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Coordination Chemistry

3-Bromo-2-Pyrone: An Alternative and Convenient Route to Functionalized Phosphinines

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Abstract: The facile access to 3-bromo-2-pyrone allows the preparation of 6-bromo-2-trimethylsilyl-phosphinine by a [4+2] cycloaddition with Me_3Si-C≡P for the first time. The regioselectivity of this reaction could be verified by means of single crystal X-ray diffraction of the corresponding W^0 complex. In the presence of $ZnBr_2$ and dppp (1,3-bis(diphenylphosphino)propane) as a bidentate ligand, the bromophosphinine quantitatively undergoes a Negishi cross-coupling reaction with PhLi that selectively leads to 6-phenyl-2-trimethylsilyl-phosphinine. This heterocycle could again be characterized by means of X-ray diffraction as a W^0 complex. These results describe a new and convenient route to 2,6-disubstituted phosphinines that makes use of readily available starting materials.

Introduction

Low-coordinate phosphorus compounds have long been regarded as "laboratory curiosities", as they were considered to violate the double bond rule and should therefore not be stable.[1] However, they have recently regained noticeable interest, particularly in the last decade. In fact, it was demonstrated in several cases that the peculiar characteristic properties of λ^3,σ^2-species can be transferred to more applied research fields, such as homogeneous catalysis, (luminescent) molecular materials, phosphorus-containing oligomers and polymers, dendrimers, and supramolecular chemistry.[2] Nevertheless, the accessibility to tailor-made low-coordinate phosphorus compounds is an important aspect for potential applications, as the steric and electronic properties of such species have to be modified accordingly.

During the last years, our group has been particularly interested in aromatic λ^3,σ^2-phosphinines, which are the higher homologues of pyridines (Figure 1). While the parent compound C_5H_5P (**1**) has been reported by Ashe et al. in 1971, the kinetically much more stable 2,4,6-triphenylphosphinine (**2**) has already been described in 1966.[3,4] The beauty of the latter compound is its synthesis by the corresponding pyrylium salt, which provides access to both **2** and the structurally related 2,4,6-triphenylpyridine. We have recently exploited this synthetic procedure extensively. Important contributions to this chemistry were made with the synthesis of various donor-functionalized phosphinines as well as axially chiral heterocycles and their corresponding transition metal complexes.[5] As an example, the phosphorus derivative of 2,2′-bipyridine (**3**) has been successfully used for the preparation of hitherto unknown phosphinine-based coordination compounds due to the chelate effect of this P,N-hybrid ligand.[6]

The direct functionalization of phosphinines towards this type of valuable bi- or polydentate heterocycles is, on the other hand, not as straightforward as for pyridines. Mathey, Le Floch, and co-workers and later Bayer et al. have shown that 2-bromo-4,5-dimethylphosphinine (**4**) undergoes Pd-catalyzed Stille- and Negishi-type coupling reactions with various substrates to afford the corresponding 2-substituted phosphinines of type **5** (Scheme 1).[7,8]

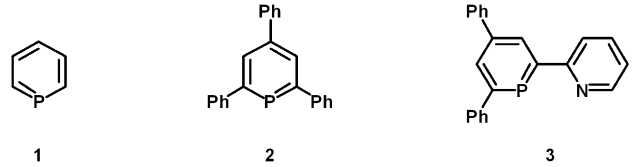
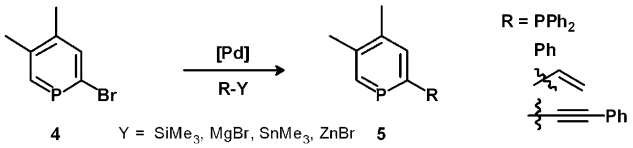


Figure 1. Parent phosphinine **1** and functionalized heterocycles **2** and **3**.



Scheme 1. Pd-catalyzed coupling reactions of bromo-functionalized phosphinines **4**.

Unfortunately, the preparation of **4** requires the use of the very expensive 2,3-dimethylbutadiene as well as the rather hazardous and potentially carcinogenic dibromomethyldibromophosphine (Br_2P-$CHBr_2$).[9] Breit et al. reported on an elegant alternative for the preparation of donor-functionalized phos-

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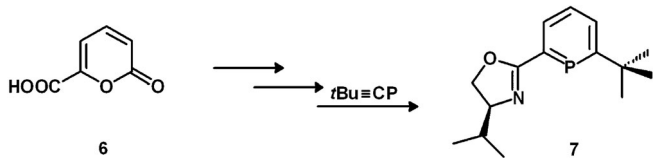
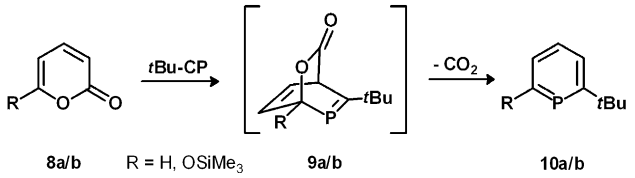


Scheme 2. Conversion of 6-carboxy-2-pyrone to the chiral 2,6-disubstituted phosphinine **7**.

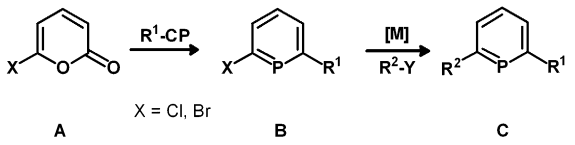
phinines with the use of 6-carboxy-2-pyrone (**6**) as the starting material. In a multistep synthetic procedure, the chiral oxazoline-substituted phosphinine **7** could be obtained (Scheme 2).[10]

This transformation is based on the original procedure for the preparation of 2-*tert*-butylphosphinine (**10a**) described by Regitz et al.[11] In this reaction, unsaturated cyclic compounds (such as pyrones) undergo a [4+2] cycloaddition reaction with *t*Bu-C≡P under formation of **10a**. In few cases, the conversion of 6-substituted pyrones with *t*Bu-C≡P to 2,6-disubstituted phosphinines has also been reported in the literature (Scheme 3).[12]



Scheme 3. [4+2] Cycloaddition of pyrones with *t*Bu-C≡P.

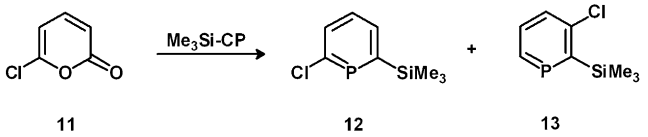
Inspired by these publications, we set out to combine the synthetic procedures shown in Schemes 1, 2, and 3 to have a convenient access to 2-substituted 6-halophosphinines. These could be used for further coupling reactions for the preparation of functionalized phosphinines according to Scheme 4. However, the [4+2] cycloaddition of a halopyrone has never been reported in the literature before.



Scheme 4. Synthetic strategy for the preparation of 2,6-disubstituted phosphinines.

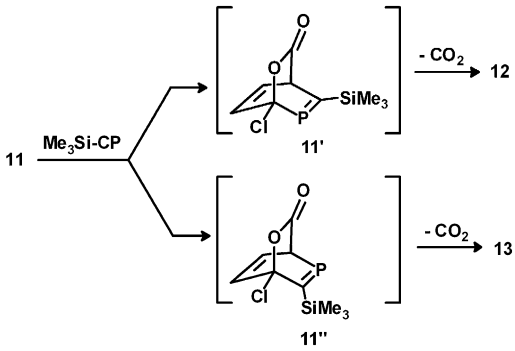
Results and Discussion

We first investigated the reaction of 6-chloro-2-pyrone (**11**) with the rather common phosphaalkyne *t*Bu-C≡P.[13] For this purpose, compound **11** was prepared according to a procedure described by Pirkle and Dines starting from glutaconic acid and phosphorus pentachloride.[14] Unfortunately, this reaction turned out to be extremely slow, showing only a minor product signal at $\delta = 196$ ppm in the $^{31}P\{^1H\}$ NMR spectrum even after one week of reaction time. We therefore turned our attention to the more reactive phosphaalkyne Me_3Si-C≡P.[15] Indeed a very fast conversion was found but, much to our surprise, only a rather poor regioselectivity was observed. In fact, two resonances were found in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 244$ and 219 ppm in a ratio of 3:7, which we assigned to the two regioisomers **12** and **13** (or vice versa, Scheme 5).



Scheme 5. Reaction of 6-chloro-2-pyrone with Me_3Si-C≡P.

Interestingly, this lack of regioselectivity has not been reported in the literature so far for the reaction of 6-substituted 2-pyrones and phosphaalkynes (vide supra). It is clear, on the other hand, that steric factors play a role during the addition of the dienophile to the diene according to Scheme 6.

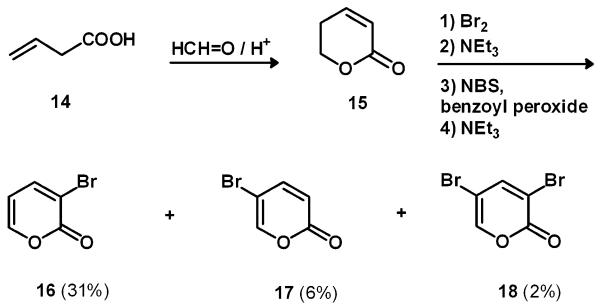


Scheme 6. Intermediates in the formation of **12** and **13** starting from **11**.

Thus, we turned our attention to bromo-substituted pyrones. Unfortunately, however, the corresponding 6-bromo-2-pyrone is unknown and has not been reported so far. Consequently, we attempted the synthesis of 3-bromo-2-pyrone (**16**), in the hope that this compound would regioselectively form the desired 2-substituted 6-bromo-phosphinine upon reaction with *t*Bu-C≡P or Me_3Si-C≡P due to the sterically demanding bromo substituent. Starting from 3-butenoic acid (**14**), the bromo-substituted 2-pyrones **16**, **17**, and **18** could be prepared according to a modified literature procedure, with the desired 3-bromo-2-pyrone (**16**) as the main product (Scheme 7).[16]

All compounds were easily separated by column chromatography. The assignment of the ^1H NMR spectra to **16**–**18** was verified crystallographically, as single crystals suitable for X-ray diffraction were obtained of all three compounds. The molecular structures of **16**–**18** are depicted in Figure 2, along with selected bond lengths and angles for **16**.

3-Bromo-2-pyrone (**16**) was first treated with *t*Bu-C≡P. Again, it unfortunately turned out that this reaction is rather slow,



Scheme 7. Synthesis of the bromo-pyrones **16**–**18**.

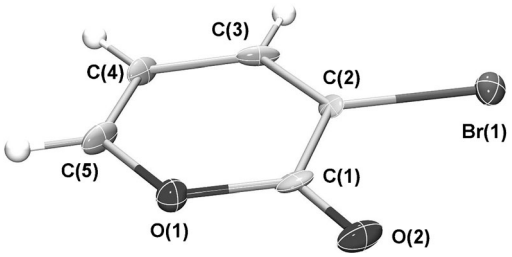


Figure 2. Molecular structure of **16** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): O(1)–C(1) 1.373(10), O(2)–C(1) 1.213(11), C(1)–C(2) 1.451(11), C(2)–C(3) 1.349(10), C(3)–C(4) 1.415(10), C(4)–C(5) 1.351(11), C(5)–O(1) 1.355(9), C(2)–Br(1) 1.891(7).

showing full conversion of the starting material only after 4 d. In contrast, the reaction of **16** with Me_3Si-C≡P is considerably faster, with full conversion already after 6 h in toluene at $T=$ 110 °C. Most strikingly, only one signal could be found in the $^{31}P\{^1H\}$ NMR spectrum at $\delta=232$ ppm, while only two small impurities occurred at $\delta=28$ and 30 ppm. This observation clearly demonstrates that the [4+2] cycloaddition reaction of **16** with Me_3Si-C≡P obviously proceeds regioselectively in the case of the bromo-substituted 2-pyrone moiety. The new phosphinine could easily be purified by column chromatography and was isolated as a fairly air and moisture stable orange oil in 75% yield. Figure 3 shows the ^1H NMR spectrum of the product (>95% purity based on ^1H NMR spectroscopy).

Unfortunately, it was not possible to assign the signals in the aromatic region (see inset) to the correct substitution pattern. We therefore treated the new phosphinine **19** with $[W(CO)_6]$ in THF under irradiation with UV light. Within 2 h, the starting material was quantitatively converted to the corresponding W^0 complex **20** according to $^{31}P\{^1H\}$ NMR spectroscopy and could be isolated as a light yellow solid. The coordination compound **20** shows a single resonance in the $^{31}P\{^1H\}$ NMR spectrum with additional satellites ($^1J_{P-W}=$ 139.3 Hz).

Crystals of **20** suitable for X-ray diffraction were obtained from THF/pentane at $T=-35$ °C and the molecular structure along with selected bond lengths and angles is depicted in Figure 4. The X-ray crystal structure analysis not only confirms the mononuclear nature of the coordination compound **20**, but also the presence of 6-bromo-2-TMS-phosphinine (**19**, TMS = trimethylsilyl) as ligand. Due to the rather sterically demanding TMS group and the Br substituent both in α-position of the phosphorus heterocycle, the planar aromatic ring is rotated out of the plane defined by three of the five carbonyl ligands and the phosphinine moiety (dihedral angle C(10)–W(1)–P(1)–C(5) = 41.9°). A similar conformation has been observed for phosphinine complexes containing a $Cr(CO)_5$ or $W(CO)_5$ fragment.[17,18]

The structural characterization of **20** nicely proves that the phosphinine **19** was regioselectively formed in a facile manner,

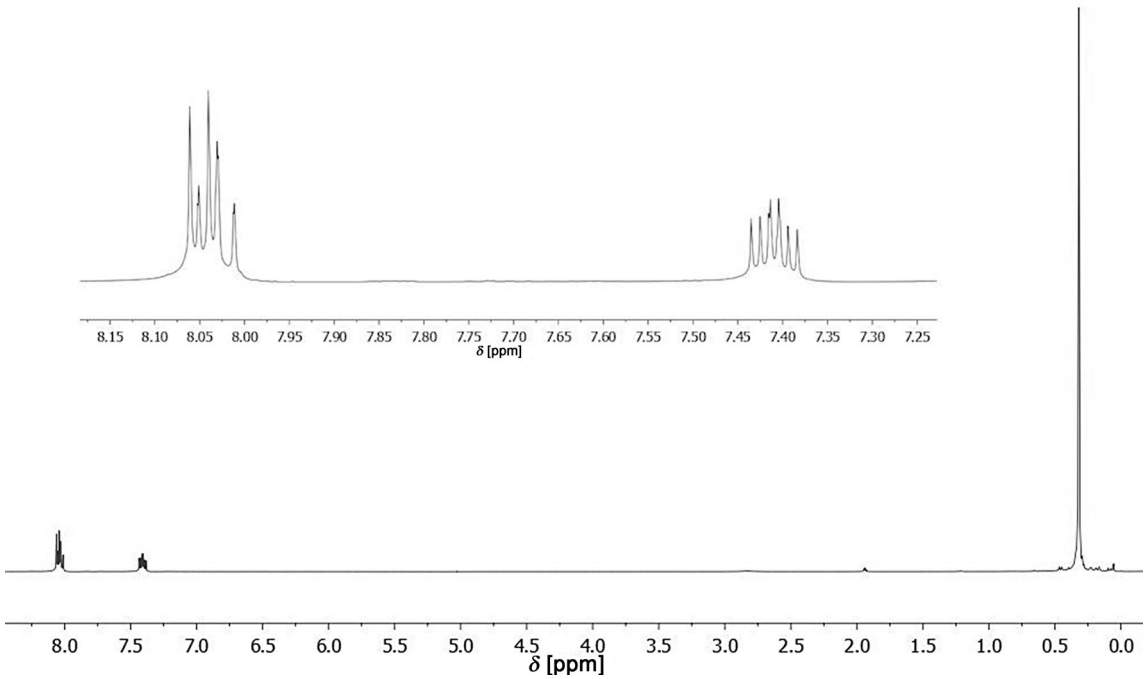


Figure 3. ^1H NMR spectrum of the phosphinine **19** in CD_3CN.

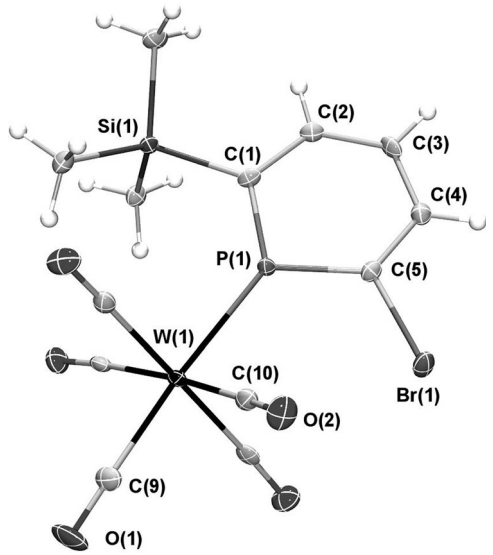
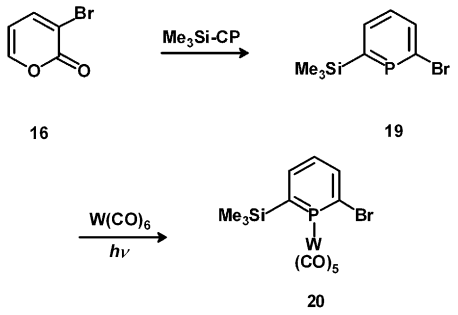


Figure 4. Molecular structure of **20** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.739(4); C(1)–C(2) 1.395(5), C(2)–C(3) 1.381(5), C(3)–C(4) 1.392(5), C(4)–C(5) 1.377(5), C(5)–P(1) 1.737(4), C(5)–Br(1) 1.902(3), C(1)–Si(1) 1.908(4), P(1)–W(1) 2.4819(9), W(1)–C(9) 2.011(4); C(9)–O(1) 1.138(5); C(1)–P(1)–C(5) 103.14.

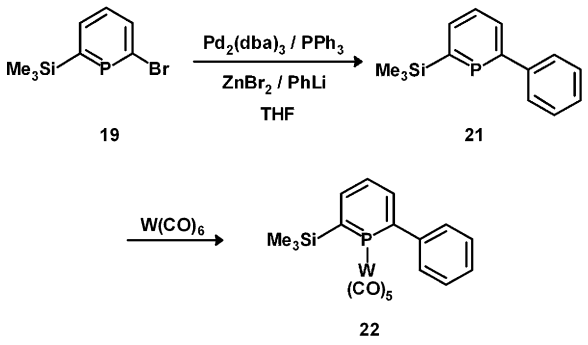


Scheme 8. Reaction sequence for the preparation of **20** starting from 3-bromo-2-pyrone.

starting from 3-bromo-2-pyrone (**16**) and Me_3Si-C≡P. This method can, thus, be used for the convenient synthesis of 6-bromo- and 2-TMS-functionalized phosphinines and the overall reaction sequence is summarized in Scheme 8.

Finally, we attempted a coupling reaction to convert 6-bromo-2-TMS-phoshinine (**19**) into the corresponding product by means of a C–C coupling reaction, which has been reported for bromo-phosphinines before (vide supra and Scheme 9).

It turned out, that the Pd-catalyzed Negishi reaction of **19** with PhLi and $ZnBr_2$ in the presence of dppp (1,3-bis(diphenylphosphino)-propane) as a bidentate ligand leads to the presence of four very broad signals in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 220.6$, 220.9, 222.6, and 255.3 ppm after 24 h at $T = 50\,^{\circ}C$. These resonances are probably caused by the presence of several phosphinine-based metal complexes, while no starting material could be detected anymore. Indeed, after column chromatography, a yellow oil was isolated in 80% yield that shows a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at $\delta =$



Scheme 9. Negishi coupling of **19** under formation of **21** and the W^0 complex **22**.

225.4 ppm. Moreover, in the ^1H NMR spectrum of **21,** additional signals in the aromatic region can be observed. The yellow oil was subsequently treated with $[W(CO)_6]$ in THF under irradiation with UV light monitored by means of NMR spectroscopy. Product **22** shows a single resonance in the $^{31}P\{^1H\}$ NMR spectrum with additional satellites ($^1J_{P-W} = 132.8$ Hz).

We were able to obtain crystals of **22** suitable for X-ray diffraction and the molecular structure along with selected bond lengths and angles are depicted in Figure 5. The X-ray crystal structure analysis confirms the presence of 6-phenyl-2-TMS-phosphinine (**20**) as ligand and the successful Pd-catalyzed Negishi-coupling between **19** and PhLi in the presence of $ZnBr_2$ and dppp as ligand (Scheme 9).

A comparison of the molecular structures of compounds **20** and **22** in the crystal further reveals that the P(1)–W(1) distance in **20** is shorter than in **22** (2.4819(9) Å vs. 2.5225(8) Å), while the C–O bond is longer in **22** than in **20** (1.153(3) Å vs.

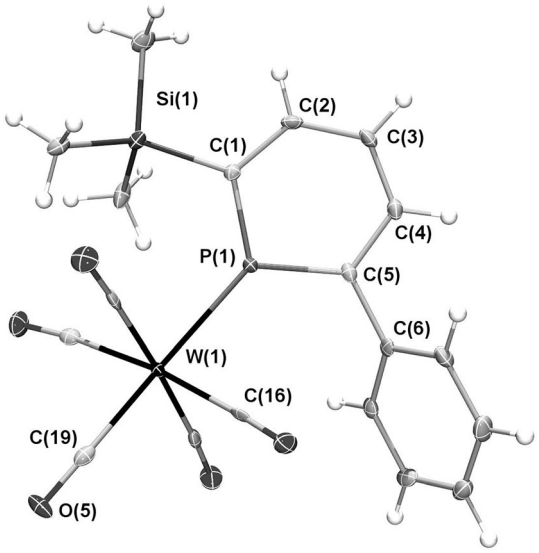


Figure 5. Molecular structure of **22** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°):P(1)–C(1) 1.735(3); C(1)–C(2) 1.398(4), C(2)–C(3) 1.390(4), C(3)–C(4) 1.379(4), C(4)–C(5) 1.400(4), C(5)–P(1) 1.737(3), C(5)–C(6) 1.486(4), C(1)–Si(1) 1.899(3), P(1)–W(1) 2.5225(8), W(1)–C(9) 1.996(3); C(19)–O(5) 1.153(3); C(1)–P(1)–C(5) 105.75.

1.138(5) Å). Although steric effects cannot be excluded, the observed data nicely reflect the stronger π-accepting character of the bromo-phosphinine **20** compared to the phenyl-substituted aromatic heterocycle **22**.

Conclusion

We have successfully developed a convenient and straightforward synthetic route to 2,6-disubstituted phosphinines starting from 3-bromo-2-pyrone. The [4+2] cycloaddition of this compound with the rather reactive phosphaalkyne Me_3Si-C≡P regioselectively as well as quantitatively gives 6-bromo-2-TMS-phosphinine, under elimination of CO_2. This could be verified by means of X-ray crystallography of the corresponding W^0 complex. By making use of the Pd-catalyzed Negishi cross-coupling reaction, the bromo-functionalized phosphinine can easily be further converted to a 2,6-disubstiuted aromatic phosphorus heterocycle. As an example, the quantitative formation of 6-phenyl-2-TMS-phosphinine could again be confirmed by means of single crystal X-ray diffraction of its W^0 complex. Experiments to investigate the scope of the reaction as well as to use the TMS substituent for further functionalizations are currently carried out in our laboratories.

Experimental Section

General. All reactions were performed under argon in oven-dried glassware using modified Schlenk techniques unless otherwise stated. All common solvents and chemicals were commercially available. Trimethylsilylphosphaalkyne[15a] and the bromo-substituted 2-pyrones **16, 17,** and **18**[16,19] were prepared according to literature procedures. The solvents were prepared by using the MBraun Solvent Purification System MB-SPS 800 filled with Al_2O_3. Silica gel plates 60 F_{254} from Merck were used for thin layer chromatography and silica gel 60 M (0.04–0.063 mm) from Macherey–Nagel was used for preparative column chromatography. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded by using a Jeol JNM-ECA 400II spectrometer. ^1H and $^{13}C\{^1H\}$ chemical shifts are referenced to the residual proton resonance of the deuterated solvents and $^{31}P\{^1H\}$ chemical shifts are referenced to an 85% aqueous solution of H_3PO_4. Electron impact mass spectra (EI-MS) were recorded on a Variant MAT 711 spectrometer. For reactions under UV radiation a UVP Black-Ray B-100AP 100 W high intensity mercury vapor lamp without filter was used at a distance of 15 cm.

6-Bromo-2-(trimethylsilyl)phosphinine (19). The pyrone **16** (0.93 g, 5.30 mmol) was added to a solution of Me_3Si-C≡P (0.62 g, 5.30 mmol) in toluene (100 mL). After refluxing for 12 h, all volatiles were removed in vacuo to obtain a dark orange residue. The crude product was purified by means of column chromatography over silica with ethyl acetate/*n*-hexane (1:9) to afford the product **19** as a yellow oil (0.97 g, 3.93 mmol, 75%). R_f = 0.78 (ethyl acetate/*n*-hexane 1:9); ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 8.03 (dd, J = 8.7, 4.1 Hz, 1H), 7.95 (dd, J = 11.4, 7.8 Hz, 1H), 7.36 (ddd, J = 8.7, 8.1, 4.1 Hz, 1H), 0.35 ppm (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 °C): δ = 175.3 (d, J = 80.2 Hz, 1C), 154.0 (d, J = 1.0 Hz, 1C), 137.8 (d, J = 12.7 Hz, 1C), 136.1 (d, J = 13.1 Hz, 1C), 130.2 (d, J = 19.7 Hz, 1C), −0.09 ppm (d, J = 6.5 Hz, 3C); $^{29}Si\{^1H\}$ NMR (80 MHz, $CDCl_3$, 20 °C): δ = 83.0 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 20 °C): δ = 231.5 ppm; MS (EI, 30 °C, 80 eV): *m/z* (%): 248.0 (29) $[M(^{81}Br)]^+$, 246.0 (28) $[M(^{79}Br)]^+$, 232.9 (100) $[M(^{81}Br)\text{-}CH_3]^+$, 230.9 (95) $[M(^{79}Br)\text{-}CH_3]^+$, 152.9 (15) $[M\text{-}(BrCH_3)]^+$, 73.0 (75) $[Si(CH_3)_3]^+$.

[W(CO)$_5$(19)] (20). The phosphinine **19** (21.1 mg, 0.09 mmol) was dissolved in THF (0.8 mL) and $W(CO)_6$ (30.0 mg, 0.09 mmol) was added. After irradiation under UV light for 2 h, the dark red reaction mixture was filtered over Celite and the filtrate was concentrated in vacuo. The crude product was recrystallized from THF/*n*-pentane to give the product **20** as a yellow solid (38 mg, 0.07 mmol, 78%). ^1H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 8.19 (ddd, J = 12.4, 8.8, 0.8 Hz, 1H), 8.02 (ddd, J = 28.1, 8.0, 0.6 Hz, 1H), 7.25 (ddd, J = 16.1, 8.0, 0.6 Hz, 1H), 0.47 ppm (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 20 °C): δ = 198.6 (d, J = 33.0 Hz, 1C), 196,0 (d, J = 9.1 Hz, 1C), 192.0 (s, $^1J_{C-W}$ = 63.5 Hz, 5C, $W(CO)_5$), 168.4 (d, J = 27.1 Hz, 1C), 141.5 (d, J = 19.4 Hz, 1C), 128.0 (d, J = 30.7 Hz, 1C), 1.70 ppm (d, J = 2.9 Hz, 3C); $^{29}Si\{^1H\}$ NMR (80 MHz, CD_2Cl_2, 20 °C): δ = 3.43 ppm (d, J = 24.0 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 198.2 ppm ($^1J_{P-W}$ = 140.9 Hz).

6-Phenyl-2-(trimethylsilyl)phosphinine (21). $ZnBr_2$ (360 mg, 1.60 mmol) was dissolved in THF (2 mL) at T = −70 °C and a solution of phenyllithium (1.8 M) in dibutyl ether (0.56 mL, 1.00 mmol) was added. After stirring for 30 min at T = −70 °C, a solution of $Pd_2(dba)_3$ (11.5 mg, 0.01 mmol, 5 mol% in Pd), dppp (10.4 mg, 0.025 mmol, 5 mol%), and **19** (124 mg, 0.50 mmol) in THF (2 mL) was added dropwise at T = −50 °C. The reaction mixture was heated for 24 h at T = 50 °C under constant stirring. Since no starting material (**19**) could be detected in the $^{31}P\{^1H\}$ NMR spectrum, the solvent was removed under reduced pressure. The crude product was purified by means of column chromatography over silica with DCM/*n*-pentane (1:9) to afford the pure product as a yellow oil (105 mg, 0.43 mmol, 86%). ^1H NMR (400 MHz, $[D_8]$THF, 20 °C): δ = 8.06 (m, 1H), 8.00 (m, 1H), 7.65 (t, J = 5.9 Hz, 2H), 7.60 (m, 1H), 7.41 (dt, J = 7.2, 5.8 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 0.39 ppm (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $[D_8]$THF, 20 °C): δ = 172.1 (d, J = 61.6 Hz, 1C), 171.6 (d, J = 77.4 Hz, 1C), 144.7 (d, J = 22.4 Hz, 1C), 137.7 (d, J = 13.1 Hz, 1C), 134.0 (d, J = 10.7 Hz, 1C), 128.6 (d, J = 1.9 Hz, 1C), 128.3 (s, 2C), 128.2 (s, 2C), 127.9 (s, 1C), 0.2 ppm (d, J = 6.6 Hz, 3C); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF, 20 °C): δ = 223.5 ppm; MS (EI, 30 °C, 80 eV): *m/z* (%): 244.0 (40) $[M]^+$, 229.0 (100) $[M\text{-}CH_3]^+$.

[W(CO)$_5$(21)] (22). The phosphinine **21** (20.0 mg, 0.08 mmol) was dissolved in THF (0.7 mL) and $W(CO)_6$ (28.8 mg, 0.08 mmol) was added. After irradiation under UV light for 6 h, the reaction mixture was filtered over Celite. The dark orange filtrate was concentrated in vacuo and the crude product was recrystallized from acetonitrile to give the product **21** as a yellow solid (33 mg, 0.06 mmol, 75%). ^1H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 8.12 (ddd, J = 26.4, 8.2, 1.2 Hz, 1H), 7.82 (ddd, J = 15.3, 8.4, 1.2 Hz, 1H), 7.45 (m, 6H), 0.54 ppm (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 20 °C): δ = 196.4 (d, J = 9.0 Hz, 5C), 145.9 (d, J = 23.4 Hz, 1C), 143.5 (d, J = 13.5 Hz, 1C), 142.2 (d, J = 19.5 Hz, 1C), 138.3 (d, J = 10.8 Hz, 1C), 130.9 (d, J = 3.5 Hz, 1C), 130.7 (d, J = 8.9 Hz, 2C), 129.2 (d, J = 0.8 Hz, 2C), 128.8 (d, J = 1.9 Hz, 1C), 126.7 (d, J = 32.6 Hz, 1C), 1.9 ppm (d, J = 2.9 Hz, 3C); $^{29}Si\{^1H\}$ NMR (80 MHz, CD_2Cl_2, 20 °C): δ = 2.41 ppm (d, J = 23.9 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$THF, 20 °C): δ = 181.2 ppm ($^1J_{P-W}$ = 132.8 Hz).

X-ray crystal structure determination of 16. Crystals suitable for X-ray diffraction were obtained from a saturated solution of **16** in methanol. Crystallographic data ($C_5H_3BrO_2$): F_W = 174.98 g mol^{-1}; 0.60×0.14×0.10 mm^3; colorless needle, orthorhombic; *Pna*2$_1$; a = 10.6142(6), b = 13.0601(8), c = 3.9163(2) Å; α = 90°, β = 90°, γ = 90°; V = 542.89(5) Å^3; Z = 4; D_x = 2.141 g cm^{-3}; μ = 7.460 mm^{-1}. 1704 reflections were measured by a D8 Venture Bruker Photon CMOS diffractometer[20] (MoK_α radiation; λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.63 Å at a temperature of 100 K. 978 reflections were

unique ($R_{int}=0.069$). The structures were solved with SHELXL-2014[21] by using direct methods and refined with SHELXS-2014[21] on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 73 parameters were refined with one restraint. $R_1=0.035$ for 904 reflections with $I>2\sigma(I)$ and $wR_2=0.117$ for 978 reflections; $S=1.136$; residual electron density −1.33–1.03 e Å^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[22] CCDC 1476987 (**16**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.[23]

X-ray crystal structure determination of 20. Crystals suitable for X-ray diffraction were obtained by cooling down a saturated solution of **20** in THF/*n*-pentane. Crystallographic data ($C_{13}H_{12}O_5BrPSiW$): $F_W=571.05$ g mol^{-1}; $0.34\times0.27\times0.08$ mm^3; yellow plate, triclinic; $P\bar{1}$; $a=9.0676(6)$, $b=10.0337(7)$, $c=10.0485(7)$ Å; $\alpha=73.056(3)^\circ$, $\beta=82.106(3)^\circ$, $\gamma=83.231(3)^\circ$; $V=863.33(10)$ Å^3; $Z=2$; $D_x=2.197$ g cm^{-3}; $\mu=9.183$ mm^{-1}. 20150 reflections were measured by using a D8 Venture Bruker Photon CMOS diffractometer[20] (MoK_α radiation; $\lambda=0.71073$ Å) up to a resolution of $(\sin\theta/\lambda)_{max}=0.63$ Å at a temperature of 100 K. The reflections were corrected for absorption and scaled on the basis of multi-scan-measured reflections by using the SADABS program (0.15–0.53 correction range).[20] 3549 reflections were unique ($R_{int}=0.031$). The structures were solved with SHELXL-2014[21] by using direct methods and refined with SHELXS-2014[21] on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 202 parameters were refined with zero restraints. $R_1=0.021$ for 3353 reflections with $I>2\sigma(I)$ and $wR_2=0.055$ for 3549 reflections; $S=1.070$; residual electron density −1.98–1.27 e Å^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[22] CCDC 1476990 (**20**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.[23]

X-ray crystal structure determination of 22. Crystals suitable for X-ray diffraction were obtained by cooling down a saturated solution of **22** in acetonitrile. Crystallographic data ($C_{19}H_{17}O_5PSiW$): $F_W=568.23$ g mol^{-1}; $0.11\times0.11\times0.03$ mm^3; yellow block, monoclinic; $P2_1/n$; $a=11.5174(6)$, $b=9.4421(4)$, $c=18.7154(10)$ Å; $\alpha=90^\circ$, $\beta=93.027(2)^\circ$, $\gamma=90^\circ$; $V=2032.43(17)$ Å^3; $Z=4$; $D_x=1.857$ g cm^{-3}; $\mu=5.848$ mm^{-1}. 35114 reflections were measured by using a D8 Venture Bruker Photon CMOS diffractometer[20] (MoK_α radiation; $\lambda=0.71073$ Å) up to a resolution of $(\sin\theta/\lambda)_{max}=0.60$ Å at a temperature of 100 K. The reflections were corrected for absorption and scaled on the basis of multi-scan measured reflections by using the SADABS program (0.57–0.53 correction range).[20] 3718 reflections were unique ($R_{int}=0.038$). The structures were solved with SHELXS-2014[21] by using direct methods and refined with SHELXL-2014[21] on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 247 parameters were refined with zero restraints. $R_1=0.019$ for 3132 reflections with $I>2\sigma(I)$ and $wR_2=0.032$ for 3718 reflections; $S=0.990$; residual electron density −0.71–0.49 e Å^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[22] CCDC 1476991 (**22**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.[23]

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FULL PAPER

Coordination Chemistry

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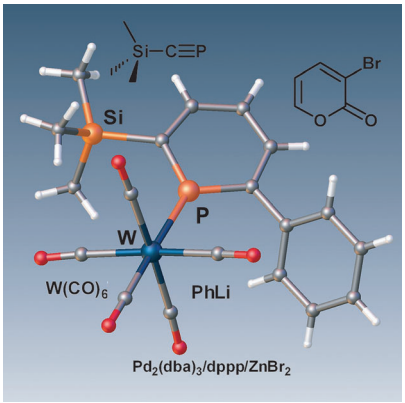
3-Bromo-2-Pyrone: An Alternative and Convenient Route to Functionalized Phosphinines



New functionalized phosphorus heterocycles: A convenient and straightforward synthetic route to 6-bromo-2-trimethylsilyl-phosphinine was developed, starting from 3-bromo-2-pyrone and $Me_3Si–C{\equiv}P$. The quantitative [4+2] cycloaddition of the starting materials turned out to be regioselective, which was verified by single crystal X-ray diffraction. A subsequent Pd-catalyzed Negishi cross-coupling reaction allows further access to 2,6-disubstiuted aromatic phosphorus heterocycles (se figrue).