

Titanocene-Mediated Formation of Phosphorus–Phosphorus Bonds

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The reaction of $\text{Cp}_2\text{Ti}(\text{btmsa})$ [$\text{btmsa} = \text{bis}(\text{trimethylsilyl})\text{acetylene}$ ($\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$)] with bulky dichlorophosphines leads to the formation of diphosphenes or dichlorodiphosphines depending on the stoichiometry used. $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)\text{PCl}_2$ (**1**) was transformed either into bis[tris(trimethylsilyl)hydrazino]dichlorodiphosphine (**2**) or bis[tris(trimethylsilyl)hydrazino]diphosphene (**3**) depending on whether an excess of **1** or $\text{Cp}_2\text{Ti}(\text{btmsa})$ was used. Depending on the starting material ratios, Cp_2TiCl_2 or $(\text{Cp}_2\text{TiCl})_2$ were obtained as byproducts besides **1** or **3**. Compounds **2** and **3** were structurally characterized by X-ray diffraction. Furthermore, the known diphosphene $\text{Mes}^*\text{P}=\text{PMes}^*$ (**4**) ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$) and the dichlorodiphosphine $\text{Mes}^*(\text{Cl})\text{PP}(\text{Cl})\text{Mes}^*$ (**5**) were prepared by reaction of $\text{Cp}_2\text{Ti}(\text{btmsa})$ with Mes^*PCl_2 . The reaction of $\text{Cp}_2\text{Ti}(\text{btmsa})$ with the sterically less demanding PhPCl_2 resulted in the isolation of a triphosphinato complex. The diphosphine $\text{Ph}_2\text{P}-\text{PPh}_2$ (**6**) was synthesized by reaction of Ph_2PCl with $\text{Cp}_2\text{Ti}(\text{btmsa})$.

1. Introduction

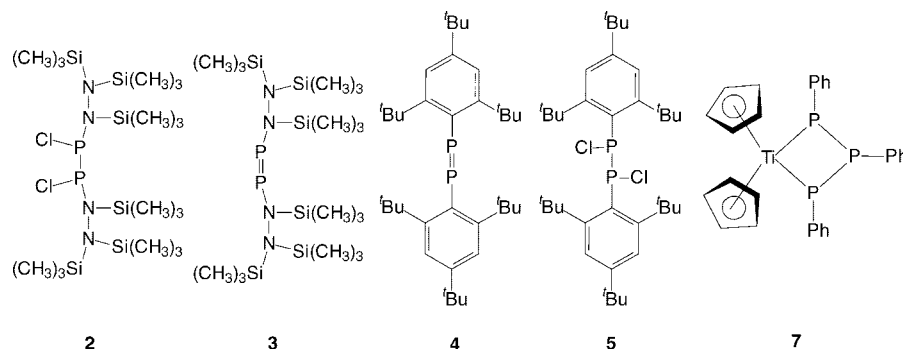
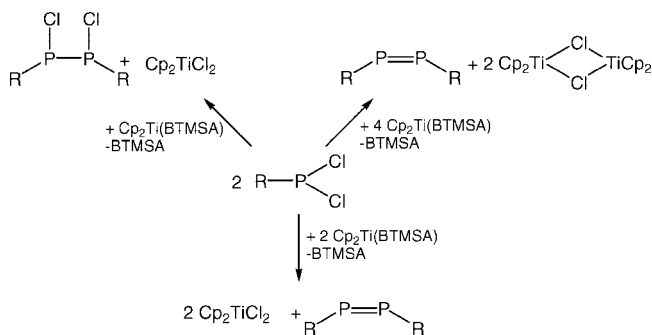
Recently, we have become interested in the chemistry of the tris(trimethylsilyl)hydrazinodichlorophosphine, $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)\text{PCl}_2$ (**1**), especially in its kinetic stability due to the presence of the bulky $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)$ substituent on the phosphorus atom and in the elimination of Me_3SiCl triggered by the action of Lewis acids such as GaCl_3 .¹ It was of interest to study the reaction of **1** with low-coordinate, highly reactive transition metal complexes such as titanocene “ Cp_2Ti ”, a species that, however, cannot be isolated.^{2–4} A useful approach to generate “ Cp_2Ti ” utilizes the weak alkyne complex $\text{Cp}_2\text{Ti}(\text{btmsa})$ [$\text{btmsa} = \text{bis}(\text{trimethylsilyl})\text{acetylene}$ ($\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$)] from which this unstable species can be generated under mild conditions by quantitative removal of the weakly bound alkyne ligand. A wide range of applications of $\text{Cp}_2\text{Ti}(\text{btmsa})$ as stoichiometric reagent or catalyst has been developed.⁵

Titanocene has been shown to be a quite useful reagent in various stoichiometric reactions³ in which new bonds between different or the same main group elements were formed. Very recently, for example, the distibene complex $\text{Cp}_2\text{Ti}[(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_2\text{Sb}_2]$ was obtained by reaction of $\text{Cp}_2\text{Ti}(\text{btmsa})$ with $(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_2\text{Sb}_2\text{H}_2$.⁶ Other examples of titanocene- or zirconocene-mediated bond formation reactions in main group chemistry are the dehydrocoupling of primary phosphines to form P–P single or double bonds.^{7,8}

The first diphosphene was reported by Yoshifuji, who introduced the bulky 2,4,6-tri-*tert*-butylphenyl group (supermesityl, Mes^*) as a substituent in 1981.⁹ The reduction of supermesityldichlorophosphine with elemental magnesium resulted in the formation of orange-red crystalline $\text{Mes}^*-\text{P}=\text{P}-\text{Mes}^*$. In general, dehalogenative coupling of halophosphines can be realized by utilization of reducing agents such as pure metals (magnesium, lithium, sodium), sodium naphthalenide, organolithium compounds, bis(trimethylsilyl)mercury, divalent germanium and tin compounds, or electron-rich olefins. Also, the

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Chart 1. Compounds Prepared in the Reactions of $\text{Cp}_2\text{Ti}(\text{btmsa})$ (i) + 1 $\rightarrow$ 2 and 3, (ii) + $\text{Mes}^*\text{PCl}_2 \rightarrow$ 4 and 5, and (iii) $\text{PhPCl}_2 \rightarrow$ 7**Scheme 1.** Ideal Product Distribution of the Reaction of 1 with $\text{Cp}_2\text{Ti}(\text{btmsa})$ (btmsa = $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3$) Depending on the Stoichiometry

elimination of hydrogen halides, salts, or trimethylsilyl halides provides other methods for diphosphene synthesis.¹⁰

We report here the titanocene-mediated coupling of dichlorophosphines to give stable diphosphenes and dichlorodiphosphines in moderate yield. The titanium alkyne complex $\text{Cp}_2\text{Ti}(\text{btmsa})$, which is readily available in a one-pot synthesis from Cp_2TiCl_2 , magnesium, and bis(trimethylsilyl)acetylene, has been found to be an excellent reagent for abstraction of chlorine from chlorophosphines to form phosphorus–phosphorus bonds. The type of product obtained in the reaction of $\text{Cp}_2\text{Ti}(\text{btmsa})$ with dichlorophosphines depends on the stoichiometry used and on the steric properties of the dichlorophosphine. The products prepared in the present study are summarized in Chart 1.

2. Results and Discussion

Synthesis and Characterization of *sym*-Dihydrazinodichlorodiphosphine (2) and Dihydrazinodiphosphene (3). The reaction of $\text{Cp}_2\text{Ti}(\text{btmsa})$ with the hydrazinodichlorophosphine $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)\text{PCl}_2$ (1)¹¹ in toluene at -78°C with an excess of $\text{Cp}_2\text{Ti}(\text{btmsa})$ resulted in formation of a deep green solution during the course of several minutes. Stepwise removal of the solvent followed by cooling to -40°C led to crystallization of a green solid; X-ray structure analysis showed this to be $(\text{Cp}_2\text{TiCl})_2$ (Scheme 1). After complete crystallization of $(\text{Cp}_2\text{TiCl})_2$ two remarkable products were isolated by evaporat-

ing the reaction mixture and extraction of the residue with *n*-hexane with subsequent stepwise removal of the solvent. After fractional recrystallization from toluene single-crystal X-ray structure analysis of the products revealed that the hitherto unknown dihydrazinodichlorodiphosphine 2 and the dihydrazinodiphosphene 3 had been formed. Especially the formation of deep yellow 3 as a stable, uncoordinated, and even preferred product is remarkable. Over the last 26 years the number of stable diphosphenes with sterically demanding substituents has steadily increased.^{9,12} However, diphosphene 3 is unusual in that it possesses a nearly planar array of NNPPNN atoms. Completely characterized diorganodichlorodiphosphines are few in number,¹³ although they can be stable without bulky substituents on the phosphorus atoms. Little is known about the reactivity and characteristics of this class of compounds. An interesting feature of 2 is that it might be a synthon for a bis(phosphazene), because it has the possibility for β -elimination of trimethylchlorosilane at each side of the P–P bond. Also, 2 might serve in the preparation for hydrazino-substituted phosphorus ring or chain compounds. Both 2 and 3 are stable over long periods in the absence of air and moisture but they are easily oxidized and hydrolyzed.

The surprising formation of a mixture of 2 and 3 in the reaction of 1 with an excess of $\text{Cp}_2\text{Ti}(\text{btmsa})$ prompted us to

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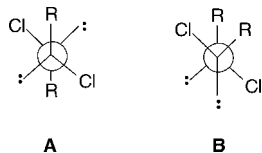


Figure 1. Two possible *anti* (with respect to the Cl atoms) isomers in $R(Cl)P-P(Cl)R$ species.

study the influence of the stoichiometry on the product distribution. Three different starting material ratios (**1** vs. $Cp_2Ti(btmsa)$) were investigated: 1:2, 1:3, and 2:1. The distribution of products in the reaction of $Cp_2Ti(btmsa)$ and **1** as the stoichiometry was varied was investigated by means of ^{31}P NMR spectroscopy. When $Cp_2Ti(btmsa)$ was added in threefold excess to **1**, diphosphene **3** ($\delta[^{31}P] = 426.5$ ppm) was almost exclusively generated. Use of a twofold excess of the titanium complex led to the formation of about 15% dichlorodiphosphine **2** ($\delta[^{31}P] = 153.4$ ppm) in addition to **3**, while for the ratio of 2:1 the formation of the dichlorodiphosphine **2** was the main product with formation of only 15% diphosphene and a considerable amount of the starting material **1** ($\delta[^{31}P] = 166.1$ ppm) was not converted.

It is interesting, that in contrast to what was formed in the case of $tBu(Cl)PP(Cl)tBu$ (two isomers in 4:1 ratio, Figure 1)^{13a} only one configurational isomer of the dichlorodiphosphine **2** was observed, as shown by its ^{31}P NMR spectrum ($\delta[^{31}P] 153.4$ ppm). For $tBu(Cl)P=P(Cl)tBu$ two different *anti* isomers (with respect to the Cl atoms) were found while for **3** only the *anti* configuration according to Figure 1A was observed in its X-ray structure determination (vide infra). Presumably, due to the considerable steric effect of the $(Me_3Si)_2N-N(SiMe_3)$ substituent, the *gauche* isomer in Figure 1B cannot be realized in **2**.

Furthermore, three resonances at $\delta[^1H] = 0.49, 0.39$, and 0.34 ppm were observed in the 1H NMR spectrum of **2**, displaying three chemically inequivalent Me_3Si groups of the hydrazino group. Obviously, there is no free rotation about the N–N bonds caused by the steric effect of the bis(trimethylsilyl)amino group.

Diphosphene **3** shows one resonance in the ^{31}P NMR spectrum at 426.5 ppm and two in the 1H NMR spectrum assigned to the Me_3Si groups at 0.20 and 0.16 ppm.

In a second series of time-dependent NMR experiments the reaction of 3 equiv of $Cp_2Ti(btmsa)$ with one of **1** was monitored by ^{31}P NMR spectroscopy with spectra recorded every 20 min at -78 °C. Already after the first 20 min the starting material **1** had disappeared. Only compounds **2** and **3** (ratio ca. 1:1) were observed. In the course of 2 days at ambient temperature, the intensity of the resonance due to **3** slowly increases whereas that due to **2** completely disappeared. After 2 days only the ^{31}P spectrum of the diphosphene **3** was observed. It can thus be assumed that in the first step **2** is generated from **1** in a fast reaction, while the second dechlorination step of **2** with $Cp_2Ti(btmsa)$ represents a much slower process.

The generation of diphosphene **3** from the dihydrazinodichlorophosphine **1** in the reaction with $Cp_2Ti(btmsa)$ is the first example of titanocene-assisted formation of a free stable diphosphene, a process that avoids the use of P–H bond containing reagents. $Cp_2Ti(btmsa)$ is a strong dechlorinating agent so that for this P–P coupling reaction, the readily available and relatively stable chlorophosphines can be used.

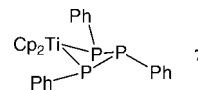
An analogous reaction in which stannylenes and germylenes were the dechlorinating agents was published by Veith and Huch¹⁴ in 1983. There is an obvious similarity between these

reagents and titanocene, all of which are carbene analogues. A free-radical mechanism has been proposed for the reduction of arylchlorophosphines with magnesium and with 1,3,1',3'-tetraethylbis(2,2'-imidazolidene), both of which lead to phosphorus-centered radicals $R(Cl)P^{\cdot}$.^{15,16} Diphosphene formation then proceeds via dimerization to the dichlorodiphosphine and subsequently further dehalogenative reduction. An analogous mechanism may be operative in the reaction of chlorophosphines with $Cp_2Ti(btmsa)$.

Synthesis of $Mes^*P=PMes^*$. Our new approach has been applied to several other dichlorophosphines. For instance, the known diphosphene $Mes^*P=PMes^*$ ⁹ ($Mes^* = 2,4,6-tBu_3C_6H_2$) (**4**) was also obtained cleanly in a reaction of $Cp_2Ti(btmsa)$ with Mes^*PCl_2 employing an excess of $Cp_2Ti(btmsa)$. The reaction of $Cp_2Ti(btmsa)$ with a twofold excess of Mes^*PCl_2 resulted in the formation of the dichlorodiphosphine $Mes^*(Cl)PP(Cl)Mes^*$ (**5**), which has been mentioned briefly before.^{13b}

Synthesis of Tetraphenyldiphosphine. The reaction of 1 equiv of $Cp_2Ti(btmsa)$ with diphenylchlorophosphine gave $(Cp_2TiCl)_2$ and tetraphenyldiphosphine (**6**) in good yields. When only 0.5 equiv of $Cp_2Ti(btmsa)$ was used, Cp_2TiCl_2 was the organotitanium product in addition to Ph_4P_2 . When an excess of $Cp_2Ti(btmsa)$ was used no coordination of the diphosphine to the titanium center could be detected.

Reaction of $Cp_2Ti(btmsa)$ with Phenylchlorophosphine. The reaction of a threefold excess of $Cp_2Ti(btmsa)$ with phenylchlorophosphine in toluene gave a deep dark red solution containing mainly one phosphorus-containing product in addition to $(Cp_2TiCl)_2$ during the course of 2 days. The latter crystallized upon addition of *n*-hexane to the toluene solution. Formation of tetraphenylcyclotetraphosphine¹⁷ or other cyclopolyphosphines¹⁸ was not observed. The ^{31}P NMR spectrum of the resulting supernatant solution showed two signals, a doublet at 191.2 ppm and a triplet at -186.3 ppm. These can be assigned to the cyclo-titanatraphosphine complex **7**, which had been described by Köpf and Voigtländer in 1981.¹⁹ Our ^{31}P NMR chemical shifts and coupling constants are in agreement with theirs. Benac and Jones²⁰ reported that this type of complex can be obtained by reacting lithium phosphides, $LiPH(R)$ ($R = Ph, tBu$), with $Cp^*_2MCl_2$ ($M = Zr, Hf; Cp^* = \eta^5-C_5H_5$).



X-ray Crystallography. Crystallographic data for **2** and **3** are summarized in Table 1. The perspective views of **2** and **3** are depicted in Figures 2 and 3. Selected structural data are given in Table 2. Dichlorodiphosphine **2** crystallizes in yellowish plates in the triclinic space group $P\bar{1}$ with one molecule per unit. As depicted in Figure 2, the asymmetric unit consists of one-half of the molecule with both phosphorus groups in a staggered position with respect to each other; all attached atoms/groups are in a trans position in agreement with symmetry

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Table 1. Crystallographic Data

	2	3
formula	C ₁₈ H ₅₄ N ₄ Si ₆ P ₂ Cl ₂	C ₁₈ H ₅₄ N ₄ Si ₆ P ₂
fw	628.03	557.13
color	yellow	yellow
cryst syst	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	8.762(2)	8.724(2)
<i>b</i> , Å	9.246 (2)	9.467(2)
<i>c</i> , Å	12.340(3)	23.224(5)
α , deg	77.45(3)	84.51(3)
β , deg	83.69(3)	80.24(3)
γ , deg	63.81(3)	66.53(3)
<i>V</i> , Å ³	875.5(3)	1733.1(6)
<i>Z</i>	1	2
ρ_{calc} , g cm ⁻³	1.191	1.068
μ , mm ⁻¹	0.50	0.35
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073
<i>T</i> , K	173(2)	228(2)
no. of reflns collected	21470	38287
no. of indep. reflns	3978	7783
no. of obsd reflns	3785	6061
<i>R</i> _{int}	0.02	0.03
<i>F</i> (000)	338	608
<i>R</i> ₁ ^a	0.020	0.04
<i>wR</i> ₂ ^b	0.06	0.11
GooF	1.063	1.072
no. of parameters	154	289

^a final *R* [*I* > 2 σ (*I*)]. ^b *R* indices (all data).

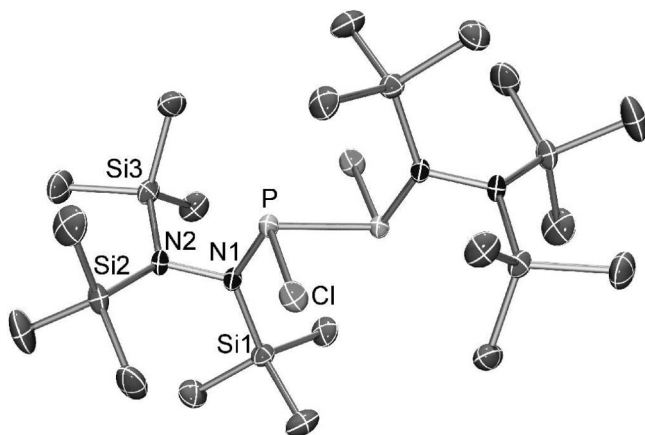


Figure 2. ORTEP drawing of the molecular structures of **2** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Selected distances in Å, angles in deg: P1–P1ⁱ 2.255(1), P1–N1 1.6795(9), P1–Cl1 2.1359(5), N1–N2 1.485(1), Cl1–P1–P1ⁱ 90.87(3), N1–P1–P1ⁱ 102.05(4), N2–N1–P1 111.46(6); P1ⁱ–P1–N1–N2 154.67(5), Cl–P1–P1ⁱ–Cl 180.00(2), N1–P1–P1ⁱ–N1ⁱ 180.00(2), Cl1–P1–N1–N2 –110.71(6), Cl1–P1–N1–Si1 60.18(7).

constraints. Compound **3** crystallizes in the form of yellow needles in the triclinic space group *P* $\bar{1}$ with two independent molecules per unit. Both molecules of the diphosphene display a trans configuration of the hydrazine groups along the P=P double bond.

Despite obvious differences in species **2** and **3**, the molecular structure of the hydrazine moiety of **3** strongly resembles that of **2**: (i) a staggered conformation with two perpendicular planes

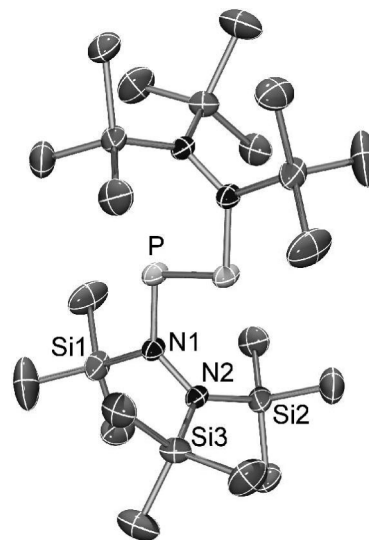


Figure 3. ORTEP drawing of the molecular structure of **3** (only one of the two independent molecules is shown) in the crystal. Thermal ellipsoids with 50% probability at 228 K. Selected distances in Å, angles in deg: P1–P1ⁱ 2.038(1), P1–N1 1.700(2), N1–N2 1.463(2); N1–P1–P1ⁱ 103.38(7), N2–N1–P1 120.8(1); P1ⁱ–P1–N1–N2 –1.4(1), N1–P1–P1ⁱ–N1ⁱ 180.00(9), P1–N1–N2–Si2 –91.1(1).

Table 2. Selected Structural Data of **2** and **3** (Bond Lengths in Å, Angles in deg)

	2	3
P1–P1 ⁱ	2.255(1)	2.038(1)
P1–N1	1.6795(9)	1.700(2)
N1–N2	1.485(1)	1.463(2)
N1–Si1	1.794(1)	1.763(2)
N2–Si3	1.758(1)	1.754(2)
N2–Si2	1.7584(9)	1.758(2)
Si1–C3	1.859(1)	1.860(3)
P1–Cl1	2.1359(5)	
$\angle$ N1–P1–P1 ⁱ	102.05(4)	103.38(7)
$\angle$ P1–N1–Si1	132.17(5)	117.00(9)
$\angle$ N2–N1–P1	111.46(6)	1208(1)
$\angle$ N2–N1–Si1	115.81(6)	122.1(1)
$\angle$ N1–N2–Si3	117.63(6)	116.2(1)
$\angle$ N1–N2–Si2	113.46(6)	115.6(1)
$\angle$ Cl1–P1–P1 ⁱ	90.87(3)	
$\angle$ N1–P1–Cl1	106.76(4)	
$\angle$ Cl1–P1–N1–N2	–110.71(6)	
$\angle$ P1 ⁱ –P1–N1–N2	154.67(5)	–1.4(1)
$\angle$ P1 ⁱ –P1–N1–Si1	–34.44	176.00(8)
$\angle$ P1–N1–N2–Si3	79.62(7)	93.1(1)
$\angle$ Si–N1–N2–Si2	104.03(6)	91.4(1)

was found,¹ (ii) both nitrogen atoms are in an ideal planar environment ($\Sigma\angle(\text{N1}) = 359.96^\circ$, $\Sigma\angle(\text{N2}) = 359.9^\circ$) with bond lengths typical for a single N–N bond, and (iii) a short P–N bond length of 1.6795(9) Å in **2** and 1.700(1) Å in **3** was found (cf. $\Sigma r_{\text{cov.}} = 1.80$ (1.76) Å).^{21,22} Moreover, in both species a center of symmetry is located in the middle of the P–P bond.

The main difference between **2** and **3** lies in the geometry of the NNPPNN-moiety. While it is almost planar in the case of **3** (dihedral angles close to 0.0° and 180.0°, respectively), the N–N–P and N–P–P planes of **2** are not coplanar but exhibit a dihedral angle of 25.33(5)°. The dihedral angle between the Cl–P–N plane and the N–N–P plane is 69.39(6)°. The central moiety in **2** consists of a Cl–P–P–Cl plane with the Cl atoms in a trans configuration. The preferred trans orientation of the P–Cl bonds in dichlorodiphosphines was proposed previously based on NMR spectroscopic data by Baudler et al.^{13a} The P–Cl

(21) The first value corresponds to the sum of covalent radii: $r(\text{P}) = 1.1$ and $r(\text{N}) = 0.7$; however, bond lengths between two elements with large differences in electronegativity are often corrected according to $d_{\text{AB}} = r_{\text{A}} + r_{\text{B}} - c|\chi_{\text{A}} - \chi_{\text{B}}|$ (Schomaker–Steveson equation): *Holleman–Wiberg Lehrbuch der Anorganischen Chemie*, 101. Aufl.; Walter de Gruyter: New York, 1995; Anhang V.

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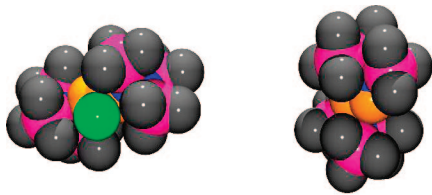


Figure 4. Space-filling models of $\text{RP}(\text{Cl})\text{--P}(\text{Cl})\text{R}$ (**2**) and $\text{RP}=\text{PR}$ (**3**) with $\text{R} = (\text{Me}_3\text{Si})\text{N--N}(\text{SiMe}_3)_2$.

bonds and the P–P bond are almost perpendicular, with a Cl--P--P angle of $90.87(3)^\circ$. Other interesting structural features are the P–P bond and the N–P–P angles. As expected, the P=P bond length in **3** of $2.038(1) \text{ \AA}$ is close to the values observed for other diphosphenes and significantly shorter than the P–P bonds in **2** ($2.255(1) \text{ \AA}$, cf. $\Sigma r_{\text{cov.}} = 2.20$). The P–P bond length in **2** corresponds to that of a typical single bond.^{16,21} Also, the N–P–P angle in **3** ($103.38(7)^\circ$) is in the range for known R–P–P angles of diphosphenes. The whole NNPPNN-moiety is almost planar so that electronic delocalization in this part of the molecule can be assumed due to hyperconjugative effects.

Dichlorophosphine **2** and diphosphene **3** are kinetically stabilized by the steric effects of the adjacent bulky $(\text{Me}_3\text{Si})\text{N--N}(\text{SiMe}_3)_2$ groups (Figure 4). Steric protection in the sandwich between the two tris(trimethylsilyl)hydrazino groups is responsible, e.g., for the impossibility of forming a titanium complex of **3**. Even when **3** is added to a large excess of $\text{Cp}_2\text{Ti}(\text{btmsa})$ no complex formation was observed in the course of several days, even when a toluene solution of $\text{Cp}_2\text{Ti}(\text{btmsa})$ and **3** was heated at 110°C . Attempted reactions of **3** with $\text{Cr}(\text{CO})_3(\text{H}_3\text{CCN})_3$ or $\text{Fe}_2(\text{CO})_9$ did not result in formation of complexes. This is somewhat surprising since some transition metal complexes of stable diphosphenes have been reported.²³

3. Experimental Section

General Information. All manipulations were carried out under oxygen- and moisture-free conditions with standard Schlenk or inert atmosphere box techniques. Solvents were dried over sodium benzophenone and were freshly distilled prior to use. Bis(cyclopentadienyl)titanium[bis(trimethylsilyl)acetylen]-adduct,²⁴ [tris(trimethylsilyl)hydrazino]dichlorophosphine,¹¹ and (2,4,6-tri-*tert*-butylphenyl)dichlorophosphine²⁵ were synthesized according to literature methods. Phenylidichlorophosphine and diphenylchlorophosphine were purchased from Acros and were distilled prior to use.

NMR: NMR spectra were obtained with Bruker ARX 300, AV 300, or AV 400 spectrometers. $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra are referenced internally to the deuterated solvent (^{13}C) or to protic impurities in the deuterated solvent (^1H). ^{29}Si and ^{31}P NMR spectra are referenced externally. Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm). MS: Finnigan MAT 95-XP from Thermo Electron. All mass spectra were recorded by chemical ionization (positive) in isobutane. CHN analysis: Truspec CHNS Microanalysator from

Leco or Analysator Flash EA 1112 from Thermo Quest. UV/Vis: Perkin Elmer Lambda 19. Melting points are uncorrected (EZ-Melt, Stanford Research Systems).

X-ray Structure Determination. X-ray quality crystals of **2** and **3** were selected in Kel-F-oil at ambient temperature and were cooled to 173 K (**2**) or 228 K (**3**) during measurement. The data were collected on a Bruker Apex X8 CCD diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$). The structures were solved by direct methods (SHELXS-97)²⁶ and refined by full-matrix least-squares procedures (SHELXL-97).²⁷ Semiempirical absorption corrections were applied (SADABS). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the refinement at calculated positions by using a riding model.

Bis[tris(trimethylsilyl)hydrazino]dichlorodiphosphine (2). $\text{Cp}_2\text{Ti}(\text{btmsa})_2$ (0.7 g , 2.0 mmol) was dissolved in 15 mL of toluene and cooled to -78°C . A solution of 1.4 g (4.0 mmol) of [tris(trimethylsilyl)hydrazino]dichlorophosphine in 15 mL of toluene was added slowly by syringe. The resulting mixture was stirred for 15 min at this temperature and then warmed to room temperature. After it had been stirred overnight, the red solution was evaporated in vacuo. The residue was extracted with 40 mL of *n*-hexane and filtered. The yellow-brown filtrate was concentrated in vacuo and cooled to -40°C . Crude **2** was obtained as a brown solid in 48% yield (0.6 g , 0.96 mmol). For further purification the crude product was recrystallized from *n*-hexane to give yellow crystals.

^1H NMR (400.13 MHz , C_6D_6): $0.49 \text{ (s, 18 H, Si(CH}_3)_3)$, $0.39 \text{ (s, 18 H, Si(CH}_3)_3)$, $0.34 \text{ (s, 18 H, Si(CH}_3)_3)$. ^{13}C NMR (100.63 MHz , C_6D_6): $4.6 \text{ (} J_{\text{CP}} = 8 \text{ Hz, Si(CH}_3)_3)$, $4.0 \text{ (Si(CH}_3)_3)$, $3.5 \text{ (Si(CH}_3)_3)$. ^{29}Si NMR (79.49 MHz , C_6D_6): $22.6, 11.4, 8.9$. ^{31}P NMR (161.98 MHz , C_6D_6): 153.4 . Raman (cm^{-1}): $2983(4)$, $2961(5)$, $2901(10)$, $1411(2)$, $1246(1)$, $984(1)$, $924(1)$, $844(1)$, $758(1)$, $688(2)$, $663(2)$, $647(4)$, $587(2)$, $484(3)$, $452(3)$, $418(3)$, $365(4)$, $231(3)$, $207(3)$. CI-MS (m/z): 591 (M - Cl) , 556 (M - 2 Cl) , $483 \text{ (M - 2 Cl - Si(CH}_3)_3)$, 313 (M/2) , 278 (M/2 - Cl) . Mp 184°C dec. Elemental Anal. Calcd for $\text{H}_{54}\text{C}_{18}\text{N}_4\text{Si}_6\text{P}_2\text{Cl}_2$: C 34.42 , H 8.67 , N 8.92 . Found: C 33.94 , H 8.89 , N 8.66 .

Bis[tris(trimethylsilyl)hydrazino]diphosphene (3). $\text{Cp}_2\text{Ti}(\text{btmsa})_2$ (2.1 g , 6.0 mmol) was dissolved in 30 mL of toluene and cooled to -78°C . A solution of 0.7 g (2.0 mmol) of [tris(trimethylsilyl)hydrazino]dichlorophosphine in 10 mL of toluene was added slowly by syringe. The resulting mixture was stirred for 15 min at this temperature and then warmed to room temperature. After it had been stirred for 40 h the yellow-green solution was evaporated in vacuo. The residue was extracted with 30 mL of *n*-hexane and filtered. The yellow-brown filtrate was concentrated in vacuo and cooled to -40°C . Crude **3** was obtained as a yellow crystalline solid in 90% yield (0.5 g , 0.9 mmol). The crude product was purified by column chromatography on silica gel with *n*-hexane. The yellow eluate was reduced to a small volume and cooled to -40°C yielding yellow needles of **3**.

^1H NMR (300.13 MHz , C_6D_6): $0.20 \text{ (s, 36 H, Si(CH}_3)_3)$, $0.16 \text{ (s, 18 H, Si(CH}_3)_3)$. ^{13}C NMR (75.48 MHz , C_6D_6): $2.4 \text{ (} J_{\text{CP}} = 4 \text{ Hz, Si(CH}_3)_3)$, $3.2 \text{ (} J_{\text{CP}} = 2 \text{ Hz, Si(CH}_3)_3)$. ^{29}Si NMR (59.62 MHz , C_6D_6): $14.1, 8.6$. ^{31}P NMR (121.5 MHz , C_6D_6): 426.5 . Raman (cm^{-1}): $2955(4)$, $2900(10)$, $1410(1)$, $1263(1)$, $1048(1)$, $848(1)$, $778(1)$, $681(1)$, $644(3)$, $621(1)$, $594(2)$, $417(2)$, $390(1)$. CI-MS (m/z): 556 (M) , $397 \text{ (M - N(SiMe}_3)_2)$, 279 (M/2 + 1) , $162 \text{ (N(SiMe}_3)_2 + 2)}$. Mp 162.2°C dec. UV/Vis: $\lambda = 415 \text{ nm}$ ($\epsilon = 5000 \text{ l/mol}\cdot\text{cm}$). Elemental Anal. Calcd for $\text{H}_{54}\text{C}_{18}\text{N}_4\text{Si}_6\text{P}_2$: C 38.81 , H 9.77 , N 10.06 . Found: C 38.78 , H 9.55 , N 9.56 .

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Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (4). $\text{Cp}_2\text{Ti}(\text{btmsa})_2$ (1.1 g, 3.1 mmol) was dissolved in 10 mL of toluene and cooled to -78°C . A solution of 0.38 g (1.1 mmol) of (2,4,6-*tert*-butylphenyl)dichlorophosphine in 7 mL of toluene was added slowly by syringe. The resulting mixture was stirred for 15 min at this temperature and then warmed to room temperature. After it had been stirred for 40 h the yellow-green solution was evaporated in vacuo. The residue was extracted with 30 mL of *n*-hexane, filtered through a small amount of silica gel, and washed with an additional 30 mL of *n*-hexane. The dark orange filtrate was concentrated in vacuo and cooled to -40°C . Compound **4** was obtained as an orange crystalline solid in 65% yield (0.2 g, 0.36 mmol).

^1H NMR (300.13 MHz, C_6D_6): 7.59 (s, 4 H, Ph-*H*), 1.57 (s, 36 H, CH_3), 1.29 (s, 18 H, CH_3). ^{31}P NMR (121.53 MHz, C_6D_6): 494.2. CI-MS (m/z): 553 ($\text{M} + 1$), 307 ($\text{M} - \text{Mes}^*$), 277 ($\text{Mes}^*\text{P} + 1$).

Bis(2,4,6-tri-*tert*-butylphenyl)dichlorodiphosphine (5). $\text{Cp}_2\text{Ti}(\text{btmsa})_2$ (0.7 g, 2.0 mmol) was dissolved in 15 mL of toluene and cooled to -78°C . A solution of 1.4 g (4.0 mmol) of (2,4,6-tri-*tert*-butylphenyl)dichlorophosphine in 15 mL of toluene is added slowly by syringe. The resulting mixture was stirred for 15 min at this temperature and then warmed to room temperature. After it had been stirred overnight the red solution was evaporated in vacuo. The residue was extracted with 40 mL of *n*-hexane and filtered. The dark orange filtrate was concentrated in vacuo and cooled to -40°C . The crude **5** was obtained as a light orange brown solid in 25% yield (0.31 g, 0.5 mmol). For further purification the crude product was recrystallized from *n*-hexane.

^1H NMR (300.13 MHz, C_6D_6): 7.54 (s, 4 H, Ph-*H*), 1.71 (s, 36 H, CH_3), 1.25 (s, 18 H, CH_3). ^{31}P NMR (121.53 MHz, C_6D_6): 76.7. CI-MS (m/z): 587 ($\text{M} - \text{Cl}$), 553 ($\text{M} - 2\text{Cl}$), 311 (Mes^*PCl), 276 (Mes^*P). Mp 253.1°C dec. Elemental Anal.: Calcd for $\text{H}_{58}\text{C}_{36}\text{P}_2\text{Cl}_2$: C 69.32, H 9.37. Found: C 68.94, H 8.68.

Reaction of $\text{Cp}_2\text{Ti}(\text{btmsa})$ with Diphenylchlorophosphine: Synthesis of Tetraphenyldiphosphine (6). $\text{Cp}_2\text{Ti}(\text{btmsa})_2$ (1.35 g, 3.9 mmol) was dissolved in 20 mL of toluene and cooled to -78°C . A solution of 420 mg (1.9 mmol) of Ph_2PCl in 5 mL of toluene was added slowly by syringe. The solution was stirred for 20 min at -78°C and then warmed to room temperature. Tetraphenyldiphosphine was isolated by evaporation of the toluene,

extraction with *n*-hexane continuing a small amount of toluene, followed by recrystallization in 59% yield (205 mg, 0.56 mmol).

^1H NMR (300.13 MHz, C_6D_6): 7.58–7.52 (m, 8 H, Ph-*H*), 6.98–6.92 (m, 8 H, Ph-*H*), 6.93 (4 H, Ph-*H*, t). ^{13}C NMR (75.48 MHz, C_6D_6): 136.6 (*i*-Ph, vt $J = 5.5$ Hz), 134.8 (*o*-Ph, vt $J = 13.4$ Hz), 128.9 (*p*-Ph), 128.5 (m-Ph, vt $J = 3.4$ Hz). ^{31}P NMR (121.53 MHz, C_6D_6): -14.2 . CI-MS (m/z): 371 (M), 294 ($\text{M} - \text{Ph}$), 187 ($\text{Ph}_2\text{P} + 2$). Mp 122°C . Elemental Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{P}_2$: C 77.82, H 5.44. Found: C 77.10, H 5.53.²⁸

Reaction of $\text{Cp}_2\text{Ti}(\text{btmsa})$ with Phenylchlorophosphine: Synthesis of Bis(cyclopentadienyl)tri(phenylphosphinato)titanium(IV) (7). $\text{Cp}_2\text{Ti}(\text{btmsa})_2$ (1.8 g, 5.2 mmol) was dissolved in 30 mL of toluene and cooled to -78°C . A solution of 310 mg (1.7 mmol) of PhPCl_2 in 5 mL of toluene is added slowly by syringe. The solution is stirred for 20 min at -78°C and then warmed to room temperature. After it had been stirred overnight the dark red mixture was evaporated in vacuo. Extraction with diethyl ether, stepwise removal of the solvent, followed by layering with *n*-hexane afforded 420 mg (0.86 mmol, 49%) of crystalline **7**.

^1H NMR (400.13 MHz, C_6D_6): 8.51 (m, 2 H, Ph-*H*), 7.68 (m, 4 H, Ph-*H*), 7.0–7.2 (m, 9 H, Ph-*H*), 5.35 (s, 5 H, Cp-*H*), 5.04 (s, 5 H, Cp-*H*). ^{31}P NMR (161.98 MHz, C_6D_6): 191.9 (d, $^1J_{\text{PP}} = 337$ Hz), -185.6 (t, $^1J_{\text{PP}} = 337$ Hz). CI-MS (m/z): 502 (M), 394 ($\text{M} - \text{PPh}$). Elemental Anal. Calcd for $\text{C}_{28}\text{H}_{25}\text{P}_3\text{Ti}$: C 66.94, H 5.02. Found: C 66.54, H 5.11.

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Supporting Information Available: Crystallographic data in CIF data format. This material is available free of charge via the Internet at <http://pubs.acs.org>. The CIF files are also available online from the Cambridge Crystallographic Data Centre (CCDC Nos. 664605 (**2**), 664606 (**3**)).

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