) = 570 (40) [M<sup>+</sup>], 334 (100) [Fe(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>SnMe<sub>2</sub><sup>+</sup>]; **2c**: C<sub>20</sub>H<sub>31</sub>FePSn<sub>2</sub>, EI MS: m/e (%) = 596 (100) [M<sup>+</sup>]; **2d**: C<sub>20</sub>H<sub>25</sub>FePSn<sub>2</sub>, EI MS: m/e (%) = 590 (100) [M<sup>+</sup>]. **2d**(**As**) is obtained in the same way as an orange oil (yield 70.5 %), using Li<sub>2</sub>AsPh. C<sub>20</sub>H<sub>25</sub>AsFeSn<sub>2</sub>, EI MS: m/e (%) = 633 (60) [M<sup>+</sup>], 467 (100) [M<sup>+</sup> - AsPh - Me].

#### *1,1'-Bis[dimethyl(diorganophosphanyl)stannyl]ferrocenes* (**3b,d**)

The same procedure as described for **2b** - **d** was applied for the synthesis of the ferrocene derivatives **3b**,**d** using LiPR<sub>2</sub>. The complexes **3b**,**d** are obtained as orange oils in 75 - 80 % yield. **3b**:  $C_{30}H_{56}FeP_2Sn_2$ , EI MS: m/e (%) = 772 (100) [M<sup>+</sup>]; **3d**:  $C_{38}H_{40}FeP_2Sn_2$ , EI MS: m/e (%) = 852 (100) [M<sup>+</sup>].

## *1,1,3,3-Tetramethyl-2-pentacarbonylmetal(phenyl)-1,3-distanna-2-phospha-[3]ferrocenophanes* (**4d, 5d, 6d**)

General procedure: A solution containing both 2d (0.15 g; 0.25 mmol) and the stoichiometric amount of the

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corresponding M(CO)<sub>6</sub> in THF (20 ml) is stirred and irradiated with UV light (Hanovia, 450 W) for 2 - 4 h. The solvent is removed *in vacuo*, and the residue is dissolved in CH<sub>2</sub>Cl<sub>2</sub>. Addition of hexane leads to precipitation of the complexes as yellow solids. **4d** (yield 85 %; m.p. 176-178 °C): C<sub>25</sub>H<sub>25</sub>Cr FeO<sub>5</sub>PSn<sub>2</sub>, EI MS: m/e(%) = 782 (25) [M<sup>+</sup>], 642 (100) [M<sup>+</sup> - 5CO]; **5d** (61 %; m.p. 177 °C): C<sub>25</sub>H<sub>25</sub>FeMoO<sub>5</sub>PSn<sub>2</sub>, EI MS: m/e(%) = 826 (10) [M<sup>+</sup>], 590 (100) [M<sup>+</sup> - Mo(CO)<sub>5</sub>]; **6d** (32 %; m.p. 186-189 °C): C<sub>25</sub>H<sub>25</sub>FeO<sub>5</sub>PSn<sub>2</sub>W, EI MS: m/e(%) = 914 (20) [M<sup>+</sup>], 590 (100) [M<sup>+</sup> - W(CO)<sub>5</sub>].

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