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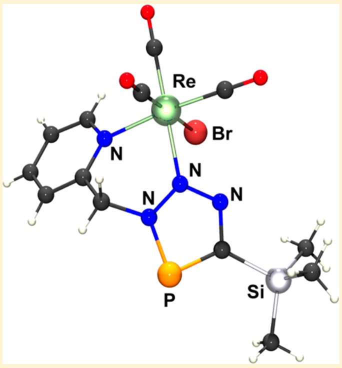
Triazaphospholes versus Triazoles: An Investigation of the Differences between “Click”-Derived Chelating Phosphorus- and Nitrogen-Containing Heterocycles

Julian A. W. Sklorz, Santina Hoof, Michael G. Sommer, Fritz Weißer, Manuela Weber, Jelena Wiecko, Biprajit Sarkar, and Christian Müller*

Institut fur Chemie und Biochemie, Anorganische Chemie, Freie Universitat Berlin, Fabeckstraße 34/36, Berlin 14195, Germany

Supporting Information

ABSTRACT: A new class of pyridyl-functionalized triazaphospholes bearing either ^{t}Bu or $SiMe_3$ substituents at the 5-position of the N_3PC heterocycle have been prepared via the “click” reaction starting from 2-(azidomethyl)pyridine and the corresponding phosphaalkynes. In order to investigate the electronic structure and donor−acceptor properties of such novel chelating and low-coordinate phosphorus heterocycles, calculations at the DFT level have been carried out. Moreover, cyclic voltammetry measurements were performed and the results were compared with those for the structurally related triazole-based systems, demonstrating a significant influence of the phosphorus atom as well as the substitution pattern on the electronic properties of the novel compounds. The P,N hybrid ligands form Re(I) complexes of the type $[(N^{\wedge m}N)Re(CO)_3Br]$ via coordination of the nitrogen atom N^2 to the metal center rather than via the phosphorus atom, as verified crystallographically.



INTRODUCTION

Low-coordinate phosphorus compounds have recently regained noticeable interest, as the very peculiar electronic and steric properties of such $\lambda^3\sigma^2$ species differ significantly from those of classical trivalent $\lambda^3\sigma^3$-phosphanes. These characteristics can be transferred to more applied research fields, such as homogeneous catalysis and material science.[1] Using a modular synthetic route, we have recently demonstrated the access to various donor-functionalized 2,4,6-triarylphosphinines, including phosphorus derivatives of 2,2′-bipyridine (**A**; Figure 1). By making use of the chelate effect, we could demonstrate that this neutral P,N hybrid ligand easily forms coordination compounds with transition-metal centers in both low as well as medium to high oxidation states.[2]

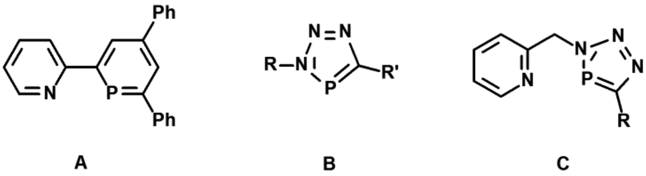


Figure 1. Pyridyl-functionalized phosphinine (**A**) and general schematic structures of a 3*H*-1,2,3,4-triazaphosphole derivative (**B**) and pyridyl-functionalized triazaphosphole (**C**).

Inspired by these findings, we started a program to investigate the access to other classes of pyridyl-functionalized, low-coordinate phosphorus compounds. We anticipated that derivatives of 3*H*-1,2,3,4-triazaphospholes (**B**) are suitable candidates, as they can generally be prepared selectively in a modular 1,3-dipolar cycloaddition reaction, starting from azides and phosphaalkynes, as shown by Regitz et al.[3] As a matter of fact, the copper-catalyzed azide−alkyne cycloaddition reaction (CuAAC, “click reaction”), introduced independently by Sharpless and Medal in 2002,[4] has found widespread application in various research areas, such as homogeneous catalysis, molecular materials, dendrimers, and supramolecular chemistry, due to a facile and atom-economical assembly of target molecules. This powerful tool can indeed be used for straightforward and simple access to functionalized ligands.[5] Interestingly, when phosphaalkynes were used instead of terminal alkynes, only one regioisomer was formed thermally and selectively without the need for a copper catalyst, because the P≡C bond is already polarized. According to Nyulászi and Regitz, 3*H*-1,2,3,4-triazaphosphole has a conjugated π system with a high degree of aromaticity, just like the corresponding triazoles containing only nitrogen.[6] In contrast to phosphinines, however, they are expected to possess a higher π density at the phosphorus atom due to a $\bar{N}{-}C{=}P \leftrightarrow N^{+}{=}C{-}P^{-}$ conjugation, particularly evident in 1,3-azaphospholes, which possess only the σ^3N atom with π-donor properties.[7] Interestingly, while the analogous donor-functionalized triazoles have been intensely investigated in coordination chemistry over the past decade,[8] the synthesis and coordination chemistry of donor-functionalized, chelating 3*H*-1,2,3,4-triazaphosphole derivatives is practically unknown.[9,10] On the other hand, the “click” reaction between donor-functionalized azides

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and phosphaalkynes would provide access to polydentate ligands, in which the stereoelectronic properties can be tuned according to the additional phosphorus heteroatom and the nature of the substituents. In this way, a whole new set of phosphorus derivatives of triazoles would be readily available, making detailed studies on the influence of the additional heteroatom on the properties of triazole derivatives possible for the first time. Surprisingly, only one example of such a species has so far been characterized crystallographically, where a tripodal tris(triazaphosphole) acts as a tridentate ligand with P coordination toward a Pt(0) center, as reported by Jones et al.[11]

Stimulated by these findings, we envisaged the access and detailed investigation of novel 2-pyridylmethyl-functionalized 1,2,3,4-triazaphospholes of type **C** (Figure 1). Due to the presence of both σ^2-phosphorus and σ^2-nitrogen atoms within one heterocycle, such ambidentate ligands contain two different potential coordination sites (**D**, **E**; Figure 2). Consequently, we were interested in investigating the coordination chemistry of these systems and the influence of additional substituents at the P═C moiety on the stereoelectronic properties of the ligands. Since these compounds have not been reported in the literature so far, we set out to synthesize the structurally related, phosphorus-lacking triazole derivatives of type **F** as well (Figure 2). It should be noted here that a detailed comparison between these heterocycles, having an otherwise identical substitution pattern, has not been reported before.

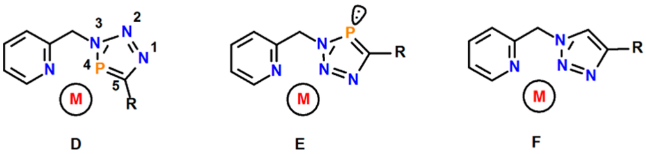


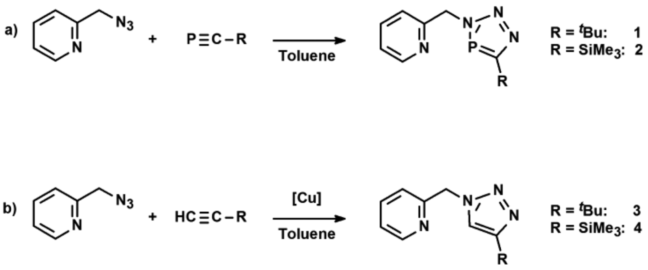
Figure 2. Possible coordination modes of chelating triazaphospholes (**D**, **E**) and 2-pyridylmethyl-functionalized triazole (**F**).

RESULTS AND DISCUSSION

Since ^{t}Bu-C≡P is accessible in a straightforward way, we decided to start our investigations with this well-known compound. Moreover, the ^{t}Bu group does obviously not prevent a possible η^1(P) coordination of the corresponding triazaphosphole to a transition-metal center.[10] In order to modify the electronic properties while retaining similar steric properties of the heterocycle, we chose to introduce a $SiMe_3$ group at the 5-position as well. It is known that silyl groups attached directly to a π-electron system show relatively strong electron-withdrawing effects due to an inverse hyperconjugation. On the other hand, the "click" reaction between an azide and the required trimethylsilylphosphaethyne has not been shown before. 2-(Azidomethyl)pyridine,[12] ^{t}Bu−C≡P,[13] and TMS−C≡P[14] were thus prepared according to standard literature procedures. Subsequently, the "click reaction" between equimolar amounts of the azide and *tert*-butylphosphaethyne was carried out at room temperature in toluene without any problem. Interestingly, it turned out that also the reaction of trimethylsilylphosphaethyne with 2-(azidomethyl)pyridine proceeded straightforwardly, leading for the first time to a TMS-substituted triazaphosphole derivative. The novel compounds **1** and **2** were respectively obtained in 93% and 94% yields as colorless solids (Scheme 1a).

Compound **1** shows a downfield shift in the $^{31}P\{^1H\}$ NMR spectrum at δ (ppm) 173.1 (CD_2Cl_2), which is typical for $\lambda^3\sigma^2$-phosphorus species with rather low π density at the phosphorus atom.[15] The $SiMe_3$ group has indeed a rather large influence on the chemical shift, as the P resonance in the $^{31}P\{^1H\}$ NMR spectrum of compound **2** was observed at δ (ppm) 216.5 (CD_2Cl_2). The ^1H NMR spectra of both **1** and **2** show a doublet at δ (ppm) 5.8 (**1**) and 5.9 (**2**), due to coupling of the methylene protons with the phosphorus atom ($^3J_{H-P}$ = 1.4, 6.1 Hz). The proton H^1 (Figure 3) is shifted the most downfield and is detected at δ (ppm) 8.54 (**1**) and 8.53 (**2**). As an example, Figure 3 shows the ^1H NMR spectrum of triazaphosphole **2**, recorded in CD_2Cl_2.

Scheme 1. Synthesis of 2-Pyridylmethyl-Functionalized Triazaphospholes (1, 2) and 2-Pyridylmethyl-Functionalized Triazoles (3, 4)



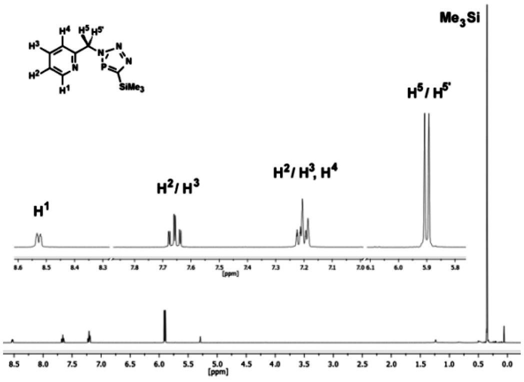


Figure 3. ^1H NMR spectrum of **2** recorded in CD_2Cl_2 and assignment of the respective protons. Inset: enlargement of the low-field region.

For comparison reasons, the nitrogen-containing triazoles **3** and **4** were obtained according to a modified literature procedure (^{t}Bu). Recently, Zhu et al.[16] and Crowley et al.[17] have demonstrated that analogous systems with different substituents at the 5-position of the triazole mojety are easily accessible. Compounds **3** and **4** were thus obtained as colorless solids in 72 and 67% yields, respectively (Scheme 1b).

In order to get insight into the electronic structure of the novel triazaphospholes, we first performed calculations at the DFT level (B3LYP) on compound **1** (R = ^{t}Bu), and the frontier orbitals are depicted in Figure 4.

Similar to the situation in $\lambda^3\sigma^2$-phosphinines, the LUMO of the low-coordinate phosphorus heterocycle shows a large coefficient of π symmetry at the phosphorus atom, indicating the π-accepting properties of such systems. The π-donor properties of triazaphospholes are obvious from the HOMO.[7] Moreover, a rather large coefficient of σ symmetry is present at the nitrogen atoms N^1 and N^2 of the heterocycle in the HOMO-1. Normally, nitrogen atom N^1 in triazoles coordinates preferentially to a transition-metal center. However, in

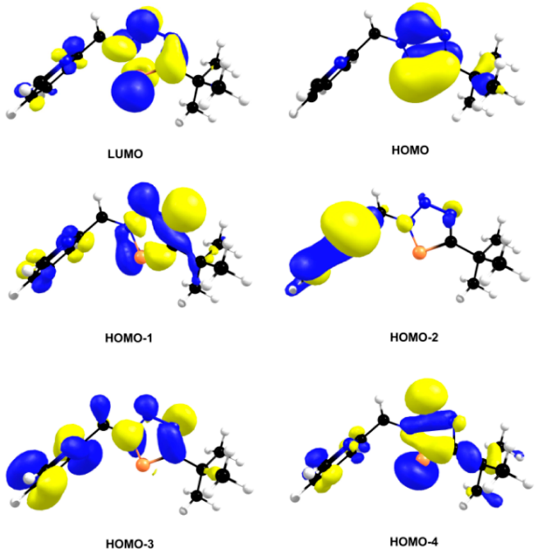


Figure 4. Frontier orbitals of the 2-pyridylmethyl-functionalized 3*H*-1,2,3,4-triazaphosphole derivative **1**.

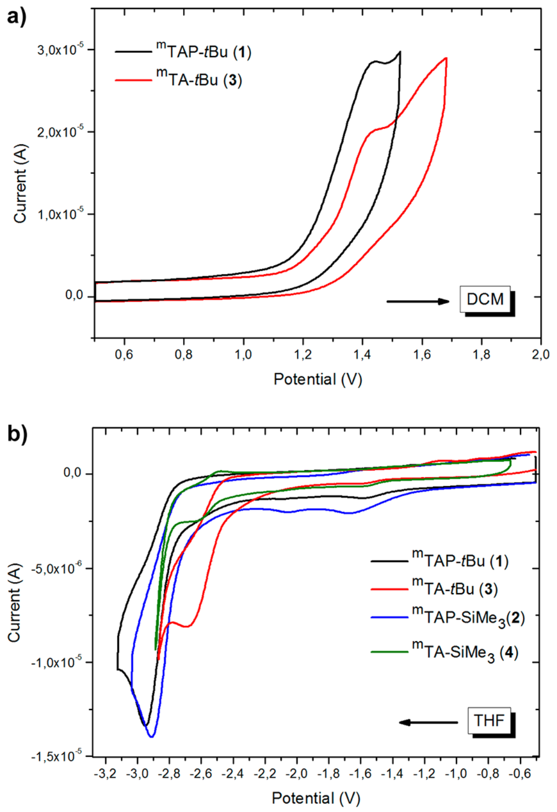


Figure 5. Electrochemical investigation of compounds **1**−**4**: (a) oxidation (measured in CH_2Cl_2); (b) reduction (measured in THF).

chelating ligands, such as in **1** and **2**, this nitrogen atom might not be suitable for σ coordination due to the chelating effect (vide infra).[8h] Very similar large coefficients of σ symmetry at both the phosphorus atom and the nitrogen atom N^2 are further present in the energetically low-lying HOMO-4. If σ coordination to a transition-metal center occurs, the energetic difference between coordinating via the pyridyl nitrogen and the nitrogen N^2 or via the pyridyl nitrogen and the phosphorus atom is thus expected to be very small and both coordination modes might consequently be possible.

In order to investigate the electronic structure of compounds **1**−**4** experimentally, their electrochemical properties were further examined by means of cyclic voltammetry (CH_2Cl_2, THF, 0.1 M Bu_4NPF_6, ν = 100 mV s^{-1}) using ferrocene (Fc) as the internal standard (Figure 5).

In DCM, compounds **1** and **3** undergo irreversible oxidation processes at $E_{\mathrm{p}}^{\mathrm{ox}}$ = +1.438 V (**1**) and $E_{\mathrm{p}}^{\mathrm{ox}}$ = +1.451 V (**3**) vs Fc/Fc^+. While **1** is slightly easier to oxidize than the corresponding triazole **3**, the $SiMe_3$-substituted compounds **2** and **4** cannot be oxidized within the solvent window of DCM. This finding is in line with the electron-withdrawing properties of the $SiMe_3$ group, directly bound to the π system of the aromatic heterocycles. In THF, compounds **1**−**4** further undergo irreversible reduction processes ($E_{\mathrm{p}}^{\mathrm{red}}$ = −2.957 V (**1**), $E_{\mathrm{p}}^{\mathrm{red}}$ = −2.691 V (**3**), E^{red} = −2.911 V (**2**), E^{red} = −2.636 V (**4**) vs Fc/Fc^+). Obviously, the phosphorus-containing heterocycles **1** and **2** are more difficult to reduce in comparison to the triazoles **3** and **4**. This can be attributed to the fact that exchanging a C−H unit in a triazole by a phosphorus atom leads, as expected, to a more electron-rich heterocycle and a LUMO located higher in energy. Complementary to the aforementioned observations, the presence of a $SiMe_3$ group (compounds **2** and **4**) leads to lower reduction potentials in comparison to the ^{t}Bu-substituted analogues due to its electron-withdrawing character, which lowers the energy of the LUMO.

As the phosphinine-based P,N ligand **A** (Figure 1) undergoes a facile reaction with $Re(CO)_5Br$ with formation of the complex [(**A**)$Re(CO)_3Br$)], we decided to explore the coordination chemistry of **1**−**4** also toward Re(I).[1d] At the same time, the [$Re(CO)_3Br$] metal fragment offers the possibility to investigate the electronic properties of **1**−**4** by means of IR spectroscopy of the resulting coordination compounds. Crowley et al. have shown that Re(I) complexes of type **F** (Figure 2, R = C_6H_5, 4-NO_2-C_6H_5, 4-$MeOC_6H_5$, Bn) can easily be prepared.[17] In those coordination compounds, the triazole moiety coordinates indeed via the N^2 atom to the [$Re(CO)_3Br$] fragment, which is the least nucleophilic part.[8h] This coordination mode can thus be attributed purely to the chelating effect. Taking the frontier orbitals of the 3*H*-1,2,3,4-triazaphosphole derivative **1** into account (Figure 4), we were thus wondering whether coordination compound **D** or **E** would be realized in combination with Re(I) (Figure 2).

We first paid attention to the coordination chemistry of the triazaphospholes. Compounds **1** and **2** were reacted with equimolar amounts of [$Re(CO)_5Br$] in dichloromethane at T = 80 °C, and the reaction was monitored by means of $^{31}P\{^1H\}$ NMR spectroscopy. After 8 h the conversions were complete and the reaction products showed a resonance in the $^{31}P\{^1H\}$ NMR at δ (ppm) 191.3 (R = ^{t}Bu, **5**) and at δ (ppm) 231.1 (R = $SiMe_3$, **6**), respectively. From the chemical shift difference (coordination compound ligand) of $\Delta\delta$ = 18.2 ppm and $\Delta\delta$ = 14.7 ppm, however, it is not conclusive whether the triazaphosphole moiety coordinates via the phosphorus lone pair or via the nitrogen lone pair to the metal center, since σ-coordinated phosphinines show a similar chemical shift difference upon coordination to a metal center. We therefore attempted a crystallographic characterization, and crystals of both products, suitable for X-ray crystal structure analysis, were obtained either by slow cooling of a saturated solution of **5** in dichloromethane or by slow diffusion of diethyl ether into a solution of **6** in dichloromethane. Compound **5** crystallized in the space group $P2_1/n$, and the molecular structure in the crystal, along with selected bond lengths and angles, is depicted in Figure 6, showing the expected facial geometry of the $[L_2Re(CO)_3Br]$ complex.

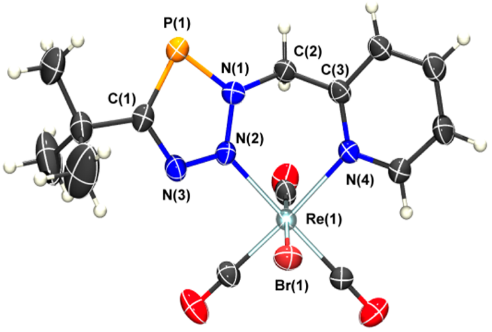


Figure 6. Molecular structure of **5** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): P(1)−C(1), 1.731(7); C(1)−N(3), 1.363(8); N(3)−N(2), 1.302(6); N(2)−N(1), 1.341(7); N(1)−P(1), 1.699(5); N(1)−C(2), 1.481(7); C(2)−C(3), 1.515(8); N(2)−Re(1), 2.163(5); N(4)−Re(1), 2.205(5); Re(1)−Br(1), 2.6258(7); N(1)−P(1)−C(1), 86.2(3); N(2)−Re(1)−N(4), 83.31(18).

The molecular structure of complex **6** (space group $P2_1/c$) is depicted in Figure 7 and shows a facial geometry comparable to that observed for compound **5**.

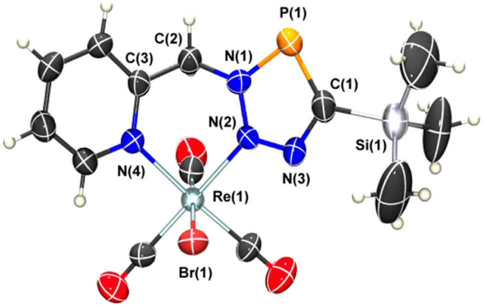


Figure 7. Molecular structure of **6** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): P(1)−C(1), 1.730(8); C(1)−N(3), 1.348(10); N(3)−N(2), 1.306(8); N(2)−N(1), 1.336(7); N(1)−P(1), 1.702(6); N(1)−C(2), 1.481(8); C(2)−C(3), 1.509(9); N(2)−Re(1), 2.163(5); N(4)−Re(1), 2.192(5); Re(1)−Br(1), 2.6248(8); C(1)−Si(1), 1.892(8); N(1)−P(1)−C(1), 86.7(3); N(2)−Re(1)−N(4), 83.7(2).

From the crystallographic characterization it is obvious that both chelating ligands **1** and **2** coordinate to the Re(I) center via the nitrogen atom N(2) of the triazaphosphole moiety, rather than via the phosphorus atom. Interestingly, the coordination of the least nucleophilic nitrogen atom N(2) to a metal center has not been observed for triazaphospholes before and is apparently enforced by the chelating effect.

In order to compare the stereoelectronic properties of the triazaphospholes **1** and **2**, Re(I) complexes containing the chelating triazoles were prepared accordingly. Since a phosphorus probe is absent, reactions of **3** and **4** with equimolar amounts of $[Re(CO)_5Br]$ in dichloromethane at $T = 85$ °C were monitored by means of ^1H NMR spectroscopy and were found to be complete within 24 h. Especially the signal of the $SiMe_3$ group in the ^1H NMR spectrum of ligand **4** and complex **8** turned out to be a useful resonance to monitor the course of the reaction. Crystals of **7** (space group $P1$) and **8** (space group $Pca2_1$) suitable for X-ray diffraction were obtained either by slow cooling of a saturated solution of **7** in hot dichloromethane or by slow diffusion of diethyl ether into a dichloromethane solution of **8**. The molecular structures, along with selected bond lengths and angles, are depicted in Figures 8 and 9, respectively.

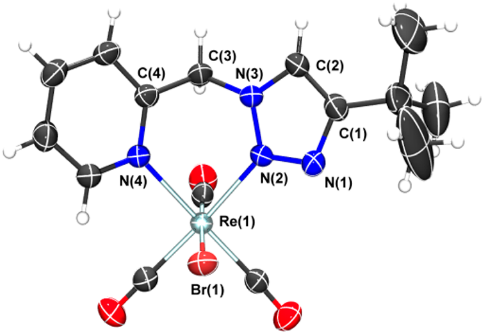


Figure 8. Molecular structure of **7** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(2)−C(1), 1.366(7); C(1)−N(1), 1.352(6); N(1)−N(2): 1.321(5); N(2)−N(3), 1.337(5); N(3)−C(3), 1.460(6); C(3)−C(4), 1.512(7); C(4)−N(4), 1.351(5); N(2)−Re(1), 2.175(3); N(4)−Re(1), 2.218(3); Re(1)−Br(1), 2.6278(6); N(3)−C(2)−C(1), 105.4(4); N(2)−Re(1)−N(4), 82.78(13).

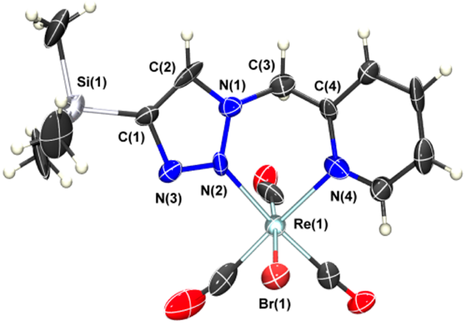
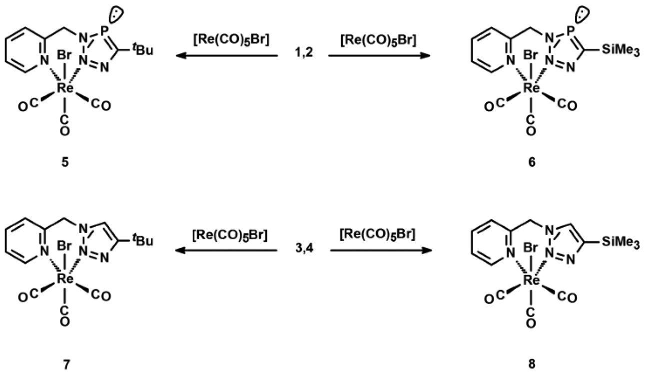


Figure 9. Molecular structure of **8** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(2)−C(1), 1.43(3); C(1)−N(3), 1.42(2); N(3)−N(2), 1.32(2); N(2)−N(1), 1.36(2); N(1)−C(2), 1.34(3); N(1)−C(3), 1.51(3); C(3)−C(4), 1.44(3); C(4)−N(4), 1.37(2); N(2)−Re(1), 2.163(16); N(4)−Re(1), 2.233(18); Re(1)−Br(1), 2.598(3); N(3)−C(2)−C(1), 107.0(17); N(2)−Re(1)−N(4), 82.5(6).

Similar to the case for compounds **5** and **6**, the graphical representations of **7** and **8** reveal the facial geometry of the complexes $[(\mathbf{3})Re(CO)_3Br]$ and $[(\mathbf{4})Re(CO)_3Br]$ with the nitrogen atoms N(2) of the triazole units coordinated to the Re(I) centers. Apparently, exchanging the phosphorus atom in **5** and **6** by an isolectronic C−H group in **7** and **8** has only a marginal effect on the bite angle N(4)−Re(I)−N(2), as values of 83.31 (**5**), 83.67 (**6**), 82.78 (**7**), and 82.48° (**8**) were found. Scheme 2 summarizes the reaction of ligands **1**−**4** with $[Re(CO)_5Br]$, leading to the corresponding Re(I) complexes **5**−**8**, in which coordination exclusively via the least nucleophilic nitrogen atom N^2 occurs.

As mentioned above, the carbonyl complexes provide the possibility to obtain information on the electronic properties of

Scheme 2. Synthesis of Re(I) Complexes 5−8



the ligands. We therefore investigated Re(I) complexes **5**−**8** also by means of infrared spectroscopy (Table 1). As already anticipated from the cyclic voltammetry measurements, a clear difference between the triazaphosphole-based complexes **5** and **6** and the triazole-based coordination compounds **7** and **8** can indeed be noticed. The $\tilde{\nu}$(CO) stretching frequencies of **7** and **8** are slightly shifted to higher wavenumbers in comparison to their phosphorus-containing analogues **5** and **6**. This indicates that the presence of a phosphorus atom leads to a ligand system, which is more electron rich. An electron-withdrawing influence of the $SiMe_3$ group on the $\tilde{\nu}$(CO) stretching frequencies, as observed by the electrochemical investigations, can, however, not be found in the IR spectra.

Table 1. Infrared Data for Coordination Compounds 5−8

compound	$\tilde{\nu}_1$(CO) (cm^{-1})	$\tilde{\nu}_2$(CO) (cm^{-1})	$\tilde{\nu}_1$(CO) (cm^{-1})
[(**1**)Re(CO_3)Br] (**5**)	2023	1919	1885
[(**2**)Re(CO_3)Br] (**6**)	2021	n.d.	1879
[(**3**)Re(CO_3)Br] (**7**)	2032	1952	1891
[(**4**)Re(CO_3)Br] (**8**)	2026	1949	1898

In addition, coordination compounds **5**−**8** were further investigated by means of cyclic voltammetry (CH_2Cl_2, THF, 0.1 M Bu_4NPF_6, ν = 100 mV s^{-1}) using ferrocene (Fc) as the internal standard (Figure 10). While the phosphorus-containing complexes **5** and **6** undergo in DCM irreversible oxidation processes (E_p^{ox} = +1.022 V (**5**), E_p^{ox} = +0.952 V (**6**) vs Fc/Fc$^+$), the triazole-based compounds **7** and **8** show quasi-reversible oxidation waves (E^{ox} = +0.909 V (**7**), E^{ox} = +0.917 V (**8**) vs Fc/Fc$^+$). In the electrochemical reduction of **5**−**8** (THF), all complexes show irreversible reduction processes (E_p^{red} = −2.56 V (**5**), E_p^{red} = −2.56 V (**7**), E_p^{red} = −2.135 V (**8**), E_p^{red} = −2.357 V (**6**) vs Fc/Fc$^+$). Similar to the observations made for the free ligands, the Re(I) complexes containing the triazaphophole ligand are slightly more difficult to reduce than the triazole-based systems, while the coordination compounds containing a ^{t}Bu group at the 5-position of the heterocycle are more difficult to reduce in comparison to those containing a $SiMe_3$ group, due to the electron-withdrawing character of that particular substituent.

In comparison to the only nitrogen-containing triazoles, both the IR spectroscopic and cyclic voltammetric measurements nicely demonstrate that there is indeed the postulated influence of the phosphorus atom and the additional substituent at the P═C moiety on the electronic properties of the novel heterocycles and the corresponding transition-metal complexes.

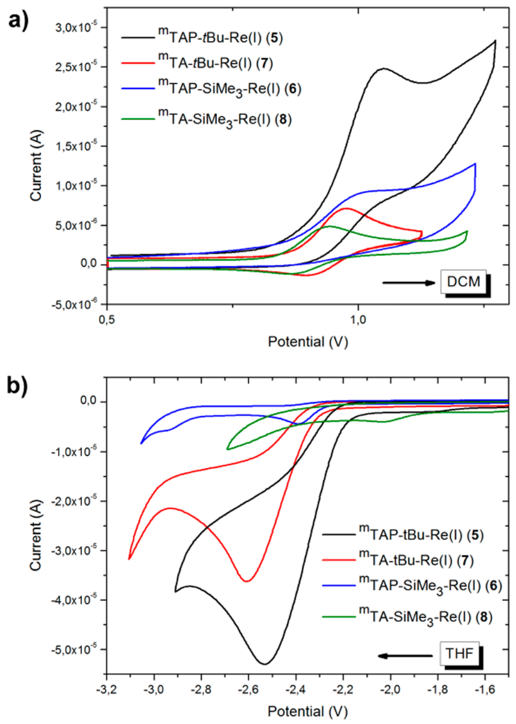


Figure 10. Electrochemical investigation of compounds **5**−**8**: (a) oxidation (CH_2Cl_2); (b) reduction (THF).

■ CONCLUSION

Using the modular synthetic procedure for the preparation of 3*H*-1,2,3,4-triazaphosphole derivatives, we have demonstrated access to a new class of chelating P,N hybrid ligands based on low-coordinate phosphorus compounds. The pyridyl-functionalized triazaphospholes bearing either ^{t}Bu or $SiMe_3$ substituents at the 5-position of the N_3PC heterocycle could easily prepared by a noncatalyzed "click" reaction, starting from 2-(pyridylmethyl)azide and the corresponding phosphaalkyne. These compounds were compared in detail with the analogous triazole-based chelates. Calculations at the DFT level have been performed in order to investigate the electronic structure and donor−acceptor properties of such low-coordinate phosphorus heterocycles. Cyclic voltammetry measurements on the triazaphospholes have been carried out, and the results were compared with those for the analogous triazole-based systems, demonstrating a significant influence of the phosphorus atom as well as the different substituents on the electronic properties of the heterocycles. The chelating triazaphospholes form Re(I) complexes of the type [(N$^{\wedge m}$N)Re$(CO)_3$Br] by coordination of the nitrogen atom N^2 to the metal center rather than via the phosphorus atom, as verified crystallographically. It should be mentioned here that the extra phosphorus atom now provides the possibility to prepare heterobimetallic complexes by additional coordination of the phosphorus atom to a second metal fragment. Moreover, the modular "click" reaction of azides with phosphaalkynes can be used to prepare also fully conjugated chelating ligands. Taking their special stereoelectronic properties into account, the corresponding Re(I) complexes could thus find application as novel and alternative bipyridine-based systems, which have been used as photocatalysts for the reduction of CO_2 or as triplet emitters in OLEDs. Experiments to investigate such coordination compounds in more detail are currently being carried out in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving full experimental details for compounds **1**−**8** and CIF files giving crystallographic data for compounds **5**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*C.N.: fax, (+) 49 (0)30 838 45004; e-mail, c.mueller@fu-berlin.de; web, www.bcp.fu-berlin.de/ak-mueller.

Notes

The authors declare no competing financial interest.

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