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2,4,6-Triphenylphosphinine and 2,4,6-triphenylposphabarrelene revisited: synthesis, reactivity and coordination chemistry†

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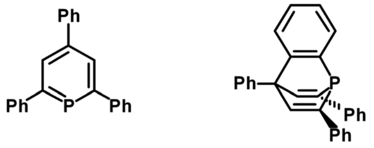
The synthesis of 2,4,6-triphenylphosphinine has been revisited and a general protocol for the preparation of such low-coordinate phosphorus compounds in good to excellent yields could be established. This allows to investigate several aspects of the chemistry of 2,4,6-triarylphosphinine, such as the reaction with *in situ* generated benzyne to give 2,4,6-triphenylphosphabarrelene. The corresponding 2,4,6-triphenylphosphabarrelene-selenide could be characterized crystallographically for the first time and the structural and electronic properties of this cage-compound in comparison to classical triarylphosphines could be evaluated. Moreover, [(L)W(CO)$_5$)] complexes of both 2,4,6-triphenylphosphinine and 2,4,6-triphenylphosphabarrelene were prepared and characterized by means of X-ray crystallography. This allowed for the first time a direct structural comparison of these related phosphorus compounds, coordinated to the same metal fragment.

Introduction

A milestone in the chemistry of low-coordinate phosphorus compounds was set with the first successful preparation of the fully unsaturated six-membered phosphorus heterocycle **1** by Märkl in 1966 and the parent compound C_5H_5P by Ashe III in 1971.[1,2] The stabilization of otherwise reactive P=C double bonds by their incorporation into aromatic systems opened up the access to formally sp^2-hybridized phosphorus(III) heterocycles with significantly different electronic and steric properties compared to classical ligands based on trivalent phosphorus. Phosphinines have long been regarded as "chemical curiosities" but state-of-the-art synthetic methodologies allow nowadays specific derivatizations and functionalizations, including the introduction of additional donor-functionalities.[3,4] Moreover, an interesting feature is the reactivity of phosphinines towards *in situ* generated benzyne as a good dienophile. These [4 + 2] cycloaddition reactions afford the corresponding phosphabarrelenes, such as **2**, which have been identified as rather bulky, mainly σ-donating phosphorus ligands towards transition metal centers (Fig. 1).[5–7]



1 **2**

Fig. 1 2,4,6-Triphenylphosphinine (**1**) and 2,4,6-triphenylphosphabarrelene (**2**).

Among the known phosphinine-derivatives having different substitution pattern, 2,4,6-triaryl-phosphinines often show a considerable kinetic stability and are inert towards water, oxygen and many acids and bases, in contrast to less substituted ones. However, despite the fact that these heterocycles are known for almost five decades, their use in more applied research fields is still comparatively rare, although several fascinating results have recently emerged.[4d,e,8–11] This also counts for the application of the corresponding phosphabarrelenes. Their efficient use as phosphorus(III) ligands in several homogeneous catalytic reaction has been recently well documented (*vide infra*). In this respect, one drawback in the use of phosphinines is certainly their often tedious synthetic procedure, especially the overall low yield. The first reported phosphinine **1** was prepared from 2,4,6-triphenylpyrylium tetrafluoroborate (**3**) and $P(CH_2OH)_3$ in refluxing pyridine, and was obtained as a yellow air- and moisture-stable solid in 24–30% yield.[1] Alternatively, $P(SiMe_3)_3$ (**4**) in refluxing acetonitrile can be used as phosphorus source, leading to only slightly higher yields.[12] Exchange of BF_4^- by I^- in the pyrylium salt can lead to even higher yields (45%) because the formation of Me_3SiI as by-

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product of the synthesis is preferred over Me_3SiBF_4.[13] Using refluxing dimethoxyethane instead of acetonitrile, the yields can range from 27% to 63%, depending on the pyrylium salt used.[14] Nevertheless, it should be mentioned here that the time-consuming preparation of larger amounts of $P(CH_2OH)_3$ and $P(SiMe_3)_3$ requires special caution, while the reported yields can differ significantly. Despite its high toxicity the use of PH_3 gives pure **1** in 77% yield after recrystallization and only H_2O as by-product.[8,15] Performing the O^+/P exchange with PH_4I as PH_3-source in butanol at $T = 110–120$ °C, **1** is obtained in 61% isolated yield.[16] PH_4I is, however, not commercially available anymore.

$P(SiMe_3)_3$ as the most often used synthon for the preparation of 2,4,6-triarylphosphinines has been initially synthesized by reaction of $NaPH_2$ (from large amounts of PH_3 and Na in liquid ammonia) and Me_3SiCl in diglyme.[17] Becker and Hölderich reported on an improved synthesis starting from P_4, Na/K alloy and Me_3SiCl.[18] A by far less dangerous procedure was reported by Niecke and Westermann. The authors started from *N*-(dichlorophosphino)piperidine, lithium and Me_3SiCl.[19]

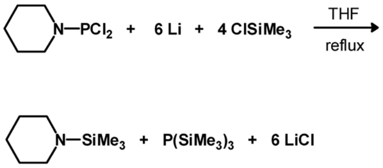
During the preparation of arene complexes of Sm, Eu, Tm, Yb, Arnold, Sergeev and Cloke reported on the use of $Li[P(SiMe_3)_2]$ (**5**) for the preparation of 2,4,6-tri-*tert*-butylphosphinine in 75% yield.[20] Inspired by these results, we started to investigate the general use of $M[(P(SiMe_3)_2]$ (M = Li, Na, K) in more detail, especially for the preparation of also 2,4,6-triarylphosphinines. In line with our recent results on the preparation of novel coordination compounds based on phosphinines and phosphabarrelenes, we also started to explore the coordination chemistry of **1** and **2** towards W(0) in order to get more information on the structural and electronic properties of these structurally related heterocycles. The results will be presented in this paper.

Results and discussion

Optimization of $P(SiMe_3)_3$ synthesis

A simple and convenient method for the preparation of tris(trimethylsilyl)phosphine is the reaction of the *N*-(dichlorophosphino)piperidine with lithium and chlorotrimethylsilane in boiling tetrahydrofuran, according to Niecke and Westermann (Scheme 1).[19]

From experience, however, this reaction is not as straightforward as reported. It strongly depends on the scale, the type and source of lithium, the order of reagents and the stirring speed. In some cases, the reaction time can vary from three days up to two weeks. It is consequently advisable that the reaction is monitored by means of ^{31}P NMR spectroscopy (unlocked), as an incomplete conversion makes the workup almost impossible. The colour of the reaction mixture is important as it turns from dark orange in the beginning to light grey. Moreover, a clear and colourless solution can be noticed at the end of the reaction when the stirrer is turned off and the LiCl has been settled.



4; 71%

Scheme 1 Synthesis of $P(SiMe_3)_3$ (**4**).

We optimized and scaled up the synthetic procedure for $P(SiMe_3)_3$ (**4**), doubling the amount and obtaining reproducible results, which are reported in Table 1. It turned out that by using lithium granulate handled under air a reaction time of 1 week was observed (Table 1, entries 1 and 2). This time period can be reduced to 30 h by stirring the lithium vigorously with a large stirring bar (5 cm, Ø = 2 cm, 34.65 g) under an argon atmosphere prior to the addition of the solvent and reactants. In this way, the passivated lithium surface can be partially removed, leading to an activation of the metal. This procedure takes approximately 4 h at a stirring speed of 1000 rpm and should not be extended, as an aggregation of the Li granulate was observed. This effect increases the reaction time again most likely due to the presence of a smaller metal surface (entries 3 and 4 *vs.* 5 and 6). Furthermore, we found that both the morphology as well as the amount of lithium has also an effect on the reaction times. The best results were obtained using lithium foil, as the reaction was complete within one day (entry 9). By doubling the amount of lithium to 14 equivalents, the reaction was complete within 16 h. It turned out that the use of sliced lithium rods is not recommended (entries 11/12). It should also be mentioned that the solvent must be removed *in vacuo* immediately after the reaction is complete, as the generation of unidentified species was otherwise observed by ^{31}P NMR spectroscopy. The crude product can be stored at $T = -20$ °C for several weeks under an argon atmosphere and can be finally worked up by suspending the grey mixture with 300 mL of dry pentane. The solid is

Table 1 Optimization of $P(SiMe_3)_3$ synthesis

Entry	Li source	Li eq.	Stirring speed [rpm]	Time	Yield
1	Granular[a]	7	750	7 d	69%
2	Granular[a]	7	750	7 d	70%
3	Granular[b]	7	1000	30 h	70%
4	Granular[b]	7	750	34 h	74%
5	Granular[c]	7	1000	2 d	72%
6	Granular[c]	7	1000	2 d	70%
7	Granular[c,d]	7	1000	2 d	71%
8	Granular[c,d]	7	1000	2 d	70%
9	Foil[c]	7	1000	20 h	68%
10	Foil[c]	14	1000	16 h	72%
11	Rod[c,e]	7	1000	7 d	69%
12	Rod[c,f]	7	1000	12 d	69%

[a] Li handled under air. [b] Li handled under air, activation by stirring. [c] Exclusively Ar atmosphere (no activation). [d] Li, 99%, trace metals basis. [e] Horizontally and vertically sliced. [f] Vertically sliced.

removed by filtration under argon atmosphere and the solvent is subsequently removed *in vacuo*. P(SiMe$_3$) in obtained in an average yield of 70% after vacuum distillation (~55 °C, 0.5 mbar).

Optimization of 2,4,6-triarylphosphinine synthesis

As mentioned above, the reaction of 2,4,6-triarylpyrylium tetrafluoroborates with P(SiMe$_3$)$_3$ gives the corresponding 2,4,6-triarylphosphinines in generally rather poor yields, although some improvements have been reported in literature. Me$_3$SiO-SiMe$_3$ as well as Me$_3$SiBF$_4$ are the by-products of this conversion. It is believed, that a nucleophilic attack of P(SiMe$_3$)$_3$ to the C$_\alpha$ atom of the pyrylium salt is initiating the reaction, with subsequent elimination of Me$_3$SiBF$_4$.[12] The neutral species undergoes ring-opening, rearrangement and ring-closing under elimination of Me$_3$SiOSiMe$_3$ and formation of the aromatic phosphorus heterocycle. Nevertheless, mechanistic investigations are lacking, although one derivative of a proposed intermediate has been isolated in one case.[12]

In order to increase the yield of the reaction, we envisaged to start from M[P(SiMe$_3$)$_2$] (M = Li, Na, K) as a phosphorus source, since the formation of MBF$_4$ as a salt, which would precipitate from the reaction mixture, should entropically favour the formation of the 2,4,6-triarylphosphinine core (Scheme 2). Moreover, [P(SiMe$_3$)$_2$]$^-$ is more nucleophilic than P(SiMe$_3$)$_3$. Therefore, we started to synthesize Li[P(SiMe$_3$)$_2$] (**5**) by reaction of the above prepared P(SiMe$_3$)$_3$ with *n*BuLi in THF, according to the literature.[21] We first examined the reaction of 2,4,6-triphenylpyrylium tetrafluoroborate (**3**) with Li[P(SiMe$_3$)$_2$] (**5**) under different reaction conditions and the results are listed in Table 2.

It turned out, that the optimal reaction time is 6 h, while the solvent of choice is THF under refluxing conditions (entry 4). Interestingly, the use of 2 equivalents of Li[P(SiMe$_3$)$_2$] has a beneficial effect on the yield of the reaction, as 76% of isolated 2,4,6-triphenylphosphinine could be obtained (entry 12).

Next to the use of Li[P(SiMe$_3$)$_2$] (**5**) we also used Na[P(SiMe$_3$)$_2$] (**6**) as well as K[P(SiMe$_3$)$_2$] (**7**) as phosphorus source for the preparation of 2,4,6-triphenylphosphinine.[21] The optimized conditions with respect to solvent, temperature and reaction time (Table 1) were used and the results are listed in Table 3.

A comparison between **5**, **6** and **7** shows that reasonable yields are obtained with all three bis-trimethylsilylphosphides, although there is no significant difference between using one or two equivalents of **6** and **7**, in contrast to **5**. However, it can be concluded that the optimal reaction conditions for the preparation of **1** are 2 equivalents of Li[P(SiMe$_3$)$_2$] (**5**) in refluxing THF and a reaction time of 6 h, leading to a highest isolated yield of 76%.

Next, we were wondering whether we can transfer our observations to the preparation of other 2,4,6-triarylphosphinines for which the isolated yields are normally rather low. We therefore chose for the synthesis of 2-(2-pyridyl)-4,6-diphenyl-phosphinine (**8**) and 2,4-diphenyl-5-methyl-6-(2,3-dimethylphenyl)-phosphinine (**9**).[22,23] Starting from the corresponding pyrylium salts and P(SiMe$_3$)$_3$, phosphinine **8** is typically obtained in an average yield of 25%, while the atropisomeric phosphinine **9** is typically isolated in only 10–15% yield (Fig. 2).

Interestingly it turned indeed out, that phosphinines **8** and **9** can be prepared in significantly higher yields under the same optimized reaction conditions as described in Table 1,

Table 2 Optimization of 2,4,6-triphenylphosphinine synthesis

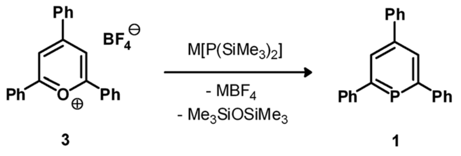
Entry	Ratio **3**/LiP(SiMe$_3$)$_2$	Time [h]	Solvent	*T* (°C)	Isolated yield [%]
1	1 : 1	16	THF	r.t	28
2	1 : 1	3	THF	100	31
3	1 : 1	1	THF	Reflux	33
4	1 : 1	6	THF	Reflux	56
5	1 : 1	16	THF	Reflux	55
6	1 : 1	6	MeCN	Reflux	—
7	1 : 1	6	DME	Reflux	44
8	1 : 1	6	Toluene	Reflux	—
9	1 : 1	6	No solvent	80	48
10	1 : 1.4	6	THF	Reflux	52
11	1 : 1.6	6	THF	Reflux	54
12	1 : 2	6	THF	Reflux	76

Conditions: pyrylium salt: 2.0 mmol, solvent: 25 mL.

Table 3 Optimization of 2,4,6-triphenylphosphinine synthesis

Entry	Ratio py-salt/ M[P(SiMe$_3$)]$_2$	M[P(SiMe$_3$)$_2$]	Isolated yield [%]
4	1 : 1	Li[P(SiMe$_3$)$_2$]	56
12	1 : 2	Li[P(SiMe$_3$)$_2$]	76
13	1 : 1	Na[P(SiMe$_3$)$_2$]	45
14	1 : 2	Na[P(SiMe$_3$)$_2$]	47
15	1 : 1	K[P(SiMe$_3$)$_2$]	46
16	1 : 2	K[P(SiMe$_3$)$_2$]	51

Conditions: pyrylium salt: 2.0 mmol, solvent: THF (25 mL, reflux), reaction time: 6 h.



Scheme 2 Improved synthesis of **1**.

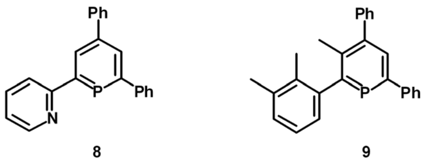


Fig. 2 Functionalized 2,4,6-triarylphosphinines **8** and **9**.

entry 12. Both compounds could be obtained in 37% isolated yield, using 2 equivalents of Li[P(SiMe$_3$)$_2$] (**5**) in refluxing THF and a reaction time of 6 h.

2,4,6-Triphenylphosphabarrelene: synthesis and reaction with selenium

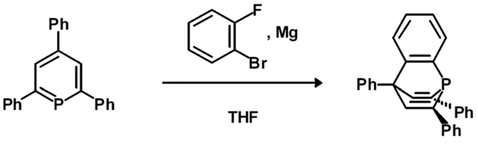
The aromatic phosphinine heterocycle can serve as the basis for the development of very interesting phosphorus-cages, the so-called phosphabarrelenes. In 1971 Märkl reported on the Diels–Alder-type [4 + 2] cycloaddition of benzyne with **1** to give the corresponding phosphabarrelene **2**.[5] These molecules have mainly σ-donating character with some π-acceptor properties as due to low lying σ* orbitals of the P–C bonds.[6,7] Breit and co-workers showed that very active hydroformylation catalysts could be generated in combination with [Rh(CO)$_2$(acac)].[6] Remarkably, internal alkenes were converted essentially free of alkene-isomerization towards internal aldehydes. Le Floch and Mézailles proved their application in the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction and the Pd-catalyzed allylation of amines.[24,25] Also very efficient Pt-complexes based on phosphabarrelenes were prepared for the hydrosilylation of alkynes under mild reaction conditions.[26] Breit and co-worker reported on Rh-catalyzed hydrogenations and our group could show that phosphabarrelenes are excellent phosphorus ligands for the Rh-catalyzed tandem-hydroformylation-cyclization reaction of allyl-functionalized imidazole derivatives.[27,28]

As 2,4,6-triphenylphosphinine can be prepared in large amounts using this improved synthetic procedure, we further converted **1** into the corresponding 2,4,6-triphenylphosphabarrelene **2**, according to the literature procedure (Scheme 3).[6] In contrast to 2,4,6-triarylphosphinines, phosphabarrelenes are prone to oxidation reactions and can easily be converted into the corresponding phosphabarrelene-oxides, sulfides and selenides.[27,29] Generally the $^1J_{31\text{P}-77\text{Se}}$ coupling constant in P–Se compounds allows for the evaluation of the s-character of the phosphorus lone pair.[30] It is consequently an important tool for the design of tailor-made phosphorus ligands and their applications in homogeneous catalysis.

It appeared thus surprising to us that only one literature reference deals with the preparation and structural characterization of phosphabarrelene-selenides.[29] We therefore converted **2** with an excess of grey selenium in refluxing toluene to **10** within 24 h and the product could be obtained as a white solid in 95% isolated yield, according to Scheme 4.

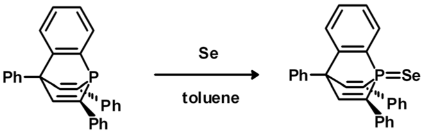
While the starting material **2** shows a signal at δ = −69.0 ppm in the ^{31}P{^{1}H} NMR spectrum, a downfield shift of 75.6 ppm to δ (ppm) = 6.6 with $^1J_{31\text{P}-77\text{Se}}$ = 834 Hz is observed for product **10**. Interestingly, the 2,4,6-triphenylphosphabarrelene **10** shows by far the largest coupling constant among the differently substituted phosphabarrelene-selenides reported in literature.[29] This shows that the s-character of the phosphorus lone-pair in **10** is significantly higher compared to other phosphabarrelenes as well as classical phosphine-selenides (Ph$_3$P=Se: $^1J_{31\text{P}-77\text{Se}}$ = 732 Hz).[30] It should be noted here that although the preparation of phosphinine–sulfides is possible, phosphinine–selenides are still unknown, making a direct comparison of the structurally related heterocycles unfortunately impossible.

The two structurally characterized phosphabarrelene-selenides, reported in literature, contain a –SiMe$_3$ group in 2- and 6-position of the heterocycle.[29] Since the molecular structure of **10** in the crystal is unknown, we attempted a crystallization and structural characterization of this 2,4,6-triphenyl-derivative. Crystals of **10**, suitable for single crystal X-ray diffraction were indeed obtained from a concentrated solution of this compound in toluene and its molecular structure is depicted in Fig. 3. The P–Se as well as the P–C bond lengths in **10** are very similar to the ones of reported phosphabarrelene-selenides. In contrast, the sum of the CPC angle in **10** is approximately 6° smaller compared to the reported values of the –SiMe$_3$-substituted phosphabarrelene-selenides. This finding could explain the larger $^1J_{31\text{P}-77\text{Se}}$ coupling constant



1 2

Scheme 3 Synthesis of phosphabarrelene **2**.



2 10

Scheme 4 Synthesis of phosphabarrelene-selenide **10**.

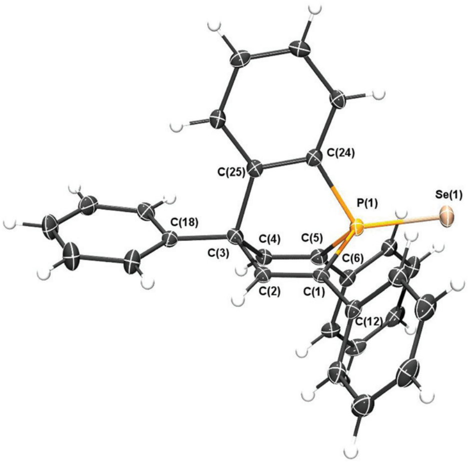


Fig. 3 Molecular structure of **10** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Only one independent molecule is shown.

Table 4 Structural parameters of **2** and **10**

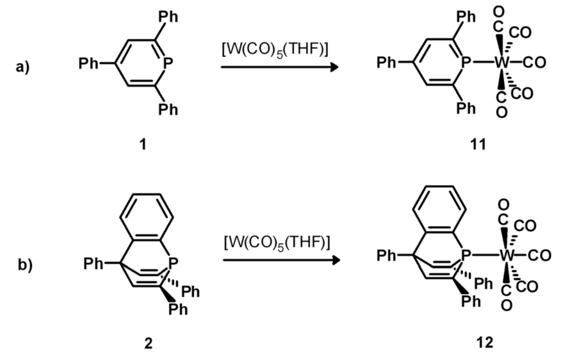
Bond length [Å]	2	10
P(1)–Se(1)	—	2.0924(7)
P(1)–C(1)	1.8454(16)	1.838(3)
P(1)–C(5)	1.8601(16)	1.839(2)
P(1)–C(24)	1.8345(18)	1.812(2)
C(1)–C(2)	1.331(2)	1.330(3)
C(2)–C(3)	1.527(2)	1.531(3)
C(3)–C(4)	1.533(2)	1.538(3)
C(4)–C(5)	1.333(2)	1.333(4)
C(3)–C(25)	—	1.563(3)
C(24)–C(25)	—	1.390(4)
Bond angles (°)		
C(1)–P(1)–C(5)	95.57(7)	97.9(1)
C(1)–P(1)–C(24)	94.95(7)	97.4(1)
C(5)–P(1)–C(24)	92.23(7)	98.4(1)
∑(CPC)	282.7	293.7

observed for **10** (*vide supra*), which in turn indicates a higher s-character of the phosphorus lone-pair of phosphabarrelene **2** in comparison to the $-SiMe_3$–substituted derivatives. The crystallographic characterization of **10** further allows for the comparison with the molecular structure of the starting material **2** in the crystal, which has been reported by Breit and co-workers (Table 4).[6]

Upon reaction of the phosphorus atom with selenium, a shortening of the three P–C bonds can be noticed, while the C–C bond distances within the cage remain essentially very similar. Moreover, a significant widening of the CPC angles upon oxidation with selenium can be observed, as the sum of the CPC angles changes from 282.7° in **2** to 293.7° in **10**. Interestingly, the ∑(CPC) angle in 2,4,6-triphenylphosphabarrelene **2** of 282.7° is indeed significantly smaller than the ones observed for the $-SiMe_3$-substituted derivatives reported in literature (287.7° and 290.1°; PPh_3: 307.2°).[29,31] Apparently, the aryl-substituted cage compounds, such as **2**, are the least σ-donating ligands among the hitherto known series of phosphabarrelenes as already anticipated from the $^{31}P\{^1H\}$ spectroscopic data (*vide supra*).

Coordination chemistry of 2,4,6-triphenylphosphinine (1) and 2,4,6-triphenylphosphabarrelene (2)

We were further interested in the coordination chemistry of **1** and **2** towards the same metal fragment. This would allow for a direct structural comparison of a phosphinine- and a phosphabarrelene-based coordination compound independently from any substituent influence. Surprisingly, although several structurally characterized metal complexes of phosphinines and phosphabarrelenes have been reported in literature, no such evaluation of the structurally related phosphorus heterocycles has been made, to the best of our knowledge. Moreover, as carbonyl-complexes provide the possibility to obtain valuable information on the electronic properties of the corresponding ligands, we aimed for the preparation of metal carbonyl complexes of **1** and **2** and were successful with the $[W(CO)_5]$-fragment for both ligands.



Scheme 5 Reaction of **1** and **2** with $[W(CO)_5(THF)]$.

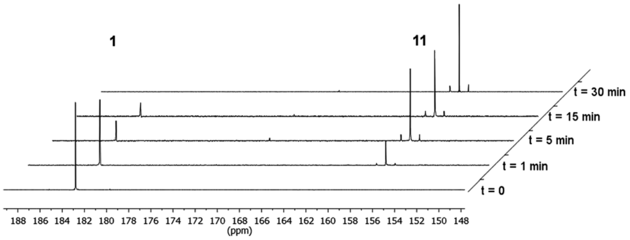


Fig. 4 Time-dependent $^{31}P\{^1H\}$ NMR spectra for the reaction of **1** with $[W(CO)_5(THF)]$.

We first looked into the synthesis of $[(\mathbf{1})W(CO)_5]$ (**11**) and stirred a suspension of $[W(CO)_6]$ in THF for 2 h under UV light in order to generate $[W(CO)_5(THF)]$, according to a modified procedure described by Deberitz and Nöth.[32] By adding a solution of **1** in THF to this intermediate we were able to prepare **11** almost quantitatively (Scheme 5a).

Compound **11** shows a resonance in the $^{31}P\{^1H\}$ NMR at δ (ppm) = 159.1 with $^1J_{31P-183W}$ = 273 Hz due to coupling to the ^{183}W NMR active nucleus (15% natural abundancy). This value is very similar to the one observed for $[W(CO)_5(PPh_3)]$ ($^1J_{31P-183W}$ = 245 Hz). The reaction of **1** with $[W(CO)_5(THF)]$ can also be directly monitored by means of $^{31}P\{^1H\}$ NMR spectroscopy in THF (Fig. 4). Within 30 min phosphinine **1** has been completely consumed under quantitative formation of **11**, as can be nicely detected by the tungsten satellites.

Similarly, reaction of 2,4,6-triphenylphosphabarrelene **2** with $[W(CO)_5(THF)]$ affords the corresponding novel tungsten complex **12** in 85% isolated yield as a white solid, according to Scheme 5b. In the $^{31}P\{^1H\}$ NMR spectrum of **12** a resonance at δ (ppm) = −8.5 with $^1J_{31P-183W}$ = 266 Hz can be detected. These values are also very similar compared to the ones reported for a tungsten complex based on a substituted triarylphosphabarrelene.[7]

We were able to grow crystals of both **11** and **12**, suitable for X-ray diffraction, by slow evaporation from a pentane solution and the molecular structures of **11** and **12** are depicted in Fig. 5 and 6, respectively. Although the preparation of compound **11** has been reported in 1973 by Deberitz and Nöth, its

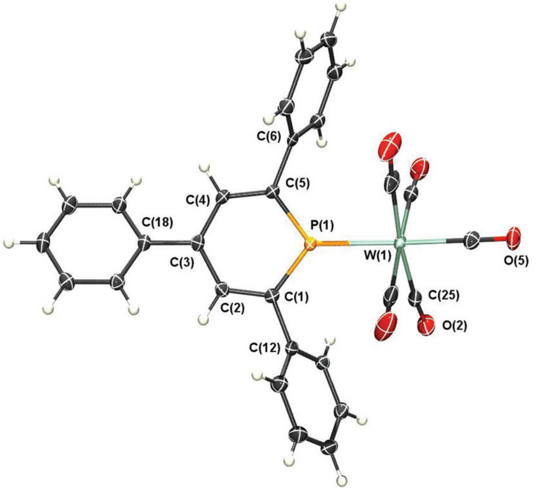


Fig. 5 Molecular structure of **11** in the crystal. Displacement ellipsoids are shown at the 50% probability level.

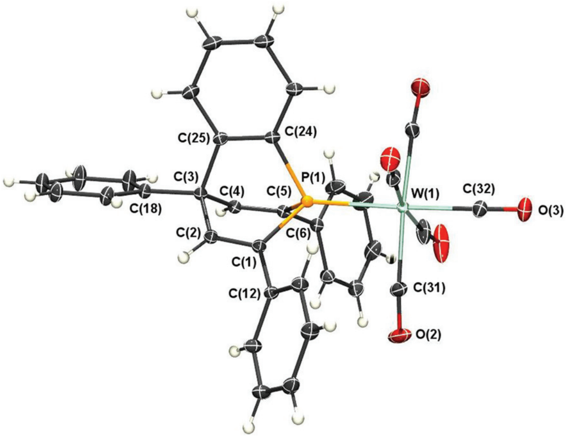


Fig. 6 Molecular structure of **12** in the crystal. Displacement ellipsoids are shown at the 50% probability level.

Table 5 Structural parameters of **1**, **2**, **11** and **12**

Bond length [Å]	**1**[36]	**11**	**2**	**12**
P(1)–W(1)	—	2.5053(7)	—	2.5276(4)
P(1)–C(1)	1.757(8)	1.737(2)	1.8454(16)	1.8528(13)
P(1)–C(5)	1.774(7)	1.733(3)	1.8601(16)	1.8445(13)
P(1)–C(24)	—	—	1.8345(18)	1.8333(13)
C(1)–C(2)	1.367(10)	1.390(4)	1.331(2)	1.3361(19)
C(2)–C(3)	1.423(10)	1.403(4)	1.527(2)	1.5325(18)
C(3)–C(4)	1.455(11)	1.390(3)	1.533(2)	1.5307(18)
C(4)–C(5)	1.461(11)	1.394(4)	1.333(2)	1.3370(19)
C(3)–C(25)	—	—	—	1.5506(19)
C(24)–C(25)	—	—	—	1.406(2)
W(1)–C(25)	—	2.049(3)	—	—
W(1)–C(28)	—	1.999(3)	—	—
W(1)–C(31)	—	—	—	2.0610(16)
W(1)–C(32)	—	—	—	1.9952(15)
C(28)–O(5)	—	1.149(3)	—	—
C(25)–O(2)	—	1.140(4)	—	—
C(31)–O(2)	—	—	—	1.139(2)
C(32)–O(3)	—	—	—	1.156(2)
Angles (°)				
C(1)–P(1)–C(5)	97.5(4)	103.6(1)	95.57(7)	95.94(6)
C(1)–P(1)–C(24)	—	—	94.95(7)	95.90(6)
C(5)–P(1)–C(24)	—	—	92.23(7)	95.46(6)
∑(CPC)	97.5(4)	103.6	282.7	287.30

structural characterization (and consequently also of **12**) has so far remained elusive.[32]

The molecular structure of **11** in the crystal shows the expected mononuclear nature of the compound and is very similar to the one reported for the corresponding Cr(0) complex $[(\mathbf{1})Cr(CO)_5]$.[33] Fig. 5 nicely shows the distortion of the aromatic 6-membered heterocycle due to the longer P–C bonds in comparison to a C–C or N–C bond in benzene or pyridine. The phosphorus–tungsten bond is 2.5053(7) Å, which is shorter than in $[(PPh_3)W(CO)_5]$ (2.545(1) Å).[34] This observation indicates the difference between a formally sp^2 and a sp^3-hybridized phosphorus atom, as well as the stronger π-accepting character of **1** in contrast to PPh_3. Upon complexation, both the P(1)–C(1) and P(1)–C(5) bonds as well as the C–C bonds within the phosphorus heterocycle shorten significantly compared to the free ligand **1** (Table 5). Interestingly, the phenyl-substituents in 2- and 4-position are rotated considerably out of the plane of the 6-membered ring (torsion angles P(1)–C(1)–C(12)–C(13) = 56.13° and P(1)–C(5)–C(6)–C(7) = 69.3°). In this way, the P-ligating ability of such 2,4,6-triaryl-substituted phosphinines is apparently not influenced as dramatically as observed for $SiMe_3$-substituted ones, which show a preference for η^6-coordination through the aromatic ring, rather than for η^1-coordination through the phosphorus lone pair.[35]

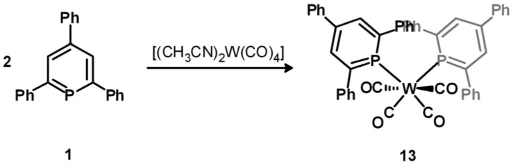
The molecular structure of the phosphabarrelene-based W(0) complex **12** in the crystal also shows the expected mononuclear nature of the compound (Fig. 6). Since both ligands **1** and **2** are coordinated to the same metal fragment, a direct structural comparison of **11** and **12** is now possible, even with the free ligands **1** and **2**. Table 5 contains all relevant structural parameters of **1**, **2**, **11** and **12**. It can be noticed, that the P–W bond length in **12** lies exactly in between the ones in **11** and $[(PPh_3)W(CO)_5]$. Both the P–C bond lengths as well as the C–C bond lengths within the phosphorus cage are very similar to the bond lengths found for the free ligand. However, the pyramidalization of the phosphorus atom is more pronounced in **12** than in the corresponding phosphabarrelene-selenide **10** (∑(CPC) = 293.7°) and in $[(PPh_3)W(CO)_5]$ (∑(CPC) = 308.6°), as the sum of the CPC angles in **12** has the smallest value of 287.30°, which is close to the one of the free ligand (282.7°).

The IR-spectroscopic investigation of **11** and **12**, in comparison with $[(PPh_3)W(CO)_5]$, reveals the expected trend of the net-donor capabilities of the corresponding ligands (Table 6). The order of increasing basicity of the donor-atom is $\mathbf{1} < \mathbf{2} < PPh_3$, which is in line with earlier observations that phosphinines are rather good π-accepting ligands.

During their investigation on the synthesis of $[(\mathbf{1})M(CO)_5]$ complexes (M = Cr, Mo, W), Deberitz and Nöth reported on the

Table 6 IR-wavenumbers $\tilde{\nu}_{(CO)}$ of **11**, **12**, **13** and [(PPh$_3$)W(CO)$_5$]

	$\tilde{\nu}_{(CO)}$ (cm)$^{-1}$
[(**1**)W(CO)$_5$] (**11**)	2073 (w); 1992 (w); 1932 (sh); 1909 (s)
[(**2**)W(CO)$_5$] (**12**)	2071 (w); 1989 (w); 1930 (sh); 1907 (s)
[(PPh$_3$)W(CO)$_5$]	2071 (m); 1985 (w); 1929 (sh); 1909 (s)
[(**1**)$_2$W(CO)$_4$] (**13**)	2024 (s); 1915 (s); 1884 (s)



Scheme 6 Synthesis of bis(phosphinine)–W(0) complex **13**.

formation of [(**1**)$_2$W(CO)$_4$] (**13**) during the photochemical reaction of **1** and [W(CO)$_6$] in THF.[32] Indeed we also observed traces of **13** during our NMR spectroscopic investigations on the formation of **11** from **1** and [W(CO)$_5$(THF)], as depicted in Fig. 4.

The resonance of **13** can be detected at δ (ppm) = 169.9 ($^1J_{31P-183W}$ = 263 Hz) in the ^{31}P{^{1}H} NMR spectrum. By using [(CH$_3$CN)$_2$W(CO)$_4$] and **1** as starting material in the ratio of 1 : 2, the authors observed the quantitative formation of **13**. Based on the IR-spectroscopic data, the presence of the *cis*-, rather than the *trans*-isomer was suggested, although a structural characterization of this coordination compound remained elusive. In order to clarify this point, we started to synthesize [(**1**)$_2$W(CO)$_4$] according to the literature procedure (Scheme 6).

We were able to obtain crystals of this compound, suitable for X-ray diffraction from slowly cooling down a saturated solution of **13** in hot acetonitrile. The molecular structure of **13** in the crystal along with selected bond lengths and angles is depicted in Fig. 7 and confirms indeed the presence of the *cis*–bis(phosphinine) complex. It is interesting to note that the formation of the *cis*-isomer is apparently preferred over the *trans*-isomer, despite the presence of two sterically rather demanding 2,4,6-triphenylphosphinine ligands. As expected, the IR-spectroscopic data of **13** show stretching frequencies at lower wavenumbers compared to the mono-substituted [(**1**)W(CO)$_5$] complex **11** (Table 6).

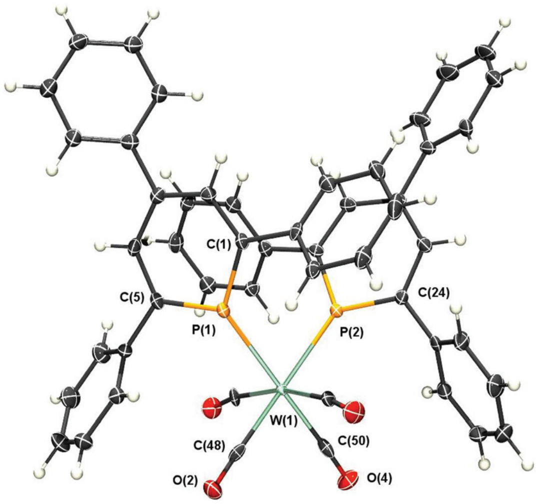


Fig. 7 Molecular structure of **13** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Solvent molecules (CH$_3$CN) are omitted for clarity. Selected bond lengths [Å] and angles (°): P(1)–W(1): 2.494(1); P(2)–W(1): 2.500(1); P(1)–C(1): 1.744(6); P(1)–C(5): 1.744(6); P(2)–C(24): 1.732(6); P(2)–C(28): 1.746(5). P(1)–W(1)–P(2): 82.88(5); C(1)–P(1)–C(5): 103.6(3); C(24)–P(1)–C(28): 104.0(3).

Experimental part

Synthesis of P(TMS)$_3$ (4)

In a 2-necked 1 L Schlenk-flask, equipped with stirring bar and dropping funnel, 9.72 g of Li (1.4 mol, 7 eq.) were suspended in 300 mL of freshly distilled THF. TMSCl (101.8 mL, 800 mmol, 4 eq.) was then added to the flask and a 120 mL THF solution of 1-(dichlorophosphanyl)piperidine (28.5 mL, 200 mmol, 1 eq.) was added to the dropping funnel. The flask was then equipped with a reflux condenser and the solution was heated up to reflux. At this point the 1-(dichlorophosphanyl)piperidine solution was added dropwise over 30 minutes and the reaction mixture was then refluxed for 4 h. Afterwards it was cooled down to room temperature and stirred until full conversion (reaction followed by ^{31}P NMR, reaction mixture becomes colorless from orange), then the volatiles were evaporated. 300 mL of dry pentane were added and the suspension was filtered. After removal of the volatiles in vacuum, the product is distilled (~55 °C, 0.5 mbar) in an average yield of 70% (35 g).

Caution: It is important to remove the solvent once the reaction is complete, to prevent side- and back-reactions. Afterwards, the crude product can be safely stored for several weeks at −20 under argon atmosphere. P(TMS)$_3$ is pyrophoric and can be destroyed under inert atmosphere by reaction with *n*-hexanol, isopropanol, ethanol and only at last, water. The same procedure should be adopted with the filter cake.

Synthesis of 2,4,6-triphenylphosphinine (1)

2,4,6-Triphenylpyrylium tetrafluoroborate (790 mg, 2.0 mmol) and Li[P(TMS)$_2$] × 0.5 THF (870 mg, 2 eq.) were put together in a 50 mL Schlenk flask under an argon atmosphere. 25 mL of THF were added. Upon addition a dark reaction mixture was obtained which was heated to reflux for 6 h. Subsequently, all volatiles were removed *in vacuo* to obtain a yellow-brown oil. The crude product was eluted through a neutral alumina plug (8 cm) with toluene to afford the pure product as a yellow solid (490 mg, 76%).

Conclusions

We have revisited several important aspects of the synthesis, reactivity and coordination chemistry of 2,4,6-triphenylphosphinine and 2,4,6-triphenylphosphabarrelene. First we optimized the synthesis of $P(SiMe_3)_3$, which has been the most frequently used phosphorus source for the preparation of 2,4,6-triarylphosphinines starting from the corresponding pyrylium salts. We could further show that $Li[P(SiMe_3)_2]$, prepared from $P(SiMe_3)_3$ and *n*BuLi in THF, is a highly recommendable alternative phosphorus source, as generally very high yields in 2,4,6-triarylphosphinines can be obtained. Structurally related to these aromatic phosphorus heterocycles are 2,4,6-triarylphosphabarrelenes. We could prepare and for the first time structurally characterize 2,4,6-triphenylphosphabarrelene-selenide, which allows for an evaluation of the structural and electronic properties of this compound in comparison to PPh_3PSe. Moreover, we could prepare and structurally characterize $[(L)W(CO)_5]$ complexes of both the phosphinine and phosphabarrelene, for which the molecular structures in the crystal remained so far elusive. This allowed for the first time the direct structural comparison of these structurally related phosphorus-compounds, coordinated to the same metal fragment. By means of X-ray crystallography and IR-spectroscopy, valuable structural and electronic information about these compound could thus be obtained. Finally we were able to characterize crystallographically a bis(phosphinine)–$W(CO)_4$ complex, which shows a *cis*-arrangement of the two phosphinine ligands.

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