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Synthesis, Spectroscopic Properties, and Reactivity of Ferrocenyl(2,4,6-tri-*tert*-butylphenyl)diphosphene

Rudolf Pietschnig and Edgar Niecke*

Institut für Anorganische Chemie, Gerhard-Domagk-Strasse 2, D-53121 Bonn, Federal Republic of Germany

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Summary: A ferrocenyl-substituted diphosphene has been synthesized and characterized, which seems to represent a borderline case concerning the dimerization of such species. Thus, the tetraphosphetane formed by dimerization readily undergoes cycloreversion to the initial diphosphene upon heating in xylene solution.

Introduction

Tetraphosphetanes and other cyclopolyphosphanes are common byproducts in the synthesis of diphosphenes.[1] Even the first diphosphene reported, the historically interesting “phosphobenzene”,[2] turned out to be a mixture of several different cyclopolyphosphanes,[3] Since the reactions of polyphosphanes often lead to the products expected in the formal reaction of the corresponding diphosphene or phosphinidene,[4] several attempts have been made to generate these compounds from the easily available polyphosphanes.[5] Up to now only few cases are known in which diphosphenes have been generated by cycloreversion of tetraphosphetanes.[6] In all of these cases the tetraphosphetane was formed by initial cycloaddition of an unsymmetrical diphosphene, whereas the products of the following cycloreversion were symmetrical diphosphenes, at least one of which proved to be stable against further cycloaddition reactions (diphosphene metathesis). The ferrocenyl substituent selected for our investigations has been characterized by its remarkable ability to stabilize a positive charge on an adjacent atom.[7] We consider this to be a very useful feature concerning the cycloreversion of tetraphosphetanes to diphosphenes under mild conditions, as shall be pointed out later.

Results and Discussion

Although the electronic properties of the ferrocenyl substituent alone are insufficient to stabilize a monomeric diphosphene,[8] we succeeded, by combining both steric and electronic features, in generating a diphosphene **(1)** that seems to represent a borderline case concerning dimerization. The ferrocenyldiphosphene **(1)** dimerizes slowly at room temperature, forming the cyclotetraphosphane **(2)**, which upon heating in xylene readily undergoes cycloreversion to the original diphosphene **(1)**. Furthermore, this process is completely reversible and strictly stereospecific.

The ferrocenyl-substituted diphosphene **(1)** is synthesized from ferrocenyldichlorophosphane and lithium (2,4,6-tri-*tert*-butylphenyl)(trimethylsilyl)phosphanide at −78 °C. The compound shows a characteristic intensive red-violet color due to a long-wavelength absorption at 515 nm. In comparison to other diphosphenes (355−484 nm)[1] this is a remarkable bathochromic shift, indicating considerable electronic interaction between the ferrocenyl group and the P═P double bond.

This hypothesis is corroborated by the NMR data. Accordingly, the ^{31}P NMR spectrum of **1** shows an AX system in the low-field range typical for *trans*-diphosphenes with $\delta(P_A)$ 471.2 ppm and $\delta(P_B)$ 442.6 ppm. In contrast, the coupling constant $^1J_{PP} = 532$ Hz is rather small for *trans*-diphosphenes in general but is in good accordance with *E*-configurated systems bearing at least one strong π-donating substituent, as for instance in aminodiphosphenes.[9] The reduced coupling constant can be explained by assuming a reduced P−P bond order, as depicted in formulation **1b** (Scheme 2), which has been confirmed for certain aminodiphosphenes by X-ray structure analysis.[10]

Evidence that formulation **1b** is of considerable importance can be found in the ^{1}H NMR spectrum of **1**, since the α-protons of the substituted cyclopentadienyl ring are chemically not equivalent. While the signals due to the β-protons of the same ring are detected indistinguishably at 4.29 ppm (2H) as a multiplet, the two α-protons are observed at different values, namely 4.76 ppm (1H) for the downfield proton and 4.65 ppm (1H) for the upfield one.[11]

Since the steric demand of the ferrocenyl moiety is comparable to that of the phenyl group[12] and the PhP═PMes* (Mes* = 2,4,6-tri-*tert*-butylphenyl) substituted diphosphene can not be isolated in the monomeric form,[13] diphosphene **1** also dimerizes slowly when exposed to daylight and ambient temperature, taking weeks, depending on temperature and concentration.[14] Remarkably, only one of the various possible isomers

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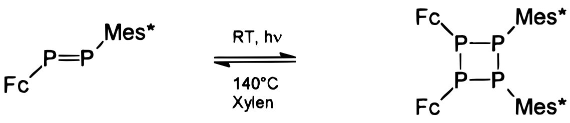
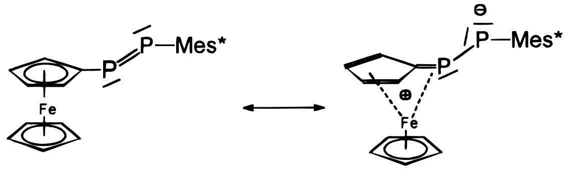
Scheme 1[a]



(1) **(2)**

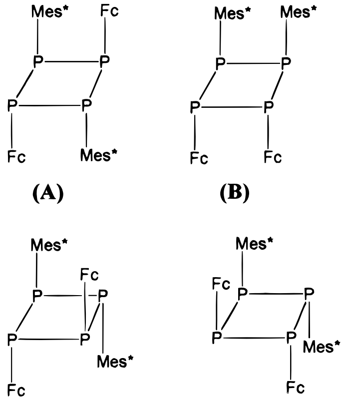
[a] Legend: Fc = ferrocenyl; Mes* = 2,4,6-tri-*tert*-butylphenyl.

Scheme 2



(1a) **(1b)**

Chart 1



(A) **(B)**

(C) **(D)**

is formed, showing an AA′BB′ spin system. At a temperature of −30 °C and in the absence of light, the ferrocenyl-substituted diphosphene remains stable in the monomeric form. When it is heated in boiling xylene to approximatly 140 °C, the tetraphosphetane **2** undergoes spontaneous cycloreversion, yielding diphosphene **1** stereospecifically in the *E* configuration. Irradiation of solid **2** with UV light leads to the same product. In neither case is Mes*P=PMes* formed.

Due to the fact that an AA′BB′ spin system is observed for tetraphosphetane **2**, only a few relative arrangements of substituents are possible (Chart 1). Simulated and measured ^{31}P NMR spectra of **2** are in good accordance, using as a set of coupling parameters $J_{AA'}/J_{BB'} = 127.6/\pm156.8$ Hz and $J_{AB}/J_{AB'} = \pm150.9/-64.8$ Hz. Assuming an arrangement of substituents as shown in **A**, the coupling constants AA′ and BB′ would be of the type $^{2}J_{PP}$, which is in contradiction to the observed values revealing a $^{1}J_{PP}$ coupling.[15] Hence, a "head to tail" dimer can be excluded. Considering a "head to head" dimer showing the observed spin system, the substituent adjacent to A is arranged either *cis* **(B)** or *trans* **(C,D)** in reference to A′. Since in these cases the coupling constants AA′ and BB′ are of the type $^{1}J_{PP}$, these structures are in good agreement with the observed values. A further decision between **B**, **C**, and **D** is not possible merely on the basis of the NMR data. However, due to possible steric interaction an arrangement as shown in **B** seems to be highly unlikely. Therefore, we presume tetraphosphetane **2** to have a structure like **C** or **D**, in which the bulky Mes* substituents are oriented *trans* to each other.

If the observed stereospecifity is not a consequence of the concerted course of reaction but of the relative stability of the resulting products, structure **C** would be the most probable one. But it should be pointed out that in all known cases where cycloreversion occurs, one of the two substituents is a π-donor. As recently proposed by Bickelhaupt *et al.*,[16] a thermal dimerization of diphosphenes is preceded by initial formation of an intermediate *cis* isomer. Similarly, structure **D** represents the adduct of this intermediate. Therefore, from the mechanistic point of view, structure **D** is the most likely one. The corresponding cycloreversion, which is the retro reaction, should also proceed *via* the generation of an initial *cis* diphosphene, followed by subsequent *cis*−*trans* isomerization. This process should, according to formulation **1b** (Scheme 2), be facilitated by an adjacent π-donor substituent.

Chemically, the ferrocenyl-substituted diphosphene **1** behaves like other diphosphenes, forming the expected [2 + 4] cycloadduct **3** with cyclopentadiene (Scheme 3). While at high temperature predominant formation of one of the two possible diastereomers **3a** or **3b** cannot be observed, at ambient temperature only one of them is formed.

Treatment of **1** with methanol or water results—as common for diphosphenes[9]— in cleavage of the P−P bond. As indicated by the polarity expressed by formulations **1a,b** (Scheme 2), Mes*PH_2 and Fc−P$(OR)_2$ are the sole products of this reaction. Products of the opposite polarity, as for instance the well-known Fc−PH_2, cannot be detected.

Stabilization of diphosphene **1** can be achieved by complexation to Pt(0) (Scheme 3). The resulting complex **4** is stable at room temperature (δ_P (121.5 MHz, toluene): P_A 25.5, P_B 24.8, P_C 26.4, P_X −16.1; $^{1}J_{AX} = -424.0$ Hz, $^{2}J_{AB} = 52.2$ Hz, $^{2}J_{AC} = 4.0$ Hz, $^{2}J_{XB} = 3.0$ Hz, $^{2}J_{CX} = 36.0$ Hz, $^{2}J_{BC} = 8.0$ Hz). In contrast, the presence of $Fe_2(CO)_9$ even seems to accelerate the formation of tetraphosphetane **2** and does not lead to the desired monomeric diphosphene complex.

Experimental Section

General Considerations. All steps were carried out under a dry argon atmosphere using common Schlenk techniques. Solvents were dried and freshly distilled from Na/K alloy before use. NMR spectra were recorded on a Bruker AMX 300. ^{31}P NMR spectra were recorded using 85% H_3PO_4 as external standard and ^{1}H NMR spectra with tetramethylsilane as external standard.

Preparation of 1. (*E*)-1-Ferrocenyl-2-(2,4,6-tri-*tert*-butylphenyl)diphosphene was synthesized from (2,4,6-tri-*tert*-butylphenyl)(trimethylsilyl)phosphane (Mes*PHTms)[17] and

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(14) As measured by ^{31}P NMR spectroscopicly the dimerization is second order in **1**. The half-lifetime at a concentration of 2.3×10^{-2} mol/L turned out to be approximately 4 days.

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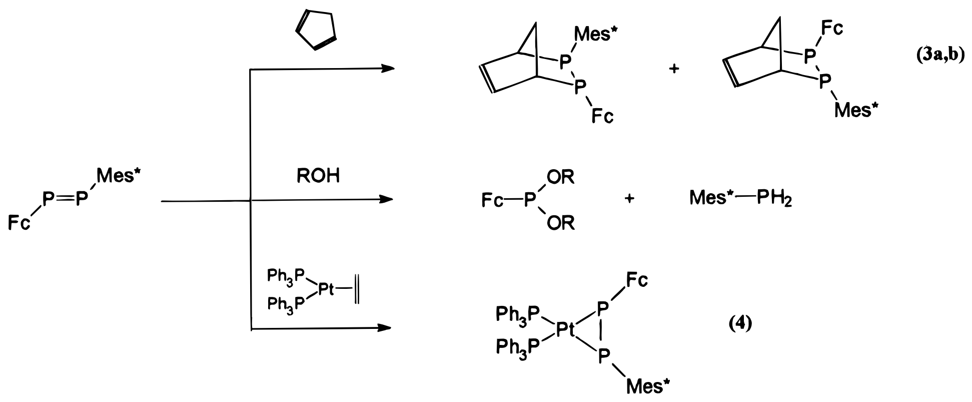
Scheme 3



dichloroferrocenylphosphane ($FcPCl_2$).[18] To a solution of Mes*-PHTms (1.75 g, 5.0 mmol) in diethyl ether (20 mL) was added a solution of *n*-butyllithium (3.4 mL, 5.5 mmol) in hexane at −78 °C. After being stirred for 30 min at −78 °C, the reaction mixture was stirred at room temperature for 1.5 h. The resulting mixture was slowly added to a cooled (−78 °C) solution of $FcPCl_2$ (1.44 g, 5.0 mmol) in diethyl ether (100 mL). After the reaction mixture was warmed to room temperature, the solvent was evaporated under vacuum. The residue was extracted with pentane and the LiCl filtered. After evaporation of the pentane under vacuum **1** was obtained as a deep red-violet solid (yield 2.02 g, 82%). On recrystallization from toluene at room temperature, **2** is obtained as a yellow solid (mp 98 °C dec).

1. δ_P (121.5 MHz, pentane): 471.2 (1P, d, $^1J_{PP} = 532$ Hz, P−Fc) and 442.6 (1P, d, $^1J_{PP} = 532$ Hz, P−Mes*). δ_H (300 MHz, C_6D_6) 7.61 (2H, s, Mes*), 4.76 (1H, s, H_α−Fc), 4.65 (1H, s, H_α−Fc), 4.29 (2H, s, H_β−Fc), 4.08 (5H, s, Cp′−Fc), 1.90 (18H, s, *ortho*-$C(CH_3)_3$), 1.40 (9H, s, *para*-$C(CH_3)_3$). δ_C (75.5 MHz, $CDCl_3$) 68.9 (s, Cp′), 68.7 (m, C_α−Fc), 69.5 (m, $C_{\alpha'}$−Fc), 69.9 (m, C_β−Fc), 31.4 (s, *para*-$C(CH_3)_3$), 34.9 (s, *para*-$C(CH_3)_3$), 31.6 (d, $^4J_{CP} = 16.4$ Hz, *ortho*-$C(CH_3)_3$), 39.8 (d, $^3J_{CP} = 4.0$ Hz, *ortho*-$C(CH_3)_3$), 149.5, 149.6, 149.9, and 123.2 (m, Mes*). MS (EI, 70 eV, 180 °C): M^+ 492.1790 (found), 492.179 08 (calculated), 62.2%; 435 (54%), $M^+ - t$-Bu; 277 (39%), Mes*PH^+; 217 (100%), $FcPH^+$; 186 (62%), FcH^+; 121 (18%), $CpFe^+$; 57 (40%), Fe/butyl$^+$. UV−vis (pentane): 515 nm ($\epsilon = 1065$ L/(mol cm), 447 nm ($\epsilon = 648$ L/(mol cm), 357 nm ($\epsilon = 3518$ L/(mol cm), 228 nm ($\epsilon = 12\,454$ L/(mol cm), 209 nm ($\epsilon = 13\,190$ L/(mol cm).

2. Anal. Calcd for $C_{56}H_{76}Fe_2P_4$: C, 68.30; H, 7.78. Found: C, 68.11; H, 7.93. δ_P (121.5 MHz, toluene): −32.0 (2P, m), −42.9 (2P, m) $^1J_{AA'} = 127.6$ Hz, $^1J_{BB'} = \pm 156.8$ Hz, $^1J_{AB} = \pm 150.9$ Hz, and $^2J_{AB'} = -64.8$ Hz. δ_H (300 MHz, $CDCl_3$): 7.21 (4H, m, Mes*), 4.43 (4H, m, H_α−Fc), 4.37 (4H, m, H_β−Fc), 4.21 (10H, m, Cp′), 1.65 (36H, m, *ortho*-$C(CH_3)_3$), 1.49 (18H, m, *para*-$C(CH_3)_3$). MS (FAB): 983.4 (20%), $M^+ - 1$; 799 (17%), M^+ − FcH; 739.2 (15%), M^+ − Mes*; 708.2 (40%) M^+ − Mes* − PH; 492.2 (42%), $M^+/2$; 217.0 (100%) $FcPH^+$.

2-Ferrocenyl-3-(2,4,6-tri-*tert*-butylphenyl)-2,3-diphosphanorborn-5-ene (3) is synthesized from **1** and cyclopentadiene. To a solution of **1** (0.3 g, 1 mmol) in pentane (15 mL) was added an excess of cyclopentadiene (CpH) (1 mL) at room temperature. After the mixture was stirred for 1.5 h, the solvent and excess cyclopentadiene were removed under vacuum, yielding 0.46 g (82.4%) of an orange oil. Satisfactory analysis could not be performed, since the product contained traces of dicyclopentadiene, which could not be removed without decomposition of the product. **3a:** δ_P (121.5 MHz, toluene) 35.9 (1P, d, $^1J_{PP} = 274.7$ Hz), −9.5 (1P, d, $^1J_{PP} = 274.7$ Hz) (isomer **3b**, obtained in mixture with **3a** when heated without solvent δ_P (121.5 MHz, toluene) 35.7 (1P, d, $^1J_{PP} = 279.8$ Hz), −7.6 (1P, d, $^1J_{PP} = 279.8$ Hz)); δ_H (300 MHz, C_6D_6) 4.3 (5H, s, Cp′), 4.4 (4H, m, $C_{\alpha/\beta}$), 1.7 (s, *o*-*t*-Bu), 1.5 (s, *p*-*t*-Bu), 2.8 (m), 3.1 (m), 5.6 (m), 5.7 (m), 1.2 (d, $J_{HP} = 7.1$ Hz), 1.7 (d, $J_{HP} = 9.3$ Hz), 7.6 (d, $J_{HP} = 2.1$ Hz); δ_C (75.5 MHz, C_6D_6) 69.9 (s, Cp′), 70.0 (d, $^1J_{CP} = 31.1$ Hz, C_{ipso}), 70.4 (d, $^2J_{CP} = 24.7$ Hz, C_α), 70.9 (s, C_β), 33.0 (d, $^4J_{CP} = 7.5$ Hz, *o*-*t*-Bu), 32.2 (s, *p*-*t*-Bu), 35.3 (s, C_q-*p*-*t*-Bu), 148.3 (d, $^1J_{CP} = 45.3$ Hz, C_{ipso}), 138.2 (d, $^2J_{CP} = 11.8$ Hz, C_{ortho}), 137.5 (d, $^3J_{CP} = 25.1$ Hz, C_{meta}), 136.1 (d, $^4J_{CP} = 2.3$ Hz, C_{para}), 136.7 (d, $^1J_{CP} = 43.9$ Hz), 132.3 (d, $^1J_{CP} = 56.2$ Hz), 47.6 (d, $^2J_{CP} = 26.1$ Hz), 45.2 (d, $^2J_{CP} = 31.1$ Hz), 53.9 (s, CH_2). MS (24 eV, 80 °C): 556 (0.5%), $M^+ - 2$; 492 (1.1%), M^+ − Cp; 484 (6.3%), $M^+ - C_2H_2$; 277 (47.3%), Mes*PH^+; 251 (6.5%), M^+ − Mes*P; 217 (18.5%), $FcPH^+$; 186 (24.0%), FcH^+; 66 (100%), Cp^+; 57 (65.1%), Fe/butyl$^+$.

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