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Tuning the electronic effects of aromatic phosphorus heterocycles: An unprecedented phosphinine with significant P(π)-donor properties

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A hitherto unprecedented electronic situation has been observed for a substituted, pyridyl-functionalized phosphinine. In contrast to previous studies, this compound shows considerable π-donor properties as the result of the rather strong +M effect of the CH_3S-substituent, changing the electronic properties of this low-coordinate and aromatic phosphorus heterocycle substantially.

Since the first successful preparation of 2,4,6-triphenylphosphinine (**A**, Figure 1) by Märkl in 1966, this low-coordinate phosphorus compound has been regarded as an aromatic heterocycle with significantly different electronic properties compared to its nitrogen counterpart (pyridine), as well as classical trivalent phosphorus(III) species.[1]

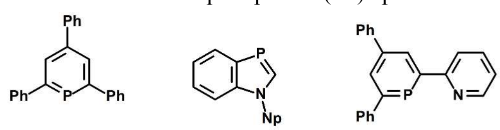

A **B** **3a**

Fig. 1 Low-coordinated $\lambda^3\sigma^2$-phosphorus compounds.

Both the reluctance of phosphorus to undergo 3*s*-3*p* hybridization and the differences in electronegativities of N (3.1), P (2.1) and C (2.5) lead to a substantial decrease in lone-pair basicity in C_5H_5P (63.8% lone-pair *s*-character) compared to C_5H_5N (29.1% lone-pair *s*-character). This special situation causes an inversion of the π-and n-orbitals sequencies between phosphinine and pyridine (Figure 2).[2]

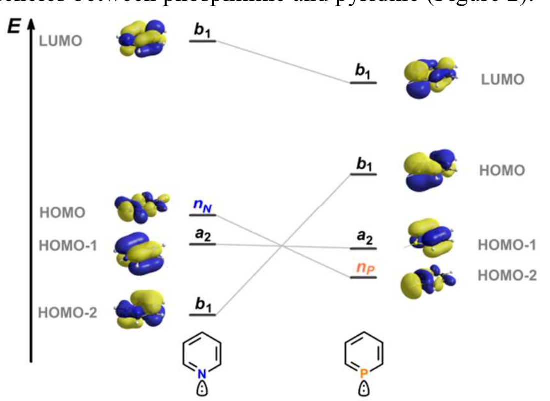
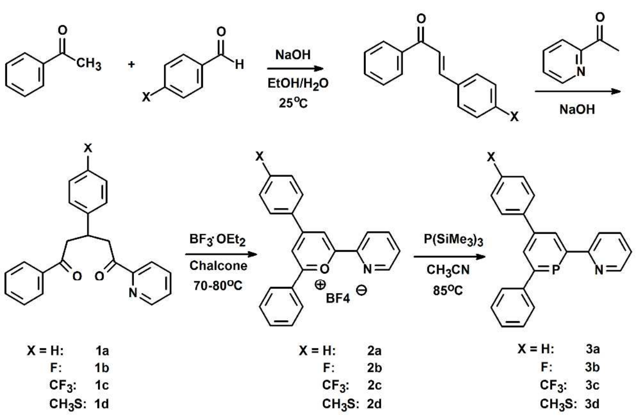


Fig. 2 Frontier orbitals of pyridine (left) and phosphinine (right).

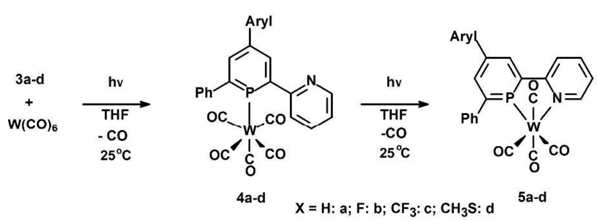
When coordinated to a metal center through the P-atom, phosphinines have been described to act as weak σ-donor (energetically low-lying HOMO-2), but rather strong π-acceptor ligands (energetically low-lying LUMO), which can stabilize efficiently metal centers in low oxidation states.[3] In contrast, the π-excess aromatic $\lambda^3\sigma^2$-benzazaphospholes (**B**, Figure 1), investigated by Heinicke *et al.*, show considerable P(π)-donor properties due to a $\bar{N}$-C=P $\leftrightarrow$ N^+=C-P^- conjugation.[4] As a matter of fact, IR-stretching frequencies of transition metal carbonyl complexes of phosphinines indicate that these aromatic heterocycles act indeed as electron withdrawing ligands with properties similar to phosphites. Interestingly, their π-accepting behaviour has led to the development of very active Rh-catalysts for the hydroformylation of (internal) alkenes.[5] It has further been suggested that the HOMO and HOMO-1 π-orbitals can participate in η^6-coordination towards a transition metal center via the aromatic ring, which accounts for the range of coordination modes observed in various transition metal complexes based on phosphinines.[6]

With respect to potential applications, it has long been discussed whether not only the steric but also the electronic properties of phosphinines can be modified successively. From the MO diagram shown in Figure 2 it is, for example, not obvious why potentially π-donor properties of σ-coordinated phosphinines have neither been considered, nor discussed in literature. Especially as the HOMO is rather high in energy, this situation should have a significant effect on the nature of the metal-phosphorus bond. On the other hand, a systematic investigation on the influence of substituents on the electronic properties of phosphinines has so far remained elusive, mainly due to synthetic reasons. During the course of our investigations on chelating phosphinines, we recently reported on the preparation and coordination chemistry of 2-(2'-pyridyl)-4,6-diphenylphosphinine, which was obtained via the classical pyrylium-salt route (**3a**, Scheme 1).[7] This P,N-hybrid ligand enforced σ-coordination to a metal center and is therefore an ideal bidentate ligand to probe influences of substituents on the electronic properties of the aromatic phosphorus heterocycle, because π-coordination can be exluded. We anticipated that the modular synthetic route towards **3a** would offer the possibility to introduce defined substituents into the phenyl group in 4-position of the heterocyclic framework. This would allow for the first time a systematic modulation of the electronic properties of **3a** not only via +/-I-effects of the substituents, but also through the participation of the P=C double bond in conjugative interactions via +/-M-effects. Starting from *p*-substituted benzaldehydes, the corresponding diketones **1a-d** were synthesized by condensation reaction of the substituted chalcones with acetylpyridine. Subsequently, the pyrylium salts **2a-d**, bearing either a H, F, CF_3, or CH_3S-group could be obtained as yellow-red solids in good yields. We were able to convert all pyrylium-salts into the corresponding phosphinines **3a-d** by reaction with $P(SiMe_3)_3$ in CH_3CN (Scheme 1), although the isolated yields of the products were rather low.[8]



Scheme 1 Synthetic route towards substituted, pyridyl-functionalized phosphinines.

Compounds **3a-d** show the characteristic downfield-shift of the phosphorus-signal in the $^{31}P\{^1H\}$ NMR spectrum at δ(ppm) = 186.7 (**3a**), 186.6 (**3b**), 192.2 (**3c**) and 185.8 (**3d**). In order to probe the electronic properties of **3a-d** we decided to prepare the corresponding $[W(\kappa\text{-}P,\kappa\text{-}N)(CO)_4]$ complexes and to analyze them by means of IR-spectroscopy. According to ^{31}P NMR spectroscopy, coordination compounds **5a-d** were obtained quantitatively by reaction of equimolar amounts of the ligand and $W(CO)_6$ in THF and under irradiation with UV-light (Scheme 2).



Scheme 2 Synthesis of phosphinine-based tungsten(0) complexes.

The reactions could be monitored by means of $^{31}P\{^1H\}$ NMR spectroscopy and the course of the reaction is depicted for the fluorine-substituted P,N-ligand **3b** in Figure 3.

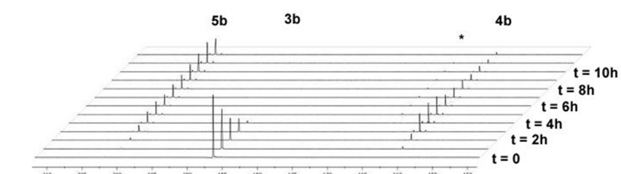


Fig. 3 Time-dependent $^{31}P\{^1H\}$ spectra for the conversion of phosphinine **3b** with $W(CO)_6$ towards **5b**.*Unidentified species.

Interestingly, an intermediate with W-satellites ($^1J_{P\text{-}W}$ = 275 Hz) is observed at δ(ppm) = 160.8 upon consumption of the ligand, while the final complex **5b** has been formed almost quantitatively after 10h (δ(ppm) = 201.0, $^1J_{P\text{-}W}$ = 278 Hz). We assume, that the observed intermediate is the mono-coordinated pentacarbonyl-species $[W(\kappa\text{-}P,N)(CO)_5]$ **4b**, depicted in Scheme 2. A similar transient species has been observed by Mathey *et al*. upon reaction of NIPHOS with *in situ* generated $[W(CO)_5THF]$.[9,10]

All complexes could be isolated as red solids after recrystallization and were analyzed by means of NMR spectroscopic techniques. Red crystals of the fluorine-substitued compound **5b** suitable for X-ray diffraction where obtained from a hot THF solution. The compound crystallizes in the orthorhombic space group $Pna2_1$ and the molecular structure is depicted in Figure 4 along with selected bond lengths and angles. The molecular structure of **5b** in the crystal shows a distorted octahedral coordination geometry around the W-center with the P,N-hybrid ligand acting as a bidentate chelate. As observed before in related transition metal complexes of the unsubstituted P,N-ligand **3a**, the metal center is not located in the ideal axis of the phosphorus lone-pair and clearly shifted towards the nitrogen atom.

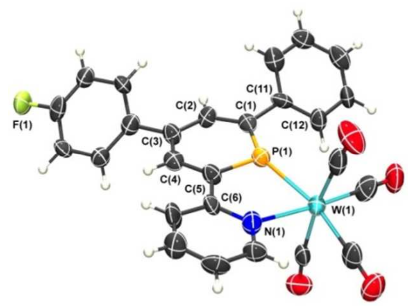


Fig. 4 Molecular structure of **5b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): W(1)-P(1): 2.464(4); W(1)-N(1): 2.31(2); P(1)-C(1): 1.77(2); P(1)-C(5): 1.72(2); C(5)-C(6): 1.49(2); C(1)-P(1)-C(5): 104.1(8).

Coordination compounds **5a-d** were further investigated by means of IR-spectroscopy. In agreement with related bypridine-$W(CO)_4$ compounds, all complexes show the characteristic wavenumbers $\tilde{\nu}_{(CO)}$ centered at around 1900 cm^{-1}. For the fluorine-substituted derivative **5b** we noticed only a marginal shift to higher wavenumbers compared to the reference compound **5a** (R = H). We attribute this minor increase in the π-acceptor capacity of the phosphinine **3b** to a +M effect of the fluorine atom, which counterbalances the –I effect of this electron-withdrawing substituent. Indeed, the IR-data of compound **5c**, which bears a $–CF_3$ as a pure –I substituent in the *para*-position proofed the higher π-accepting properties of the ligand **3c**. For the presence of an electron-donating group in the same position of the heterocycle, one would expect a shift to lower wavenumbers due to an increased electron density in the antibonding π*(C-O) orbitals. Much to our surprise, however, we clearly observed a significant opposite effect for coordination compound **5d**, which contains a CH_3S-substituent in the *para*-position. As a matter of fact, we detected a considerable shift of the IR bands to higher wavenumbers, rather than to lower ones. In order to explain this unusual observation we carried out DFT-calculations at the B3LYP/6-311+G(d,p) level on the pridyl-functionalized phosphinines **3a-d** and compared the relative energies of the frontier orbitals. The results are depicted in Figure 5. For comparison, we included the H_3C-substituted coordination compound in the calculations, although the corresponding P,N-ligand could not be synthesized.[8]

Table 1. IR-wavenumbers $\tilde{\nu}_{(CO)}$ of **5a-d** [in cm^{-1}]

	5a (-H)	**5b** (-F)	**5c** (-CF_3)	**5d** (-SCH_3)
$\tilde{\nu}_1$	2008	2012	2014	2014
$\tilde{\nu}_2$	1893	1893	1920	1971
$\tilde{\nu}_3$	1870	1877	n.d.	1889
$\tilde{\nu}_4$	1836	1840	1857	1858

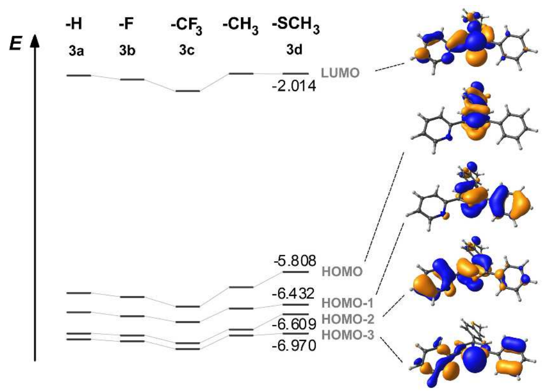


Figure 5. Frontier orbitals of **3a-d** and the CH_3-derivative.

Figure 5 (right side) shows the shape of the frontier orbitals of the CH_3S-substituted phosphinine **3d**. Qualitatively, both the sequence and the shape of the π- and n-orbitals resemble the ones depicted in Figure 2 for the parent compound C_5H_5P with the exception that the HOMO-1 in C_5H_5P is now represented by the HOMO-1 and HOMO-2 in **3d**. This is also the case for phosphinines **3a-c**. By introducing a fluorine substituent (**3b**), the frontier orbitals are slightly stabilized. This is in line with our chemical intuition, that the electron withdrawing fluorine substituent should lower the energy of the LUMO which would consequently lead to stronger π-accepting properties as observed also in the IR stretching frequencies in **5b**. This effect, however, seems to be only marginal and might be attributed to the +M effect of the fluorine substituent. Remarkably, by introducing a CH_3- or CH_3S-substituent (**3d**), the frontier orbitals are destabilized compared to the reference compound **3a**, while especially the HOMO is now much higher in energy than the HOMO in **3a**. We believe that the rather strong +M effect of especially the CH_3S-group increases the π-donor properties of **3d** by conjugative interactions through the HOMO. This situation leads consequently to an energetically high-lying HOMO and at the same time to stronger π-donor properties. However, this does not clarify why the IR-stretching frequencies in **5d** are shifted to higher wavenumbers compared to **5a**. We anticipate that the particular electronic properties of phosphinines might deliver a plausible explanation: In contrast to common π-donor ligands, such as halides, S^{2-} or SCN^- (see spectrochemical series), the LUMO (π-accepting properties) and the HOMO (π-donor properties) in **3d** have particularly large coefficients at the phosphorus donor-atom, which are similar in shape and which point into the same direction (Figure 5). These molecular orbitals would therefore interact with the same filled metal-centered *d*-orbital in an octahedral complex, leading to a repulsion and a net weakening of the P-M bond and, consequently, to a shift of the IR stretching modes to higher wavenumbers, i.e. close to uncomplexed $W(CO)_6$ ($\tilde{\nu}$ = 1998 cm^{-1}).

We have demonstrated, that the electronic properties of 2,4,6-triarylphosphinine derivatives can be modulated systematically and rather efficiently by introducing substituents into specific positions of the heterocyclic framework. Furthermore, we found evidence that the HOMO and HOMO-1 of π-symmetry do play a significant role for the properties of metal complexes containing σ-coordinated phosphinine ligands, which has so far been neglected for this class of compounds. This particular electronic situation is caused by the special shape and orientation of the LUMO and the HOMO of the phosphinine ligand and is unique in comparison with other π-donors.

Notes and references

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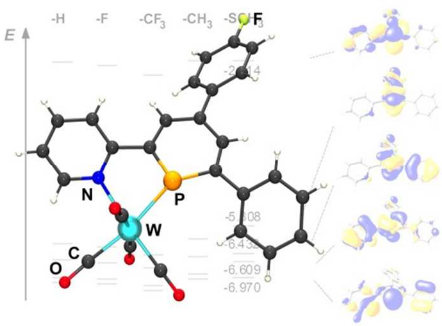

Substituent effects in phosphinine chemistry has been studied systematically and revealed for the first time considerable π-donor properties of these aromatic phosphorus heterocycles.