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Pyridyl-Functionalized 1-Phosphabarrelene: Synthesis, Coordination Chemistry and Photochemical di-π-Methane Rearrangement

Marlene Bruce, Martin Papke, Andreas W. Ehlers, Manuela Weber, Dieter Lentz, Nicolas Mézailles, J. Chris Slootweg, and Christian Müller

Dedicated to the element phosphorus on the 350th anniversary of its discovery.

Abstract: The [4+2] cycloaddition of 2-(2'-pyridyl)-4,6-diphenyl-1,3-phosphinine with the highly reactive dienophile hexafluoro-2-butyne has been studied and the first pyridyl-functionalized 1-phosphabarrelene was obtained and structurally characterized. Although monodentate CF₃-1-phosphabarrelenes show only a poor coordination ability, the chelating nature of the novel PN-hybrid ligand gives access to various transition-metal complexes. Upon irradiation with UV light, the pyridyl-functionalized 1-phosphabarrelene undergoes a rather selective di-π-methane rearrangement in the coordination sphere of the metal center, leading to the formation of a complex based on a hitherto unknown pyridyl-functionalized 5-phosphasemibullvalene derivative. DFT calculations provide first insights into the mechanism of this reaction.

Introduction

During the last decade, 1-phosphabarrelenes have emerged to a fascinating class of phosphorus compounds, which have proven to be powerful ligands in various homogenous catalytic reactions.[1] Depending on the substitution pattern, these phosphorus-containing [2.2.2] bicycles can be regarded as rather rigid, sterically demanding phosphine derivatives with some degree of π-accepting character due to the strong pyramidalization of the phosphorus atom.[1,2]

The first 1-phosphabarrelene derivative (2) was prepared by Märkl and Lieb in 1968 by a [4+2] cycloaddition reaction of the aromatic 2,4,6-triphenyl-1,3-phosphinine (1) with hexafluoro-2-butyne (Figure 1). A more common dienophile is in situ generated benzyne, which gives the corresponding substituted benzo-1-phosphabarrelene 3.[1a,4-9,2,4-8] Bidentate ligands featuring at least one phosphabarrelene moiety, such as the chiral 1-phosphabarrelene-phosphite 4, are very rare, whereas PN-donor combinations have not been reported in literature.[1b,11] In 2017, we described for the first time the quantitative and selective photochemical di-π-methane rearrangement of 1-phosphabarrelene 3 to a racemic mixture of 5-phosphasemibullvalene 5, the isolobal phosphorus congener of semibullvalene.[5] This novel, rigid phosphorus cage has similar electronic properties as 1-phosphabarrelene 3 and was successfully applied as monodentate ligand in the Au^-catalyzed cycloisomerization of N-2-propynyl-1-ybenzamide.[9b] With this in mind, we now started to investigate the synthesis, coordination chemistry, and reactivity of potentially chelating 1-phosphabarrelene and 5-phosphasemibullvalene derivatives based on 2-(2'-pyridyl)-4,6-diphenylphosphinine (6).[9]
magnesium—to the corresponding pyridyl-functionalized 1-phosphabarrelene 7 (Scheme 1). Apparently, the pyridyl-functionality interferes with the species involved in the formation of the aryne. Several reagents known to generate benzyne in situ were also tested without any success, such as 2-iodophenoltosylate in combination with iPrMgCl or benzene diazonium-o-carboxylate.\[^3a, 12–14\] Similarly, the use of diethyl acetylenedicarboxylate or maleic anhydride as typical dienophiles did not lead to the desired 1-phosphabarrelene, either.\[^3a\]

In light of the successful \([4+2]\) cycloaddition reaction between phosphinines and hexafluoro-2-butyne, we treated 6 with an excess of hexafluoro-2-butyne at \(T = 85^\circ C\) in methylcyclohexane as solvent for 72 h.\[^5\] According to \(^{31}P\{^1H\}\) NMR spectroscopy, an almost complete conversion to a new phosphorus-containing species (8) was observed, which was isolated as a colourless solid after column chromatography and recrystallization from ethanol/water (20:1). Compound 8 shows a quartet in the \(^{31}P\{^1H\}\) NMR spectrum at \(\delta = -68.8\) ppm and a P–F coupling constant of \(J = 38.8\) Hz. We further found that the chosen reaction temperature needs to be strictly applied, because a retro-Diels–Alder reaction was observed at higher reaction temperatures, which caused regeneration of phosphinine 6. This observation indicates that 8 is only slightly lower in energy than the mixture of the starting materials 6 and hexafluoro-2-butyne. Figure 2 shows the frontier orbitals of phosphinine 6 and hexafluoro-2-butyne. Their energetic positions suggest a Diels–Alder reaction with a normal electronic demand between an electron-rich diene and an electron-poor dienophile (HOMO\(_{\text{diene}}\)–LUMO\(_{\text{dienophile}}\)).

Moreover, the shape of the HOMO of 6 and the LUMO of hexafluoro-2-butyne nicely demonstrates that the cycloaddition reaction should exclusively occur in 1,4-position of the phosphorus heterocycle, as also observed experimentally.

Crystals of 8 suitable for X-ray diffraction were obtained from a solution of 8 in an ethanol/water mixture (20:1). The compound crystallizes in the space group \(P2_1/c\) with one molecule in the asymmetric unit and the molecular structure of 8 along with selected bond lengths and angles is depicted in Figure 3. The structural analysis reveals a strong pyramidalization of the phosphorus atom (\(\Sigma\chi(CPC) = 281.5^\circ\)). This results in a much higher s-character of the lone pair compared with a classical \(\text{P}^{3-}\) compound.\[^15\]

![Figure 1. Organophosphorus compounds derived from 2,4,6-substituted triarylphosphinines.](image1)

Figure 2. Frontier orbital interactions in the \([4+2]\) cycloaddition reaction of phosphinine 6 (diene) with hexafluoro-2-butyne (dienophile; B3LYP-D3/def2TZVP).

Clearly, given that the phosphorus atom is P-stereogenic, compound 8 is formed as a racemic mixture, which was further confirmed by protonating the pyridyl-functionality of \(\text{rac}-8\) with enantiomerically pure \((1S,1R)-(+)-10\)-camphorsulfonic acid (Scheme 2).

The product clearly shows two sets of quartets at \(\delta(^{31}P\{^1H\}) = -69.70\) and \(-69.65\) ppm with \(J_{P,F} = 38.4\) Hz due to the presence of the diastereomers 9 and 9’ in a 1:1 ratio (Figure 4).

![Scheme 1. Synthesis of pyridyl-functionalized phosphabarrelene 8.](image2)
Despite the fact that we accessed the first pyridyl-substituted 1-phosphabarrelene, we expected that the presence of CF$_3$ groups close to the phosphorus donor will have a drastic effect on its coordination properties. As a matter of fact, we recently showed that monodentate CF$_3$-substituted 1-phosphabarrelenes neither react with selenium or sulfur to the corresponding P$^\text{V}$ species, nor with in situ generated [M(CO)$_5$(thf)] (M = Cr, Mo, W) complexes. This is most likely due to an unfavorable combination of steric bulk around the phosphorus atom along with weak net-donating properties.

However, we anticipated that the possible chelating nature of the P,N-hybrid ligand 8 should provide access to coordination compounds which would not be favorable in the case of the monodentate 1-phosphabarrelene 2. Thus, 8 was reacted with various metal sources, such as [Rh(cod)$_2$]BF$_4$ (cod = 1,5-cyclooctadiene), [Rh(CO)$_2$Cl]$_2$, [W(CO)$_4$(CH$_3$CN)$_2$], and [Fe$_3$(CO)$_{12}$] (Scheme 3).

Pleasantly, in all cases a distinct reaction between the ligand and the metal precursor was observed. Upon reaction of 8 with [Rh(cod)$_2$]BF$_4$ in dichloromethane, an orange-red solution is immediately formed, the $^{31}$P{$_1^\text{H}$} NMR spectrum shows exclusively one resonance at $\delta =$ 9.2 ppm and a $^1J_{P@Rh}$ coupling constant of 182.2 Hz as well as a $^3J_{P@F}$ coupling constant of 14.2 Hz. These data are consistent with the formation of [(8)Rh(cod)]BF$_4$ (10).

Using 0.5 equivalents of [Rh(CO)$_2$Cl]$_2$ in dichloromethane gives a brown solution which shows again the quantitative formation of a metal complex of 8 with a doublet of quartets at $\delta =$ 21.5 ppm in the $^{31}$P{$_1^\text{H}$} NMR spectrum ($^1J_{P@Rh}$ = 198.2 Hz, $^3J_{P@Cl}$ = 14.2 Hz). In the $^{13}$C{$_1^\text{H}$} NMR spectrum of the reaction product, a doublet of doublets at $\delta =$ 187.3 ppm is observed, which is indicative for the presence of a CO ligand ($^1J_{C@Rh}$ = 67.8, $^2J_{C@P}$ = 16.9 Hz). The magnitudes of both the $^2J_{P@C}$ and the $^1J_{C@P}$ coupling constants are in line with the P atom trans to Cl and the N atom trans to the CO ligand, as expected for square planar Rh(CO)Cl complexes containing P,N-hybrid ligands. The IR spectroscopic data of the new compound reveals a strong absorption band at $\tilde{\nu} =$ 2014 cm$^{-1}$ for the stretching vibration of the coordinated CO.

Upon heating a 1:1 mixture of 8 and [W(CO)$_6$(CH$_3$CN)$_2$] at reflux in tetrahydrofuran for 1 h, only one resonance was detected in the $^{31}$P{$_1^\text{H}$} NMR spectrum at $\delta =$ 2.4 ppm with a coupling constant of $^3J_{P@F}$ = 17.7 Hz and tungsten satellites.

**Figure 3.** Molecular structure of 8 in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [: P(1)--C(1): 1.865(2); P(1)--C(5): 1.954(2); P(1)--C(23): 1.866(3); C(1)--C(2): 1.325(3); C(2)--C(3): 1.532(3); C(3)--C(4): 1.540(3); C(4)--C(5): 1.325(3); C(23)--C(24): 1.328(3); C(11)--P(1)--C(23): 94.43(10); C(11)--P(1)--C(5): 95.18(10); C(5)--P(1)--C(23): 91.86(10).

**Figure 4.** $^{31}$P{$_1^\text{H}$} NMR spectrum of the 1:1 mixture of diastereomers 9 and 9'.
The substitution of two acetonitrile ligands from the starting complex by the chelating P,N-hybrid ligand is also evidenced in the \(^{13}C\)\(_{(1)}\)H NMR spectrum, because four signals for four different CO ligands were found. They all show coupling to the phosphorus atom and appear at \(\delta = 201.7\) (\(^2J_{C,P} = 6.4\) Hz), 204.3 (\(^2J_{C,P} = 7.9\) Hz), 209.6 (\(^2J_{C,P} = 39.9\) Hz), and 210.6 ppm (\(^2J_{C,P} = 5.3\) Hz). The wavenumbers of the respective IR-stretching frequencies were found at \(\tilde{\nu} = 2022, 1891\) (br) and 1846 cm\(^{-1}\) (br). The coordination compound [(8)W(CO)\(_4\)] (12) was thus formed.

Reaction of 8 with [Fe\(_3\)(CO)\(_{12}\)] leads mainly to the 1-phosphabarrelene iron carbonyl complex 13, which was purified by column chromatography and isolated in 46% yield. Compound 13 was characterized by a resonance in the \(^{31}P\)\(_{(1)}\)H NMR spectrum at \(\delta = 27.0\) ppm with \(^3J_{P,F} = 15.3\) Hz and shows carbonyl-stretching absorptions in the IR spectrum at \(\tilde{\nu} = 2001, 1946,\) and 1900 cm\(^{-1}\). Scheme 3 illustrates a summary of the coordination chemistry of 8. Compounds 10–13 were obtained in high yields as yellow to red/brown solids after workup. It should be mentioned that complexes 10–13 are thermally stable at least up to the boiling temperature of the solvent used for their preparation and no sign of any retro-Diels–Alder reaction was observed. Moreover, 10–13 were obtained as racemic mixtures, because rac-8 was used as the starting material.

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a solution of 10 in dichloromethane and pentane into a solution of 12 and 13 in tetrahydrofuran. The molecular structures of 10, 12, and 13 in the crystal along with selected bond lengths and angles are depicted in Figure 5, Figure 6, and Figure 7. The crystallographic characterizations of complexes 10, 12, and 13 indeed reveal their mononuclear nature and show that the expected complexes (Scheme 3) have been formed.

In all cases, the pyridyl-functionalized 1-phosphabarrelene acts as a chelating P-N-hybrid ligand with corresponding P-M-N bite-angles of 77.2–84.3°. Upon coordinating 8 to the metal fragment, the pyramidalization of the phosphorus atom in 10

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$\Sigma \chi (\text{CPC}) = 290.5^\circ$, $\Sigma \chi (\text{CPC}) = 286.7^\circ$, and $\Sigma \chi (\text{CPC}) = 285.5^\circ$ is slightly reduced compared with the free ligand $\Sigma \chi (\text{CPC}) = 281.5^\circ$, whereas the C–C double bonds C(1)–(2) and C(4)–(5) of the [2.2.2] bicycle are only marginally elongated in complexes 10 and 12.

We have recently demonstrated that 1-phosphabarrelene 3 undergoes a photochemical di-π-methane rearrangement towards a racemic mixture of the 1-phosphasemibullvalene 5 (see Figure 1).\cite{5,19} In light of this quantitative and selective conversion, it was consequently of interest to evaluate 1-phosphabarrelene 8 in the same photochemical process. Zimmermann and Liu showed that the bis-trifluoromethyl-substituted barrelene A also undergoes a di-π-methane rearrangement in the presence of a photosensitizer.\cite{20} However, in this particular case, the reaction is not selective and three different CF$_3$-substituted semibullvalenes (B–D) in the ratio of 4:2:1 were identified (Scheme 4).

These isomers were formed because all three double bonds are potentially involved in the mechanism of the di-π-methane rearrangement, also the CF$_3$-substituted one.\cite{20} In the case of 1-phosphabarrelene 8, the chirality at the phosphorus atom is likely to complicate even more this process. As anticipated, the photolysis of a tetrahydrofuran solution of 1-phosphabarrelene 8 under UV light for a prolonged time unfortunately resulted in the formation of several products. However, we reasoned that the photolysis of coordinated phosphabarrelene 8 might be more selective. Indeed, exposing a solution of Rh(I) complex 11 in tetrahydrofuran to sunlight, the slow transformation of 11 into a new species (14) was noticed after several hours (Figure 8, spectra (a) and (b)).
Like 11, this new compound shows a doublet of quartets with $J_{P,ph} = 188.2$ and $J_{P,p} = 7.6$ Hz at $\delta(^{31}P{^1H}) = 109.2$ ppm.

Upon further irradiating 11 with UV light, a second Rh complex (15) is formed, which was detected as a minor species at $\delta = 100.6$ ppm with $J_{P,rh} = 9.1$ Hz. The full conversion of 11 into 14 and 15 is finally achieved after 6 hours (Figure 8, spectrum (f)). We further found that exposing a solution of 11 in tetrahydrofuran to daylight for 5 days led to a similar conversion as the irradiation 11 with UV light for only 2 hours (Figure 8, spectra (d), (e)). Compounds 14 and 15 were obtained in a ratio of 10:1.

Much to our delight, we were able to isolate the major Rh species (14) and single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a solution of 14 in dichloromethane. Figure 9 shows the crystallographic representation of 14 along with selected bond lengths and angles.

From the structural characterization of complex 14 it is indeed clear that a chelating 5-phosphasemibullvalene deriv-
tive has been formed. The P(1)-Rh(1)-N(1) bite angle of 81.77(8°) is very similar to the Rh complex 10, containing the 1-phosphabarrelene 8 as ligand. As expected, the CO group is located trans to the pyridine ring, presumably because the nitrogen atom is a stronger σ-donor than the P atom of the 5-phosphasemibullvalene moiety. The wavenumber of the corresponding asymmetric stretching vibration of the CO ligand was found at 3008 cm⁻¹ in the IR spectrum. This shows that the pyridyl-substituted 5-phosphasemibullvalene has similar net-donor properties compared to the pyridyl-functionalized 1-phosphabarrelene 8 (ν = 2014 cm⁻¹ in 11). According to the 31P(1)H NMR spectra shown in Figure 8, it is clear that the minor product 15 must be a Rh complex that is based on a phosphorus- and fluoride-containing ligand. However, given that no structural data of 15 are available, we can at this stage only propose that an isomer of the chelating 5-phosphasemibullvalene derivative is present in 15 (see below).

Motivated by these results, we also started to investigate the reactivity of tungsten complex 12 towards light and found again that this coordination compound is quantitatively converted into the two new complexes 16 and 17 upon irradiation with either daylight or UV light (see Figure S24, Supporting Information). Similarly, the products were formed in this case in a ratio of nearly 10:1 and we were able to isolate the major product 16. Unfortunately, the poor quality of the single crystals allowed only for determining the connectivity of the atoms. It turned out, however, that the same isomer as observed for complex 14 was formed (Figure S25, Supporting Information). The wavenumbers of the corresponding asymmetric stretching vibrations of the CO ligands in 16 were found at 2024, 1898, and 1861 cm⁻¹. This shows again that the 5-phosphasemibullvalene has similar net-donor properties as the pyridyl-functionalized 1-phosphabarrelene 8 (ν = 2022, 1891 (br) and 1846 cm⁻¹ (br) in 12).

As evident from our studies, the photochemical di-π-methane rearrangement of a 1-phosphabarrelene in the coordination sphere of a metal center seems to be a general reaction and is much more selective than observed for the uncomplexed bis-CF₃-1-phosphabarrelene 8 (Scheme 5).

To get insight into the initial step of the mechanism of this rather selective photochemical transformation, we started to perform time-dependent (TD)-DFT calculations at the B3LYP/6-31G*/B3LYP-D3/Def2-TZVP level of theory. In contrast to the metal-free barrelenes, the theoretical investigations revealed that the initial photoexcitation of 11 proceeds from metal-centered d-type orbitals into one of the almost degenerated π* orbitals of the 1-phosphabarrelene (Figure 10).[30] This occurs either through a lower-energy (593.4 nm), low-intensity (f = 0.001) transition from the HOMO into the LUMO at the range of visible light, or a higher energy (507.6 nm) and more effective (f = 0.008) excitation from the HOMO–1 into the LUMO (for a graphical representation of the molecular orbitals see Figure S26 in the Supporting Information).

In fact, the vertical-excited triplet state of 11 shows the spin density to be concentrated on the carbon atoms C1, C2, and C3 (Figure 11). Thus, excitation into the LUMO (ε = −0.111 eV) creates a bonding interaction (overlap) between C2 and C3, resulting in biradical 11a with a newly formed bond between these two atoms (Scheme 6).

Starting from biradical 11a and based on the known mechanism of the photochemical di-π-methane rearrangement reaction of barrelenes, we propose the subsequent formation of complex 14 via 11b, which is in line with our experimental findings (Scheme 6, see also Figure S27, Supporting Information).

Interestingly, the theoretical calculations further show that excitation from the HOMO into the LUMO+1 (ε = −0.092 eV) at slightly higher energies (468.5 nm, f = 0.006) causes a bonding interaction between C2 and C4 under formation of biradical 11c. The corresponding photochemical rearrangement would then lead to isomer 15 via 11d. Moreover, complex 15 is calcu-
Conclusions

We have investigated the [4+2] cycloaddition reaction of the reactive dienophile hexafluoro-2-butyn to 2-(2’-pyridyl)-4,6-diphenylphosphinine and obtained a hitherto unknown pyridyl-functionalized 1-phosphabarrelene as a racemic mixture, which was characterized by single crystal X-ray diffraction. DFT calculations suggest a normal HOMO\textsubscript{dienophile}–LUMO\textsubscript{dienophile} Diels–Alder reaction, whereas the shape of the frontier orbitals of both phosphinine and hexafluoro-2-butyn explain the exclusive addition of the dienophile to the 1,4-position of the phosphorus heterocycle. Although monodentate bis-CF\textsubscript{3}-substituted 1-phosphabarrelenes show only poor coordination abilities due to a combination of poor nucleophilic properties of the phosphorus atom and steric factors, we were able to synthesize and structurally characterize a series of transition-metal complexes based on the novel P,N-hybrid ligand by making use of its chelating nature. Moreover, we demonstrate here for the first time that the photochemical di-\pi-methane rearrangement of the bis-CF\textsubscript{3}-substituted 1-phosphabarrelene moiety is a much more selective process when it occurs in the coordination sphere of a metal center, leading to chelating 5-phospahasemibullvalene derivatives and their respective transition-metal complexes. Such compounds might play an interesting role as novel (chiral) P,N-hybrid-based complexes in transition-metal-mediated transformations and homogeneous catalysis. In this respect, we found that the pyridyl-substituted 5-phosphasemibullvalene has similar net-donor properties as the pyridyl-functionalized 1-phosphabarrelene. DFT calculations give insights into the first step of the mechanism of the photochemical rearrangement of a 1-phosphabullvalene based ligand bound to a transition-metal fragment.[21]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: coordination chemistry · DFT calculations · di-\pi-methane rearrangement · phosphabarrelene · phosphorus ligands

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[17] The reaction of B with [Fe(CO)]₉ also affords two minor byproducts, according to TLC analysis, which most likely correspond to [Fe(CO)]₉ and [Fe₂(CO)]₇ as observed for the reaction of [Fe₃(CO)]₁₀ with bipyridines. See for example: M. DeaVarga, R. Costa, R. Reina, A. Nuhez, M. Angel Maestro, J. Mahia, J. Organomet. Chem. 2003, 677, 101.
[20] a) H. E. Zimmerman, R. S. Givens, R. M. Pagni, J. Am. Chem. Soc. 1968, 90, 6096; b) R. S. H. Liu, J. Am. Chem. Soc. 1968, 90, 215. [21] CCDC 1895749 (8), 1895750 (14), 1895751 (13), 1895755 (12), and 1895756 (10) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.