Bis(pentamethylcyclopentadienyl)-Substituted Phosphanes: Synthesis and Structure

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The bis(1,2,3,4,5-pentamethyl-1,3-cyclopentadien-1-yl)phosphanes **3**−**7** are formed in good yields by the reaction of the halogenophosphanes **2a** or **2b** with the appropriate nucleophile. Following another route, the dialkylaminobis(pentamethylcyclopentadienyl)phosphanes **11a**−**c** have been synthesized by the treatment of dichloro(dialkylamino)phosphanes with two equivalents of (pentamethylcyclopentadienyl)lithium. The compounds **3**−**11** have been characterized by multinuclear NMR spectroscopy and **3**, **5**, **6**, and **11a** have also been characterized by single-crystal X-ray diffraction studies. The molecular structure of **11a** is governed by steric congestion, which typically would lead to a parallel arrangement of the two pentamethylcyclopentadienyl ligands at the phosphorus atom. However, surprisingly, the crystal structure of the (dimethylamino)phosphane **11a**, exhibits a tilted, rather than a parallel, conformation of the pentamethylcyclopentadienyl groups [tilt angle: 130.6(1)°].

Previous comprehensive investigations of the main-group cyclopentadienyl (Cp) compounds[1][2][3] have revealed a variety of unusual structures and bonding modes analogous to those observed for the cyclopentadienyl transition-metal compounds[4]. Depending on the availability of the valence orbitals and the geometric parameters of the central atom, mono-, di-, tri-, and pentahapto complexation has been achieved[5][6][7][8]. Moreover, by replacing Cp with the permethylated Cp* substituent, a significantly increased kinetic stability of the resulting complexes could be achieved, which made the isolation of several new types of compounds possible[3][4].

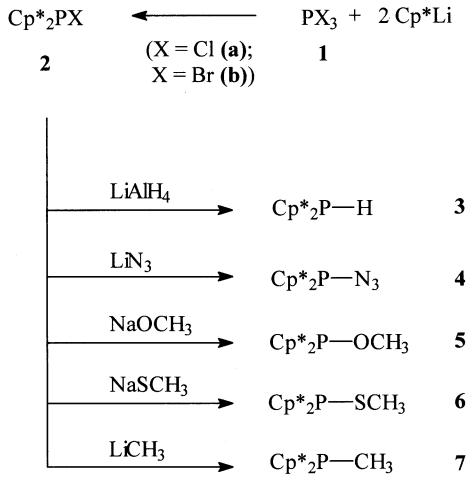
In the course of studies dealing with the dynamic behaviour of such systems (1,5-sigmatropic rearrangements) several pentamethylcyclopentadienyl-(Cp*-)substituted phosphanes have been synthesized[9][10]. On heating these Cp*-substituted phosphanes were shown to be thermally stable, which is not the case for the corresponding Cp compounds[11][12]. Recently, in the case of Cp*-substituted phosphenium cations and iminophosphanes, the haptotropic rearrangement has been proven to occur[13].

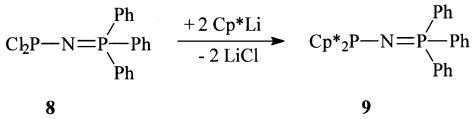
Results

Halogeno-Substituted Bis(Cp*)phosphanes

The synthesis of the chloro- and bromobis(Cp*)phosphanes[10] has been optimized, to enable characterisation by X-ray crystallography[23]. Treatment of PCl_3/PBr_3 with 2.5 equivalents of Cp*Li[10][14] at 0°C in pentane and after stirring for 10 h affords the desired halogenobis(Cp*)phosphanes **2a** and **2b**. Both compounds are obtained as yellow, thermally stable solids, that can be distilled in vacuo.

Scheme 1. Synthesis of new bis(Cp*)phosphanes by nucleophilic displacement





Starting from these halogenophosphanes **2a** and **2b** a variety of previously unknown bis(Cp*)phosphanes could be obtained by a nucleophilic displacement reaction. There-

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fore, the reduction to the phosphane **3**, on reaction of **2a**, **b** with lithium tetrahydridoaluminate in ether, proceeds in the usual manner. Due to the coupling with the directly bonded proton ($^1J_{PH} = {}_1$90.0 Hz) and the six methyl protons ($^3J_{PH} = {}_1$6.5 Hz) the ^{31}P-NMR spectrum of compound **3** exhibits a characteristic pattern of a doublet of septuplets.

The reaction of the halogenophosphanes with lithium azide in pyridine produces the azidophosphane **4** in good yield. The reaction time depends strongly on the nature of the halogen atom. While the reaction takes several days for **2a**, in the case of **2b** the exchange is completed after 1−2 h, which may be due to the weaker P−Br bond compared to the P−Cl bond.

In general, owing to the high steric congestion of the two Cp* substituents, a prolonged reaction time is necessary. However, in the case of the thermally stable compounds the reaction rate can be increased by heating the reaction mixture. Since the displacement of the Cp* moiety is a common side reaction of the nucleophilic attack at **2a**, **b**, a detailed balance of the reaction parameters is necessary. Reaction of **2a**, **b** with sodium methoxide at 40−50°C in methanol readily furnishes **5** as a crystalline compound. However, the corresponding (methylthio)phosphane **6** could be obtained at lower temperatures (0°), if a highly polar solvent such as DMF is used. With respect to this conversion the bromo derivative **2b** is seen to be more reactive than the chloro congener **2a**. Since sodium thiomethoxide is unsoluble in pure toluene or other unpolar solvents, a mixture of toluene/DMF is used as solvent in order to achieve a good solubility of the nucleophile. Methyllithium also reacts with **2a** and **2b** by displacement of the halide group at low temperature, despite the transition state of this reaction being more strained than in the previous cases. The conversion of **2a**,**b** into compound **7** is optimized in ether.

The identity of the compounds **3**−**7** was confirmed by NMR spectroscopy and elemental analysis. In addition, crystals suitable for an X-ray structure determination have been obtained for **3**, **5** and **6**.

NMR Spectra: In contrast to the compounds Cp*PR_2, which exhibit a mirror plane perpendicular to the ring, molecules of the type Cp*$_2$PR show diastereotopic methyl groups, which is similar to the situation in the phosphanes Cp*PRR′. All methyl groups are anisochronous, which corresponds to the observation of five sets of signals in the proton-NMR spectra.[10] However, these signals sometimes do not appear resolved, as, for instance, in the case of the compounds **3** and **4**, where the chemical shift of the methyl groups in positions 3 and 4 are almost the same.[15]

Figure 1. The NMR data were assigned according to the depicted numbering

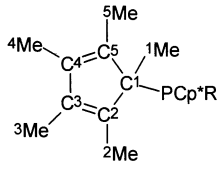


Table 1. ^{1}H-NMR data of **3**−**7** (C_6D_6)

	3	**4**	**5**	**6**	**7**
2,5-Me_2	1.72	1.89 1.81	1.90 1.78	2.07 1.94	1.85 1.69
3,4-Me_2	1.61	1.70	1.71 1.64	1.78 1.74	1.41 1.29
1-Me	0.95 d ($^3J_{HP}$ = 16.3 Hz)	1.33 d ($^3J_{HP}$ = 16.5 Hz)	1.26 d ($^3J_{HP}$ = 15.2 Hz)	1.42 d ($^3J_{HP}$ = 16.8 Hz)	1.35 d ($^3J_{HP}$ = 11.2 Hz)
R	R = H 3.48 d ($^1J_{HP}$ = 190.0 Hz)	R = N_3 −	R = OMe 3.50 d ($^3J_{HP}$ = 12.9 Hz)	R = SMe 2.29 d ($^3J_{HP}$ = 13.7 Hz)	R = Me 1.3 d ($^2J_{HP}$ = 10.4 Hz)

Table 2. ^{13}C-NMR data of **3**−**7** (C_6D_6)

	3	**4**	**5**	**6**	**7**
C-2−5	139.5 d (J_{CP} = 1.5 Hz) 137.4 d (J_{CP} = 8.8 Hz) 134.9 d (J_{CP} = 4.6 Hz) 134.0 (s)	138.9 d (J_{CP} = 2.0 Hz) 136.5 d (J_{CP} = 5.9 Hz) 135.3 d (J_{CP} = 2.8 Hz 134.6 (s)	139.4 d (J_{CP} = 1.2 Hz) 135.3 d (J_{CP} = 2.4 Hz) 134.9 d (J_{CP} = 9.1 Hz) 134.2 d (J_{CP} = 15.0 Hz)	140.0 d (J_{CP} = 2.3 Hz) 137.3 d (J_{CP} = 14.1 Hz) 135.5 d (J_{CP} = 4.1 Hz) 134.6 d ($^1J_{CP}$ = 18.9 Hz)	137.9 d (J_{CP} = 10.4 Hz) 136.3 d (J_{CP} = 12.9 Hz 134.4 d (J_{CP} = 11.9 Hz) 133.3 d (J_{CP} = 12.6 Hz)
C-1	56.3 d ($^1J_{CP}$ = 27.0 Hz)	60.7 d ($^1J_{CP}$ = 35.4 Hz)	62.3 d ($^1J_{CP}$ = 26.3 Hz)	60.1 d ($^1J_{CP}$ = 38.5 Hz)	58.6 d ($^1J_{CP}$ = 27.7 Hz)
2−5-Me	11.8 11.4 11.2	12.5 11.6 11.3 11.0	12.3 11.5 11.3 11.2	13.1 11.7 11.6 11.4	11.9 11.7 11.1 11.0
1-Me	20.4 d ($^2J_{CP}$ = 22.0 Hz)	19.4 d ($^2J_{CP}$ = 18.8 Hz)	19.4 d ($^2J_{CP}$ = 18.6 Hz)	21.5 d ($^2J_{CP}$ = 19.6 Hz)	22.5 d ($^2J_{CP}$ = 10.4 Hz)
R	R = H −	R = N_3 −	R = OMe 61.2 (s)	R = SMe 22.3 d ($^2J_{CP}$ = 27.2 Hz)	R = Me 21.6 d ($^1J_{CP}$ = 60.6 Hz)

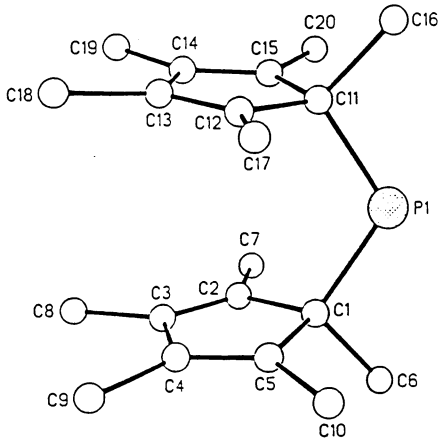
An incidental isochrony of the methyl groups 3 and 4, not only in the ^{1}H- but also in ^{13}C{^{1}H}-NMR spectra, can be observed in compound **2**. A borderline case of this situation may be ascribed to compounds **5** and **7**, in which the ^{13}C-NMR signals of the carbon atoms appear very close to each other but are still distinguishable. Owing to the greater dispersion of ^{13}C-NMR shifts, the influence of the substituents attached to the phosphorus atom on the shielding of the methyl groups 3 and 4 is more significant in ^{13}C-NMR than ^{1}H-NMR spectroscopy.

X-ray Structures of 3, 5, and 6: The molecular structures of **3**, **5**, and **6** in the crystal show significant similarities. The X-ray structures agree well with the results from multinuclear NMR spectroscopy and confirm the presence of

two η^1-bounded Cp* rings in all three cases. These rings are planar (deviation < 1 pm) and exhibit an almost parallel relative arrangement. However, these rings adopt no ecliptic conformation but are slightly twisted, probably in order to minimize repulsive interactions of the methyl groups. The planarity of these rings causes a deviation from ideal tetrahedral angles at the saturated, sp^3-hybridised carbon atoms (angles: C5−C1−C2 and. C12−C11−C15). These findings correspond well with the results for other bis(η^1-Cp*)-substituted congeners, for which X-ray structures are available, e.g. Cp^*_2S[16] or $Cp^*_2SiCl_2$[17]. The proton in the secondary phosphane **3** can not be localized in the differential Fourier-analysis, due to the proximity of the phosphorus atom. The P−C bond lengths in all the three molecules are in the range of 187.7−190.6 pm, as expected for such compounds, but are slightly elongated with respect to the standard bond length of 185 pm.[18]

The largest P−C value in this series has been found for compound **6**. However, the P−S distance (211.7 pm) in this compound, as well as the P−O distance (164.1 pm) in **5** are completely normal and in the range for regular P−chalkogene single bonds.[18]

Figure 2. Molecular structure of Cp^*_2PH **3**[a]



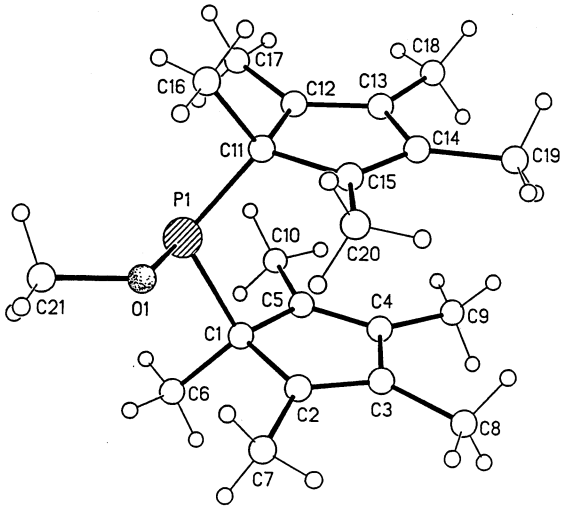
[a] Selected bond lengths [pm] and angles [°]: P1−C1 187.7 (4), P1−C11 188.9 (5); C1−P1−C11 112.6 (2), P1−C1−C6 104.1 (3), P1−C11−C16 103.4 (3); interplanar angle between Cp* planes: 9.6(3)°.

Amino-Substituted Bis(Cp*)phosphanes

The formation of amino-functionalized bis(Cp*)phosphanes can be accomplished by an inverse strategy, connecting the P−N bond prior to the P−C bonds. Therefore the corresponding aminodichlorophosphane was treated with 2.2 equivalents of Cp*Li in pentane as solvent.

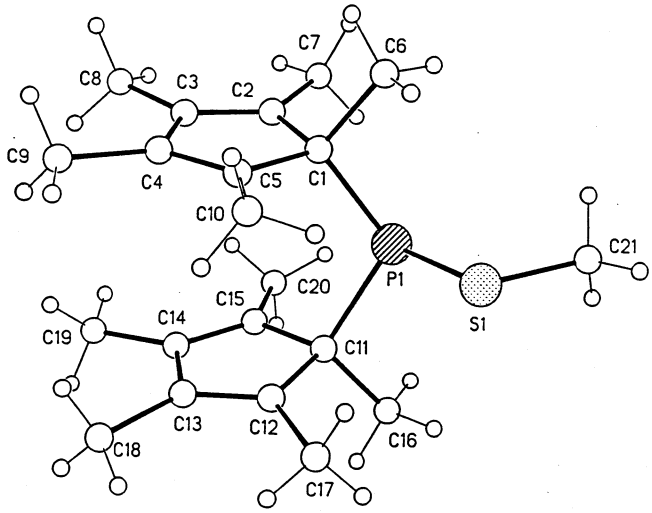
For convenience an exess of Cp*Li was used, which reduces the reaction time significantly. The presence of two Cp* moieties at the same phosphorus atom limits, due to steric hindrance, the variety of possible substituents at the nitrogen atom. An imino group should be a suitable nitrogen-containing substituent because it has a small steric bulk. Following this concept the phosphoraneimino-substituted bis(Cp*)phosphane **9**, was readily obtained as pale

Figure 3. Molecular structure of Cp^*_2POMe **5**[a]



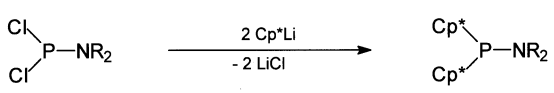
[a] Selected bond lengths [pm] and angles [°]: P1−O1 164.1 (3), P1−C1 188.0 (4), P1−C11 187.8 (4); C1−P1−C11 110.5 (2), P1−C1−C6 104.0 (2), P1−C11−C16 105.0 (2), O1−P1−C1 100.2 (2), O1−P1−C11 100.2 (2), P1−O1−C21 118.7 (3); interplanar angle between Cp* planes: 7.0(2)°.

Figure 4. Molecular structure of Cp^*_2PSMe **6**[a]



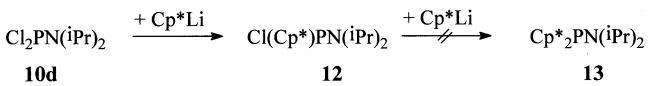
[a] Selected bond lengths [pm] and angles [°]: P1−S1 211.7 (1), P1−C1 190.6 (3), P1−C11 189.7 (3); C1−P1−C11 110.3 (1), P1−C1−C6 106.3 (2), P1−C11−C16 104.8 (2), S1−P1−C1 104.1 (1), S1−P1−C11 102.6 (1), P1−S1−C21 101.3 (1); interplanar angle between Cp* planes: 7.5(2)°.

Scheme 2. Synthesis of the aminobis(Cp*)phosphanes **11**



10 **11**

(R= CH_3, **a**; C_2H_5, **b**; $(CH_2)_5$, **c**)



10d **12** **13**

yellow solid starting from the corresponding dichlorophosphane **8** and two equivalents of Cp*Li[15].

Moreover, the syntheses of the dimethylamino (**11a**) and diethylamino (**11b**) derivatives were also sucessful by this method, while in contrast the introduction of an diisopropylamino group failed. In the latter case the reaction of dichloro(diisopropylamino)phosphane (**10d**)[19] with excess Cp*Li produces the monosubstituted phosphane **12**[20].

NMR Spectra: Similar to the ^{1}H-NMR spectra of the compounds **3**−**7**, the anisochrony of all methyl groups in the bis(Cp*)aminophosphanes **11a**−**c** can be observed as well. However, the signals for the latter compounds appear clearly separated and do not overlap as in the previously described case.

Figure 5. The NMR data were assigned according to the depicted numbering

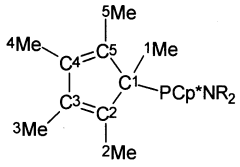


Table 3. ^{1}H-NMR data of **11a**−**c** (C_6D_6)

	11a	**11b**	**11c**
2,5-Me	1.85 1.76	1.87 1.81	1.87 1.80
3,4-Me	1.74 1.69	1.75 1.69	1.76 1.70
1-Me	0.96 d ($^3J_{HP}$ = 15.5 Hz)	0.90 d ($^3J_{HP}$ = 15.2 Hz)	0.91 d ($^3J_{HP}$ = 15.3 Hz)
R	R = NMe_2 2.63 d ($^3J_{HP}$ = 7.9 Hz)	R = $N(CH_2CH_3)_2$ CH_2: 2.94 (m) CH_3: 0.87 d ($^3J_{HH}$ = 7.1 Hz)	R = N[−$C^1H_2C^2$- $H_2C^3H_2CH_2CH_2$−] C^1H_2: 2.93 (m) $C^{2,3}H_2$: 0.87 (m)

X-ray Structure of **11a**: The dimethylamino-substituted bis(Cp*)phosphane **11a** crystallizes as colourless prisms and in the space group $P\bar{1}$. Similarly to the previously described structures both rings are bonded in an η^1 manner and are perfectly planar. However, a significantly different feature of this molecule is the surprisingly nonparallel orientation of the Cp* rings, which are tilted by 130.6(1)°. This compound represents the first example of a bis(Cp*)-phosphane with a nonparallel arrangement of the Cp* rings.

It is unlikely that this unusual geometry is due to a direct interaction of the nitrogen atom and its lone pair with the twisted Cp* ring, since the almost planar environment at this center [$\measuredangle$ N: 358.8(1)°] is a common feature of aminophosphanes[21][22]. Any influence of the phosphorus atom, which is pyramidalized to the same extent [$\Sigma\measuredangle$ P: 325.3(1)°]

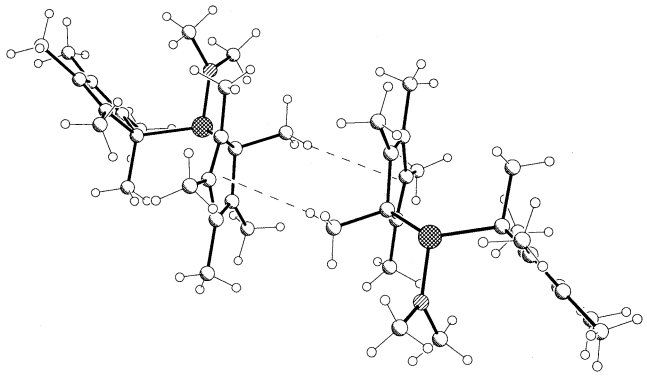
Table 4. ^{13}C-NMR data of **11a**−**c** (C_6D_6)

	11a	**11b**	**11c**
C-2−5	140.1 d (J_{CP} = 1.9 Hz) 140.0 d (J_{CP} = 11.4 Hz) 135.1 d (J_{CP} = 1.5 Hz) 134.6 d (J_{CP} = 3.8 Hz)	141.1 d (J_{CP} = 3.4 Hz) 141.0 d (J_{CP} = 10.7 Hz) 135.2 d (J_{CP} = 1.9 Hz) 134.7 d (J_{CP} = 3.4 Hz)	141.0 d (J_{CP} = 3.4 Hz 140.6 d (J_{CP} = 9.5 Hz) 134.8 d (J_{CP} = 1.9 Hz) 134.3 d (J_{CP} = 3.4 Hz)
C-1	65.3 d ($^1J_{CP}$ = 43.1 Hz)	65.6 d ($^1J_{CP}$ = 46.1 Hz)	65.5 d ($^1J_{CP}$ = 45.4 Hz)
2−5-Me	13.0 d (J_{CP} = 6.9 Hz) 12.3 d (J_{CP} = 11.4 Hz) 11.7 d (J_{CP} = 5.3 Hz)	13.3 d (J_{CP} = 8.4 Hz) 12.5 d (J_{CP} = 12.6 Hz) 11.7 d (J_{CP} = 5.0 Hz)	13.1 d (J_{CP} = 8.8 Hz) 12.2 d (J_{CP} = 11.4 Hz) 11.6 d (J_{CP} = 8.8 Hz)
1-Me	19.7 d ($^2J_{CP}$ = 21.0 Hz)	19.1 d ($^2J_{CP}$ = 19.1 Hz)	19.4 d ($^2J_{CP}$ = 21.0 Hz)
R	R = NMe_2 46.9 d ($^2J_{CP}$ = 18.8 Hz)	R = $N(CH_2CH_3)_2$ CH_2 : 34.7 (s) CH_3 : 15.4 d ($^3J_{CP}$ = 1.9 Hz)	R = N[−$C^1H_2C^2$- $H_2C^3H_2CH_2CH_2$−] C^1H_2 : 34.5 (s) C^2H_2 : 27.9 d ($^3J_{CP}$ = 5.0 Hz) C^3H_2 : 24.9 (s)

as in other bis(Cp*)phosphanes, on the arrangement of the rings can also be discounted.

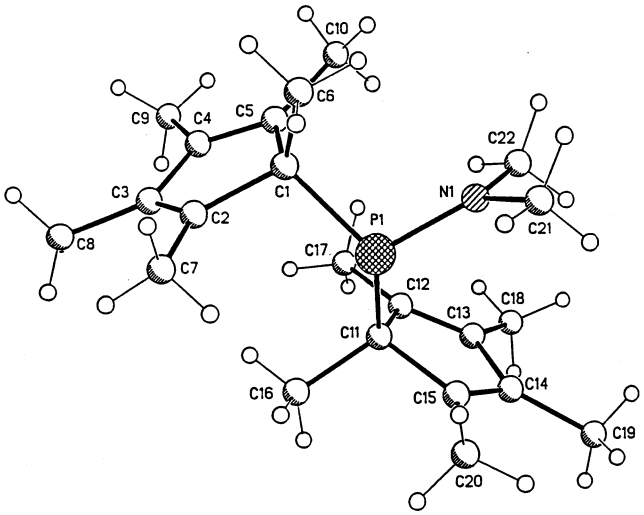
The most probable reason for this unusual geometric feature arises from the packing of the molecules within the crystal. There is an orientation of one proton of the methyl group in the 4-position towards the twisted Cp* ring of another molecule, generated by symmetry transformation $-x$, $2 - y$, $2 - z$, and vice versa.

Figure 6. Intermolecular interactions of the aminophosphane **11a** in the crystal



The P−C bond lengths in **11a** [191.1(3) pm] are even longer than in the previously mentioned compounds. Additionally, the P−N bond appears slightly shortened [168.0(3) pm]. These findings may be ascribed to tendency towards partial ionic character in **11a**.

Figure 7. Molecular structure of Cp_2PNMe_2 **11a**[a]



[a] Selected bond lengths [pm] and angles [°]: P1−N1 168.0 (3), P1−C1 191.1 (3), P1−C11 191.0 (3), N1−C21 145.7 (5), N1−C22 144.6 (5); C1−P1−C11 112.7 (1), N1−P1−C1 106.8 (1), N1−P1−C11 105.8 (1), P1−N1−C21 116.5 (3), P1−N1−C22 128.8 (3), C21−N1−C22 113.5 (3); interplanar angle between Cp* planes: 130.6(1)°.

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Experimental Section

All reaction steps were carried out under dried argon in order to exclude air and moisture; glassware, reagents and solvents were similarly prepared. − ^{31}P NMR: Bruker AMX 300 (121.5 MHz); external standard 85% H_3PO_4. − ^{13}C NMR: Bruker AMX 300 (75.5 MHz); external standard tetramethylsilane. − ^{1}H NMR: Bruker AMX 300 (300 MHz); external standard tetramethylsilane. ^{31}P- and ^{13}C-NMR spectra were recorded with ^{1}H decoupling. A positive sign means low field with respect to the standard. − MS: Kratos MS 50 and VG Instruments VG 12-250 (EI, direct inlet). The given *m/z* values refer to the isotope of highest abundance for each element. − M.p.: Measured without correction in sealed capillaries in a melting point apparatus supplied by Firma Büchi, Flawil/Switzerland. − Elemental analyses: Heraeus CHN-O-Rapid. − The literature procedure for the syntheses of the bis(Cp*)halogenophosphanes **2a** and **2b** has been slighly modified[10].

Chlorobis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)phosphane (**2a**) *and Bromobis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)phosphane* (**2b**): 1.8 ml (20 mmol) of PCl_3 or 19 ml (20 mmol) of PBr_3 was added slowly at 0°C to a suspension of 3.4 g (24 mmol) of Cp*Li in 50 ml of pentane. The mixture was cooled to room temp. and stirred vigorously for a further 10 h. The insoluble precipitate was removed by filtration and washed several times with pentane. The volume of the combined filtrate was reduced to approximately 10 ml, the product crystallised on cooling to −35°C. − **2a**: Yield: 5.5 g (87%, rel. PCl_3). − ^{31}P{^{1}H} NMR (C_6D_6): δ = 165.5 (s). − **2b**: Yield: 6.4 g (82%, rel. PBr_3). − ^{31}P{^{1}H} NMR (C_6D_6): δ = 167.8 (s).

Bis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)phosphane (**3**): A solution of 1.5 g (4.5 mmol) of **2a** in 3 ml of diethyl ether was added, at 0°C, to a suspension of 70 mg of $LiAlH_4$ in 5 ml of diethyl ether. After warming to room temp. and further stirring, the solvent was removed. The residue was extracted with pentane and, after separation from the unsoluble precipitate, the filtrate was concentrated. On cooling to −35°C, the product was obtained as colorless crystals. Yield: 0.8g (59%), m.p. 108°C. − ^{31}P{^{1}H} NMR (C_6D_6): δ = −42.2 (s). − MS (180°C/70 eV); *m/z* (%): 302 (8) [M^+], 167 (100) [M^+ − Cp*], 135 (13) [Cp*$^+$] and further fragments. − $C_{20}H_{31}P$ (302.2): calcd. C 79.43, H 10.33; found C 77.71, H 10.33.

Azidobis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)phosphane (**4**): 3.5 g (9.2 mmol) of **1b** was dissolved in 5 ml of pyridine. While cooling with ice, 0.47 g (9.5 mmol) of LiN_3 was added as pure solid. Under continuous stirring, the mixture was warmed to room temp. within 0.5 h and the pyridine was removed in vacuo. The residue was extracted with pentane and, after separation from the unsoluble precipitate, the filtrate was concentrated. On cooling to −35°C the product was obtained as colorless solid, which was then recrystallised several times to remove impurities. Yield: 2.3 g (73%), m.p.. 70°C (dec.). − ^{31}P{^{1}H} NMR (C_6D_6): δ = 138.2 (s) − MS (100°C/70 eV), *m/z* (%): 343 (8) [M^+], 315 (6) [$M^+ - N_2$], 301 (4) [$M^+ - N_3$], 270 (29) [Cp*$_2^+$], 208 (39) [M^+ − Cp*], 135 (13) [Cp*$^+$] and further fragments. − UV/Vis (pentane): λ_{max} (lgε) = 215 nm, 230, 265. − $C_{20}H_{30}N_3P$ (343.5): calcd. C 69.94, H 8.80, N 12.23; found C 68.69, H 8.67, N 12.02.

Methoxybis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)phosphane (**5**): 0.64 g (1.9 mmol) of **1a** was dissolved in 10 ml of pentane and added, under continuous stirring, to 0.05 g (2.1 mmol) of sodium in 20 ml of methanol at room temp. After the addition was completed, the mixture was stirred for a further 3 h at 40°C. The volatile components were removed in vacuo, and the residue extracted with pentane. After filtration and on cooling to −70°C, the product was obtained as white needles. Yield: 0.46 g (73%), m.p. 84−88°C. − ^{31}P{^{1}H} NMR (C_6D_6): δ = 184.8 (s) − MS (100°C/40 eV); *m/z* (%): 332 (3) [M^+], 301 (0.5) [$M^+ - OCH_3$], 197 (100) [M^+ − Cp*], 135 (70) [Cp*$^+$] and further fragments. − An analysis was not performed.

Methylthiobis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)phosphane (**6**): 0.54 g (1.5 mmol) of **1b**, dissolved in 3 ml of toluene/DMF (2:1), was added to an equivalent amount of $NaSCH_3$ (0.1 g) in 2 ml of DMF at 0°C. The solution was stirred for 1 h at ambient temp. The solvents were evaporated under reduced pressure and the residue extracted with pentane. After separation of the solid precipitate, the filtrate was concentrated and the product crystallised at −35°C. Recrystalisation at the same temp. yielded the product as pale yellow crystals. Yield 0.46 g (88%), m.p. 95−100°C. − ^{31}P{^{1}H} NMR (C_6D_6): δ = 85.1 (s) − MS (100°C/35 eV); *m/z* (%): 348 (15) [M^+], 301 (15) [$M^+ - SCH_3$], 270 (3) [Cp*$_2^+$], 213 (100) [M^+ − Cp*], 166 (30) [Cp*P$^+$], 135 (50) [Cp*$^+$] and further fragments. − $C_{21}H_{33}PS$ (348.5): calcd. 348.2041; found 348.2046 (MS).

Methylbis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)phosphane (**7**): 3.5 ml (2.2 mmol) of CH_3Li (1.6 M in diethyl ether) was added slowly to 0.67 g (2 mmol) of **1a** in 5 ml of diethyl ether at −78°C. After warming to room temp., the volatile parts of the mixture were removed in vacuo. The residue was extracted with pentane and, after separation from the unsoluble precipitate, the filtrate was concentrated. On cooling to −35°C, the product was obtained as a solid which was recrystallised several times, finally at 0°C to yield 0.5 g (79%) of white crystals. m.p. 138−140°C. − ^{31}P{^{1}H} NMR (C_6D_6): δ = 72.9 (s) − MS (100°C/35 eV); *m/z* (%): 316 (15) [M^+], 301 (5) [$M^+ - CH_3$], 270 (1) [Cp*$_2^+$], 181 (100)

[M^+ − Cp*], 166 (20) [Cp*P^+], 135 (60) [Cp*$^+$] and further fragments. − $C_{21}H_{33}P$ (316.5): calcd. 316.2322; found 316.2327 (MS).

Bis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)-(triphenylphosphoranylimino)phosphane (**9**): A suspension of 0.6 g (4.0 mmol) of Cp*Li in pentane (10 ml) was treated dropwise with 0.8 g (2 mmol) of dichloro(triphenylphosphoranylimino)phosphane[15] at −40°C. The solution was stirred for a further 12 h and warmed to room temp. After filtration, the solution was concentrated and the product isolated after crystallisation from ether/THF at 5°C. The product **8** was obtained as yellow crystals. Yield 0.8 g (70%), m.p. 170°C (dec.). − $^{31}P\{^1H\}$ NMR (ether/C_6D_6): δ = 93.0 (d, $^2J_{PP}$ = 109 Hz), 17.8 (d, J_{PP} = 109 Hz). − ^1H NMR ([D_8]THF): δ = 7.9−7.6 (m, 2 H), 7.5−7.4 (m, 3 H) H arom., 2.0 (s, 3 H), 1.7 (s, 6 H), 0.7 (d, 3 H, $^3J_{PH}$ = 14.1 Hz) C_5Me_5. − $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 141.7 (d, 2.1 Hz), 138.7 (s), 138.0 (s), 136.6 (d, 1.5 Hz), 63.0 (dd, $^1J_{PC}$ = 39.5 Hz, $^3J_{PC}$ = 9.6 Hz) C_5 ring; 133.7 (d, 2.6 Hz), 133.1 (dd, $^1J_{PC}$ = 45.2 Hz, $^3J_{PC}$ = 2.7 Hz), 129.1 (s), 128.5 (s) C_{arom}; 22.1 (d, $^2J_{PC}$ = 11.6 Hz), 13.7 (d, 2.7 Hz), 12.5 (s), 11.5 (s), 11.4 (s) C_5Me_5. − MS (300°C/40 eV); *m/z* (%): 577 (6) [M^+], 576 (13) [M^+ − H], 443 (60 [M^+ − Cp*], 308 (100) [M^+ − 2Cp*], 262 (65) [PPh_3^+], 135 (44) [Cp*$^+$] and further fragments. − $C_{38}H_{45}NP_2$ (577): calcd. C 79.00, H 7.85, N 2.42; found C 78.91, H 8.05, N 2.39.

(Dialkylamino)bis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)-phosphanes (**11a**−**c**): A suspension of 0.68 g (4.8 mmol) of Cp*Li in pentane was treated dropwise with 2 mmol of **10a**−**c** at room temp. The solution was stirred for a further 12 h and filtered afterwards. The solution was concentrated and the product isolated after crystallisation at −35°C. In all three cases yellow crystals were obtained.

(Dimethylamino)bis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)-phosphane (**11a**): Yield: 0.59 g (86%), m.p. 103−105°C. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 117.3 (s). − MS (25°C/70 eV); *m/z* (%): 345 (0.2) [M^+], 301 (0.4) [M^+ − $N(CH_3)_2$], 270 (0.7) [Cp*$_2^+$], 213 (100) [M^+ − Cp*], 166 (20) [Cp*P^+], 135 (20) [Cp*$^+$] and further fragments. − An analysis was not performed.

(Diethylamino)bis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)-phosphane (**11b**): Yield: 0.61 g (81%), m.p. 53−55°C. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 116.5 (s). − MS (200°C/25 eV); *m/z* (%): 373 (2) [M^+], 301 (1) [M^+ − $N(C_2H_5)_2$], 270 (15) [Cp*$_2^+$], 238 (90) [M^+ − Cp*], 166 (20) [Cp*P^+], 135 (100) [Cp*$^+$] and further fragments. − $C_{24}H_{40}NP$ (373.6): calcd. C 77.17, H 10.79, N 3.75; found C 76.91, H 10.85, N 3.53.

Bis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)piperidinophosphane (**11c**): Yield: 0.58 g (75%), m.p. 83−85°C. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 116.8 (s). − MS (200°C/25 eV); *m/z* (%): 385 (4) [M^+], 301 (1) [M^+ − $N(CH_2)_5$], 250 (90) [M^+ − Cp*], 166 (35) [Cp*P^+], 135 (100) [Cp*$^+$] and further fragments. − $C_{25}H_{40}NP$ (385.6): calcd. C 77.88, H 10.46, N 3.63; found C 77.41, H 10.02, N 3.48.

X-ray Structure Determination of **3**, **5**, **6**, *and* **11a**: The structures were solved by direct methods (SHELXTL-Plus[24]). The non-hydrogen atoms were refined anisotropically, H atoms were refined using a riding model [full-matrix least-squares refinement on F (**3**, **5**: SHELXTL-plus[24]) and F^2 (**6**, **11a**: SHELXL-93[25]), respec-

Table 5. Crystallographic data and summary of data collection and refinement

	3	**5**	**6**	**11a**
formula	$C_{20}H_{31}P$	$C_{21}H_{33}OP$	$C_{21}H_{33}PS$	$C_{22}H_{36}NP$
M_r	302.4	332.4	348.5	345.5
dimensions [mm]	0.90×0.90×0.90	0.30×0.50×0.90	0.45×0.40×0.25	0.40×0.35×0.20
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	10.374(2)	13.491(4)	8.664(1)	8.837(2)
b [Å]	11.237(2)	10.497(2)	14.509(3)	11.531(3)
c [Å]	16.529(3)	14.435(5)	16.805(3)	11.928(3)
α [°]	90	90	90	72.99(2)
β [°]	91.08(1)	99.34(3)	97.22(1)	72.61(2)
γ [°]	90	90	90	78.59(2)
V [Å^3]	1931(1)	2017(1)	2095.7(6)	1101.0(5)
Z	4	4	4	2
ρ [g cm^{-3}]	1.04	1.10	1.11	1.04
μ [mm^{-1}]	0.132	0.135	0.230	0.128
F(000)	664	728	760	380
diffractometer	Nicolet R3m	Enraf-Nonius CAD4	Nicolet R3m	Nicolet R3m
radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
λ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	298(2)	193(2)	293(2)	293(2)
$2\theta_{max.}$ [°]	50	48	50	50
	$-12 \le h \le 12$	$-15 \le h \le 15$	$-10 \le h \le 10$	$-10 \le h \le 10$
	$0 \le k \le 13$	$0 \le h \le 12$	$0 \le h \le 17$	$-13 \le h \le 13$
	$0 \le h \le 19$	$0 \le h \le 16$	$0 \le h \le 20$	$0 \le h \le 14$
no. of measured data	3747	3493	3815	4106
no. of unique data	3417	3148	3680	3901
no. of obs. data/s for [$F > s\sigma(F)$]	2550/4	2209/3	2419/4	2505/4
R_{int}	0.146	0.012	0.020	0.046
refinement on	F	F	F^2	F^2
no. of parameters	191	208	219	229
R [for $F > \sigma(F)$]	0.101	0.062	0.053	0.063
wR	0.123	0.073		
$wR2$ (all data)			0.146	0.180
max./min. difference peak [e/Å^3]	0.42/−0.43	0.81/−0.27	0.44/−0.17	0.32/−0.25

tively]. In **3** an extinction correction was applied and the H(P) could not be localized. Further details are given in Table 5. Additional information on the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-407789 (**3**), -407790 (**5**), -407791 (**6**), -407792 (**11a**), the names of the authors, and the journal citation.

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