2-(2′-Pyridyl)-4,6-diphenylphosphinine *versus* 2-(2′-pyridyl)-4,6-diphenylpyridine: an evaluation of their coordination chemistry towards Rh(I)†‡

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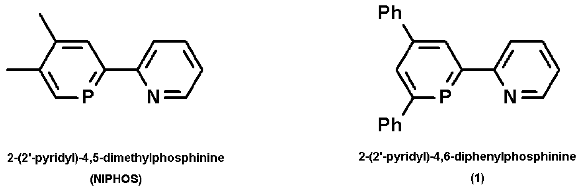
The coordination chemistry of the bidentate P,N hybrid ligand 2-(2′-pyridyl)-4,6-diphenylphosphinine towards Rh(I) has been investigated and compared to the structurally analogous 2,2′-bipyridine derivative. Considerable differences in the molecular structures of the mononuclear $[\mathrm{Rh(cod)L_2}]\mathrm{BF_4}$ complexes were observed and attributed to the different steric and electronic properties of functionalized phosphinines compared to pyridines.

2,2′-Bipyridine (bpy) and its derivatives are well studied nitrogen ligands and their rich coordination chemistry has often been exploited for the development of molecular devices, homogeneous catalytic systems or modern materials with interesting photophysical properties.[1] The replacement of a pyridine unit by a π-accepting phosphinine[2,3] entity leads to 2-(2′-pyridyl)phosphinine, a semi equivalent of bpy containing a low-coordinated "soft" phosphorus and a "hard" nitrogen heteroatom. Such chelates are intriguing bidentate hybrid ligands, which have first been described by Mathey and co-workers in 1982 with the synthesis of 2-(2′-pyridyl)-4,5-dimethylphosphinine (NIPHOS, Fig. 1).[4,5]

However, only a few studies were devoted so far to its coordination chemistry as this particular ligand requires a multistep synthesis and is, at the same time, difficult to handle due to its high sensitivity towards nucleophilic attack at the phosphorus atom and facile protonation at the nitrogen center.[6] The few examples reported in the literature are complexes of the type $[\mathrm{M(NIPHOS)(CO)_4}]$ (M = Cr, Mo, W),[7] the highly water-sensitive Pd(II) and Pt(II) complexes $[\mathrm{MCl(L)(NIPHOS)}]$-$[\mathrm{MCl_3(L)}]$ (L = tertiary phosphine),[8] as well as Rh(I) and Ir(I) dimers of the type $[\mathrm{Ir_2(cod)_2(NIPHOS)_2}][\mathrm{X}]_2$ and $[\mathrm{Rh_2(nbd)_2(NIPHOS)_2}][\mathrm{X}]_2$ (X = $\mathrm{SbF_6}$, cod = 1,5-cyclooctadiene, nbd = norbornadiene),[9] in which the phosphinine ligand adopts a μ^2-bonding mode. Interestingly, latter studies have also shown that NIPHOS binds stronger to Ir(I) and Rh(I) than bpy.



2-(2′-pyridyl)-4,5-dimethylphosphinine (NIPHOS)

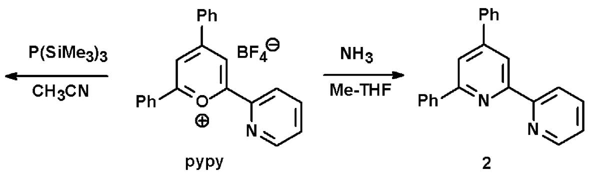
2-(2′-pyridyl)-4,6-diphenylphosphinine (1)

Fig. 1 Phosphorus analogues of 2,2′-bipyridine.

We have recently started to investigate the synthesis and coordination chemistry of functionalized 2,4,6-triaryl-substituted phosphinines, which are generally accessible *via* the modular pyrylium-salt route.[10–12] It turned out that 2-(2′-pyridyl)-4,6-diphenyl-phosphinine **1** (Fig. 1) is readily available from the pyridyl-functionalized pyrylium salt **pypy** and $\mathrm{P(SiMe_3)_3}$ (Scheme 1).[13] Interestingly, this route also allows the preparation of pyridine-derivatives with identical substitution pattern, which consequently makes for the first time the direct structural comparison of these heterocycles feasible. We report here on our primary results concerning the detailed investigation of the P,N hybrid ligand **1** and describe its coordination chemistry towards Rh(I). The results are compared with the structural N,N analogue 2-(2′-pyridyl)-4,6-diphenylpyridine **2**.

Since no theoretical data on phosphorus containing semi-equivalents of 2,2′-bipyridine have been reported in the literature so far, we first evaluated the electronic properties of the parent compound 2-(2′-pyridyl)phosphinine by means of DFT calculations and a selection of relevant frontier orbitals is illustrated in Fig. 2.[14,15]

For comparison reasons the corresponding frontier orbitals of 2,2′-bipyridine are depicted in Fig. 3.[14,15] As evident from the distribution and size of coefficients, the LUMO enables the



Scheme 1 Pyrylium salt route towards structurally equivalent phosphinines and pyridines.

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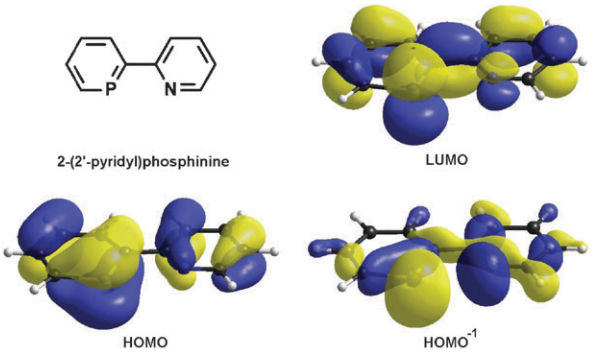


Fig. 2 Selected frontier orbitals of 2-(2′-pyridyl)phosphinine, assuming a planar geometry of the ligand.

phosphinine-moiety to act as a strong π-acceptor upon coordination of the phosphorus atom to a metal center. In contrast, the most important coefficients of the pyridine moiety are localized on the carbocyclic part, demonstrating the weaker π-acceptor properties of this subunit. This is also apparent from the representation of the LUMO of 2,2′-bipyridine, shown in Fig. 3. Judging from the sign of the coefficients, the electronic population of the LUMO *via* π-back bonding from an electron rich metal center should result in a shorter intracyclic C–C, and an elongated N–C (bridge) and P–C_α distance in 2-(2′-pyridyl)phosphinine.[16]

The HOMO of 2-(2′-pyridyl)phosphinine contributes to π-donation from the phosphorus atom towards a metal-centred d-orbital, while the HOMO^{-1} represents the lone-pairs at the heteroatoms for participation in σ-bonding with a metal center. The pronounced spherical character and larger coefficient of the phosphorus lone-pair compared to nitrogen reflects its less-directional and more diffuse nature. In 2,2′-bipyridine, the order of these frontier orbitals is reversed, indicating the pronounced σ-donor properties of this ligand.

The structural N,N analogue of the P,N ligand **1**, 2-(2′-pyridyl)-4,6-diphenylpyridine **2**, was obtained in high yields from 2-(2′-pyridyl)-4,6-diphenylpyrylium tetrafluoroborate **pypy** and NH_3, according to a modified literature procedure (Scheme 1).[17,18] Reaction of **1** and **2** with one equivalent of $[Rh(cod)_2]BF_4$ leads instantaneously and quantitatively to the corresponding Rh(I) complexes [Rh(cod)(**1**)]BF_4 (**3**) and [Rh(cod)(**2**)]BF_4 (**4**), respectively (Scheme 2). The ^{31}P NMR spectrum of **3** shows a doublet at $\delta = 175.5$ ppm (CD_2Cl_2, $^1J_{(P-Rh)} = 188.6$ Hz) and a chemical shift difference upon coordination of $\Delta\delta = +12$ ppm, which is in the expected region for phosphinine–metal complexes with an η^1-coordination mode of the phosphorus atom. As a matter of fact, the observed NMR data for complex **3** are very similar to the reported values for $[Rh(cod)L_2]BF_4$ containing two mono-dentate 2,3,5,6-tetraphenyl-phosphinine ligands ($\delta = 175$ ppm, d, $^1J_{(P-Rh)} = 166.5$ Hz).[19] We further assume that the additional phenyl-substituents in 4- and 6-position of the heterocyclic framework might also contribute to a kinetic stabilization of the metal complex, as no particular sensitivity could be observed for **3**, in contrast to some reported NIPHOS–metal complexes (*vide supra*).

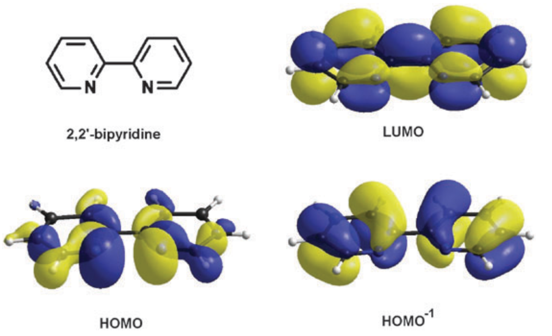
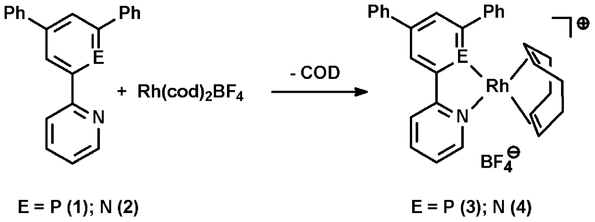


Fig. 3 Selected frontier orbitals of 2,2′-bipyridine, assuming a planar geometry of the ligand.



Scheme 2 Synthesis of [(**1**)Rh(cod)]BF_4 (**3**) and [(**2**)Rh(cod)]BF_4 (**4**).

Orange crystals of **3** suitable for X-ray diffraction were obtained from a 1 : 1 mixture of $[Rh(cod)_2]BF_4$ and **1** in THF/CH_2Cl_2 upon standing. **3** crystallizes in the space group $P\bar{1}$ (no. 2) and the molecular structure is depicted in Fig. 4. In case of **4** orange crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a 1 : 1 reaction mixture of **2** and $[Rh(cod)_2]BF_4$ in THF/CH_2Cl_2. Complex **4** crystallizes in the

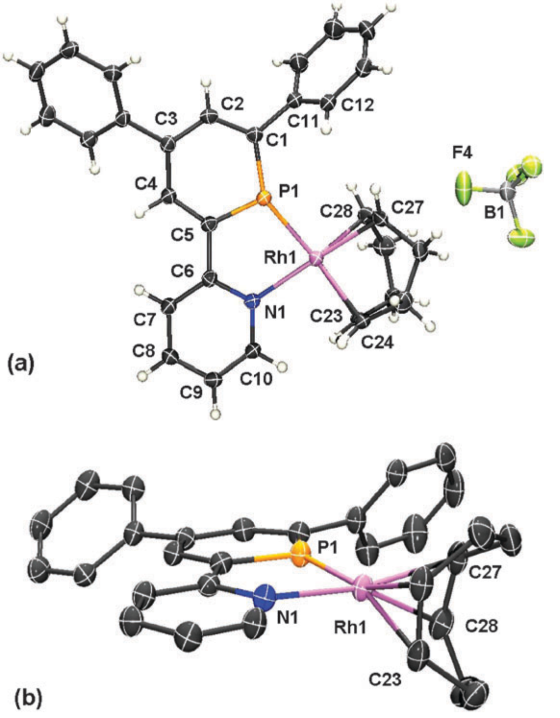


Fig. 4 (a) Molecular structure of **3** in the crystal. Displacement ellipsoids are shown at the 50% probability level. The solvent molecule CH_2Cl_2 is omitted for clarity. (b) Side-view of the cationic part of **3**, hydrogen atoms are not represented.

space group $P2_1/c$ (no. 14) and the molecular structure is shown in Fig. 5 along with selected bond lengths and angles.

The crystallographic representation of **3** in Fig. 4 confirms the observed spectroscopic data and reveals the mononuclear nature of **3** with a slightly distorted square-planar coordination geometry around the metal center. It should be noted here that NIPHOS forms the binuclear complex $[Rh_2(nbd)_2(NIPHOS)_2][SbF_6]_2$ rather than mononuclear species upon reaction with the Rh(I) precursor $[Rh(nbd)(bpy)]SbF_6$.[8] Fig. 4a nicely shows the difference between the pyridine moiety and the aromatic phosphinine ring, which is best described as a distorted hexagon due to the larger phosphorus atom in comparison to nitrogen. The two heterocyclic rings in **3** are essentially coplanar with respect to one another (interplanar angle between the least-square planes = 5.73(13)°), with an intercyclic C–C bond of 1.472(4) Å. The P–C(1) and P–C(5) bond lengths are with 1.729(3) Å and 1.721(3) Å somewhat shorter than in free 2,4,6-triarylphosphinines (1.74–1.76 Å), while the internal C(1)–P–C(5) angle is with 105.25(14)° larger compared to free 2,4,6-triarylphosphinines (101.24°–101.76°).[20] The carbon–carbon bond lengths in the aromatic phosphinine subunit are in the usual range (1.392(4)–1.404(4) Å) observed for both free and complexed phosphinine ligands.

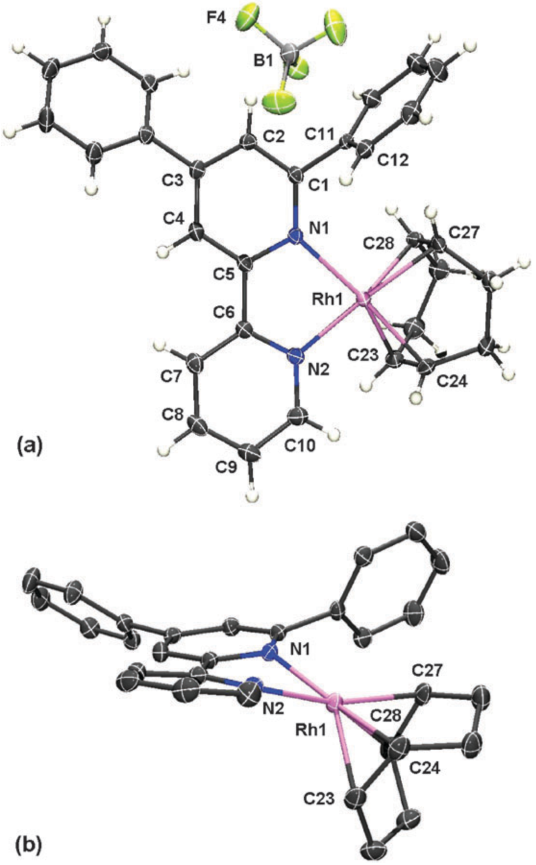


Fig. 5 (a) Molecular structure of **4** in the crystal. Displacement ellipsoids are shown at the 50% probability level. (b) Side-view of the cationic part of **4**, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(1): 1.353(2), N(1)–C(5): 1.368(2), N(2)–C(6): 1.354(2), N(2)–C(10): 1.346(2), N(1)–C(1)–C(11)–C(12): −61.1(2).

The Rh-center in **3** is essentially located in the plane formed by the phosphinine–pyridine backbone (torsion angle N(1)–Rh(1)–P(1)–C(5) = −4.01(12)°). The Rh–P bond length in **3** is with 2.2250(8) Å shorter than in $[Rh(cod)L_2]BF_4$ (L = 2,3,5,6-tetraphenyl-phosphinine) (2.281 and 2.301 Å), which might be a consequence of steric repulsion between the α,α′-diphenyl-substituents of the two monodentate phosphinine ligands in the latter complex. Moreover, the metal center in **3** is not located in the ideal axis of the phosphorus lone-pair and clearly shifted towards the nitrogen atom (C(5)–P(1)–Rh(1) = 107.89(10)°, C(1)–P(1)–Rh(1) = 146.23(10)°). Obviously, this non-directional coordination mode is necessary for a proper complexation of the Rh atom by the chelating P,N ligand and enabled by the more diffuse lone pair of the low-coordinated phosphorus atom compared to the sp^2-hybridized nitrogen atom in pyridines. Consequently, this phenomenon is not observed for the N(1)–Rh interaction (N(1)–Rh(1) = 2.159(2) Å), Rh(1)–N(1)–C(6) = 121.35(18)°, Rh(1)–N(1)–C(10) = 121.23(19)°. A *trans* influence of the P-atom can further be noticed in the longer Rh–cod bonds Rh(1)–C(23) (2.136(3) Å) and Rh(1)–C(24) (2.213(3) Å) compared to the corresponding bonds *trans* to the N-atom (Rh(1)–C(27) = 2.167(3) Å, Rh(1)–C(28) = 2.150(3) Å).[21]

Interestingly, the phenyl-substituent in the α-position of the P-heterocycle is shifted away from the coordination site and additionally rotated out of the plane of the P-heterocycle (torsion angle P(1)–C(1)–C(11)–C(12) = −53.8(4)°). In this way, the P-ligating ability of such 2,4,6-triaryl-substituted phosphinines is apparently not influenced dramatically as observed for $-SiMe_3$ substituted ones, which show a preference for η^6-coordination *via* the aromatic ring, rather than for η^1-coordination *via* the phosphorus lone-pair.[19,22]

In contrast to these observations, the molecular structure of the bipyridine-based complex **4** reveals a strong distortion (Fig. 5). The two pyridine rings are not only twisted (interplanar angle between the least-square planes = 13.67(8)°) but also slightly bent towards one another (Fig. 5b). The intercyclic C(5)–C(6) bond distance is 1.480(2) Å and thus not significantly shorter than in free 2,2′-bipyridine (1.490(3) Å), while the N(1)–C(5) bond is with 1.368(2) Å slightly longer than the corresponding bond in 2,2′-bipyridine (1.346(2) Å).[23] Most remarkably, the Rh-center is shifted significantly below the planes of the two heteroaromatic rings, which is more pronounced for the Rh(1)–N(1) interaction (torsion angle N(2)–Rh(1)–N(1)–C(5) = −22.99(11)°). The Rh(1)–N(1) bond length is slightly longer than the Rh(1)–N(2) bond length (2.1639(14) *vs.* 2.0807(14) Å). This difference is also found for the bonding of the metal center to the diene ligand (Rh(1)–C(27) = 2.1653(17), Rh(1)–C(28) = 2.1714(18) Å, *vs.* Rh(1)–C(23) = 2.1097(17), Rh(1)–C(24) = 2.1433(18) Å). Clearly, this ligand does not behave like a typical 2,2′-bipyridine. The observed differences in the N–Rh and the Rh–cod bond lengths is most likely due to the fact that the additional phenyl-substituent in α-position of the N(1)-pyridine ring of **2** is much closer to the coordination site compared to the situation in the corresponding pyridine–phosphinine ligand **1**. The steric interaction between the α-phenyl group and the cod ligand in **4** might consequently cause the strong distortion around the metal center, which is essentially absent in complex **3** and also in the related parent 2,2′-bipyridine complex [Rh(cod)(bpy)]PF_6.[24] As a matter of fact, the close proximity of the α-phenyl-group in such types of substituted 2,2′-bipyridine ligands can lead to C–H activation under the formation of cyclometalated NNC complexes[25] as observed several times before, and which we do not expect for the pyridine–phosphinine ligand **1**.

Conclusions

In summary, we have prepared and structurally characterized the square-planar Rh(I) complexes of the type [Rh(cod)L_2]BF_4, containing either the chelating P,N-hybrid ligand 2-(2-pyridyl)-4,6-diphenylphosphinine or the structurally analogous 2,2′-bipyridine derivative 2-(2′-pyridyl)-4,6-diphenylpyridine, making for the first time a direct comparison of these heterocycles possible. The electronic properties of the P,N ligand were evaluated by means of DFT calculations and compared to 2,2′-bipyridine. Due to the presence of electronically and sterically rather different phosphorus and nitrogen centers within the same structure, significant differences in the coordination behaviour of the P,N ligand towards Rh(I) were observed, compared to the structurally related N,N ligand. The latter one causes a strong distortion of the corresponding Rh(I) complex, due to steric interactions between the ligand framework and the coordinated Rh(cod) fragment. This repulsion is much less pronounced in the related phosphinine–pyridine ligand, mainly as a result of the larger phosphorus atom.

Experimental section

2 was prepared according to a modified literature-procedure.[17,18] 2-(2′-Pyridyl)-4,6-diphenylpyrylium tetrafluoroborate[13] (1.2 g, 3.0 mmol) was suspended in dry Me–THF (20 mL) and heated to T = 60 °C. NH_3 was bubbled through the reaction mixture for t = 30 min and a yellow-orange suspension was formed. The solid was filtered off and MeOH (20 mL) was added to the filtrate. An off-white solid was formed immediately, which was filtered off, washed with MeOH and dried under vacuum. Yield: 0.8 g (2.6 mmol, 87%). The analytical data of **2** are identical with those reported in the literature.[17]

Orange crystals of **3** suitable for X-ray diffraction were obtained under argon by slow crystallization from a 1 : 1 mixture of [Rh(cod)$_2$]BF_4 (25 mg, 0.0615 mmol) and **1** (20 mg, 0.0615 mmol) in THF/CH_2Cl_2 (2.0 mL) after filtration over Celite. ^{31}P NMR (162 MHz, CD_2Cl_2): δ (ppm) = 175.5 (d, J_{P-Rh} = 188.6 Hz).

Orange crystals of **4** suitable for X-ray diffraction were obtained under argon by slow diffusion of pentane into a 1 : 1 mixture of [Rh(cod)$_2$]BF_4 (26.3 mg, 0.065 mmol) and **2** (20 mg, 0.065 mmol) in THF/CH_2Cl_2 (2.0 mL) after filtration over Celite. ^{1}H NMR (CD_2Cl_2): δ (ppm) = 1.82 (d, b, J_{H-H} = 7.2 Hz, 4H, $(CH_2)_{COD}$), 2.27 (b, 4H, $(CH_2)_{COD}$), 3.79 (b, 4H, $(CH)_{COD}$), 7.63 (m, 6H), 7.79 (m, 2H), 7.88 (s, 1H, cent. pyridine-H_β), 7.93 (m, 4H), 8.26 (t, J_{H-H} = 7.6 Hz, 1H), 8.48 (d, J_{H-H} = 8.2 Hz, 1H), 8.53 (s, 1H, cent. pyridine-$H_\beta{}'$).

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