Phosphorus Analogs of Bipyridines: Their Synthesis and Coordination Chemistry

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The synthesis and coordination chemistry of 2-(2-pyridyl)phosphinines and 2,2′-biphosphinines are reviewed. A noteworthy series of homoleptic complexes of 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (tmbp) with Cr(0), Mo(0), Wo(0) and Ni(0) are described. A [Cu(bpy)(tmbp)]$^+$ cationic polymer has been characterized by X-ray analysis. Ruthenium, manganese and rhenium chelates were also obtained. With $Mn_2(CO)_{10}$, a (tmbp)-$Mn_2(CO)_6$ complex is formed where tmbp acts as an eight electron donor.

In coordination chemistry, 2,2′-bipyridines are among the ligands most frequently used for the stabilization of a given metal in various oxidation states. The prototypical ruthenium(II) complex $[Ru(bpy)_3]^{2+}$ is an example; it shows one reversible oxidation and three reversible reduction waves[1]. Reduction occurs primarily at the ligand which possesses a low-lying π* LUMO. In addition, this complex shows fascinating photochemical and photophysical properties[2]. In its first photoexcited state, one electron is transferred to the bpy ligands; then either oxidative or reductive quenching can occur[3]. As a result of these unique properties, $[Ru(bpy)_3]^{2+}$ has found numerous applications, for example in the photodecomposition of water[4] and in photovoltaic cells[5].

The replacement of a pyridine by a phosphinine nucleus in bipyridines should enhance the π-acceptor properties of these ligands because the phosphinine LUMO is significantly lower in energy than the LUMO for the pyridine ring[6]. Furthermore, a Mulliken charge analysis shows that the heteroatom bears a positive charge in phosphinine (+0.55) and a negative charge in pyridine (−0.67)[7]. Conversely, the σ donor properties are certainly weaker for the phosphorus analogs since the phosphinine lone-pair orbital is only at the third highest occupied level[7]. This qualitative analysis suggests that the phosphorus analogs of bipyridines should be more efficient for the stabilization of low oxidation states and will favor the electronic transfers from the complexed metal to the ligand better than bipyridines.

We started our investigations on the synthesis and coordination chemistry of the phosphorus analogs of bipyridines in 1982[8] based on this reasoning. Today, we are confident that our expectations are being fulfilled. This report summarizes what has been done in this new field.

2-(2-Pyridyl)phosphinines

Synthesis

The first synthesis of pyridylphosphinines is shown in Scheme 1.

The synthesis involves the ring expansion of phospholes

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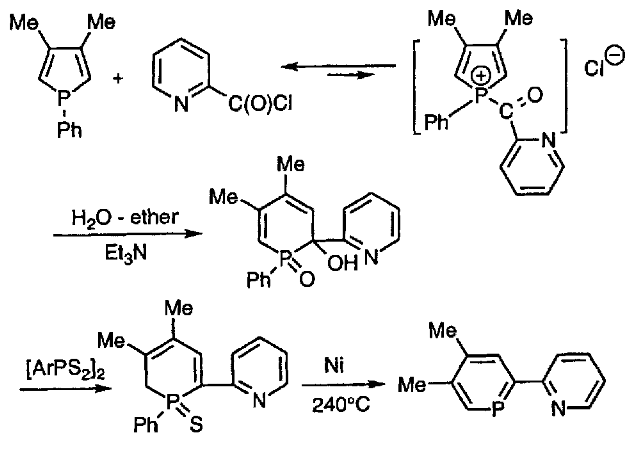
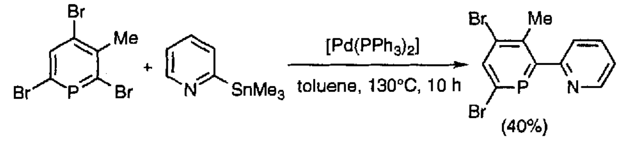
Scheme 1



by nickel and thermal aromatization, is more classical. This synthesis is difficult to perform on a large scale, but it remains the simplest route to pyridylphosphinines.

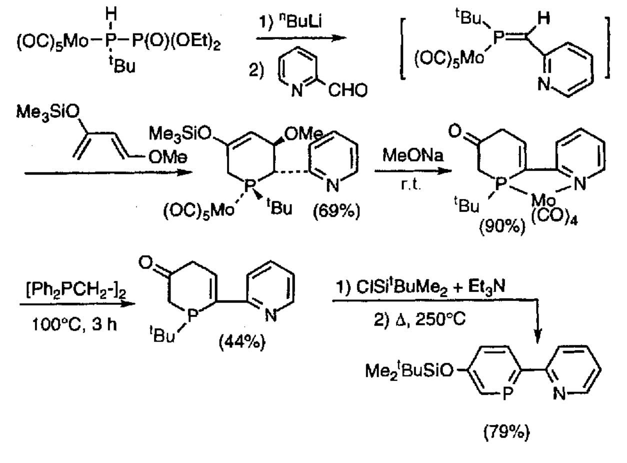
While studying the activation of the C-2−Br bond of 2-bromophosphinines by Pd(0), we found that 2-stannylpyridines can be cross-coupled with these derivatives (Scheme 2)[9]. 2,6-Disubstitution appears to be impossible and the 2-pyridyl-6-bromophosphinine is unstable.

Scheme 2



Very recently we reported that 2-pyridylphosphinines are accessible from 2-pyridinecarboxaldehyde[10]. In the first step, a pyridyl-substituted phosphaalkene is made by a "Phospha-Wittig" reaction. Then the phosphinine ring is created by the reaction between the P=C double bond and a siloxydiene (Scheme 3).

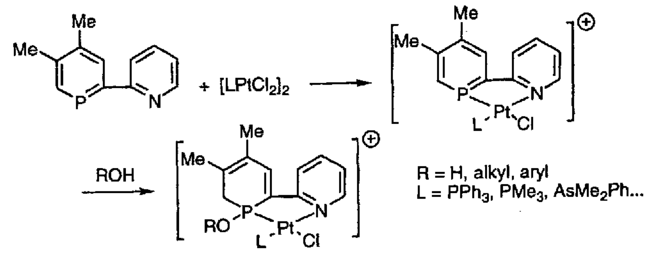
Scheme 3



Coordination Chemistry

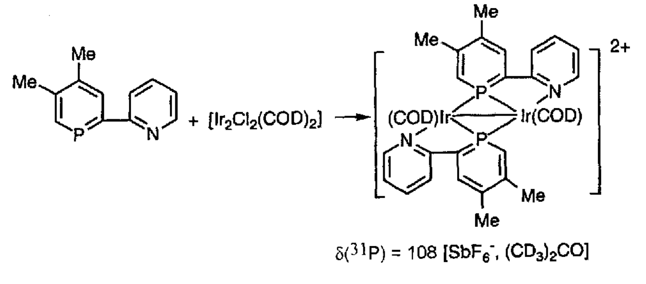
All the reactivity studies were performed with the 4,5-dimethyl derivative, which is prepared as shown in Scheme 1. In preliminary work, it was shown that protonation takes place selectively at the nitrogen atom as expected[11]. Conversely, complexation by zero-valent metals (Cr, Mo, W) initially takes place at the P atom prior to chelate formation. The X-ray analysis of the $Cr(CO)_4$ chelate shows two coplanar rings and no shortening of the C−C bridge. More interesting results were obtained by the group of Venanzi. Complexation of pyridylphosphinine by Pd(II) and Pt(II) leads to an activation of the P=C-6 formal double bond which makes it susceptible to the addition of protic reagents[12]. Dihydrophosphinine complexes are thus obtained (Scheme 4).

Scheme 4



It is clear that the pyridine ring plays a role in this activation since well-defined Pd(II) and Pt(II) complexes of 2-phenyl-4,5-dimethylphosphinine can be prepared[13]. In a related study on iridium(I) complexes, the same group has found an unusual coordination mode of the phosphinine ring where the phosphorus atom bridges two iridium centers (Scheme 5)[14].

Scheme 5



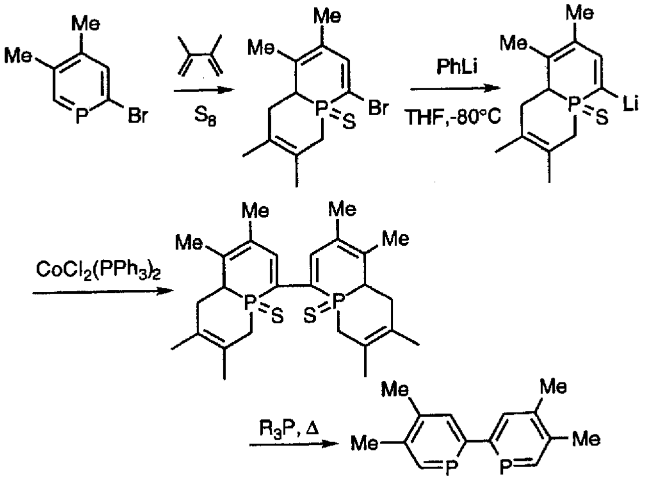
From this brief survey, it appears that pyridylphosphinines are highly reactive molecules whose coordination chemistry is relatively difficult to master.

2,2′-Biphosphinines

Synthesis

Most of the available syntheses of 2,2′-biphosphinines start from the readily available 2-bromophosphinines[15]. Since there is always a potential competition between the reactivities of the C-2−Br and P=C bonds in these species, it is advisable to either protect the P=C bond or to activate the C-2−Br bond. The first synthesis of the 2,2′-biphosphinines belongs to the first category[16]. The P=C bond is protected by a combined sulfurization/[4+2] cycloaddition (Scheme 6).

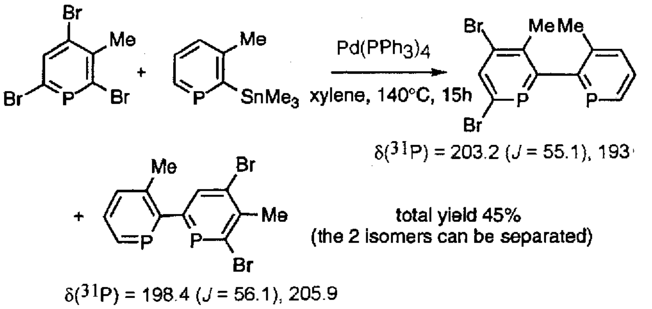
Scheme 6



After a classical C−C coupling, the P=C bonds are unmasked by desulfurization/cycloreversion. The key to the success of this protection-deprotection approach is that the phosphinine ring loses its aromaticity upon sulfurization of phosphorus; this allows the cycloaddition. After desulfurization occurs, the rearomatisation of the ring drives the cycloreversion.

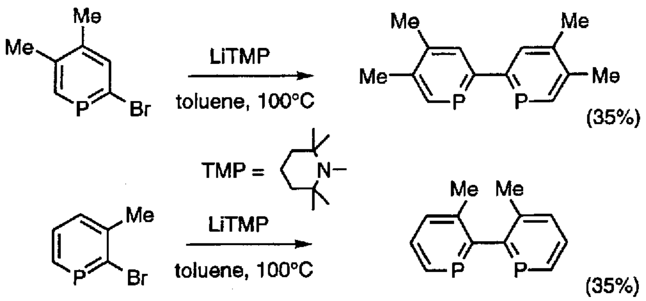
A second method takes advantage of the regioselective activation of the C-2−Br bonds of 2-bromophosphinines by palladium(0). The catalyzed cross-coupling of a 2-bromo- with a 2-stannylphosphinine led to a 2,2′-biphosphinine (Scheme 7)[17].

Scheme 7



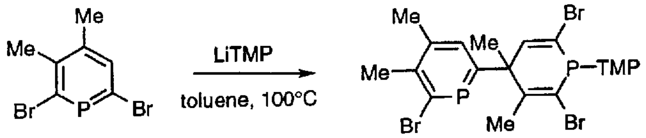
At present, the simplest access to 2,2′-biphosphinines needs neither P=C protection nor C-2−Br activation. A direct reductive coupling of 2-bromophosphinines takes place upon reaction with a bulky lithium amide (Scheme 8)[18]

Scheme 8



In some cases, the reaction yields a C-2−C-4′ derivative (Scheme 9), thus suggesting that the initial step of the mechanism is a nucleophilic attack of LiTMP at the phosphorus atom.

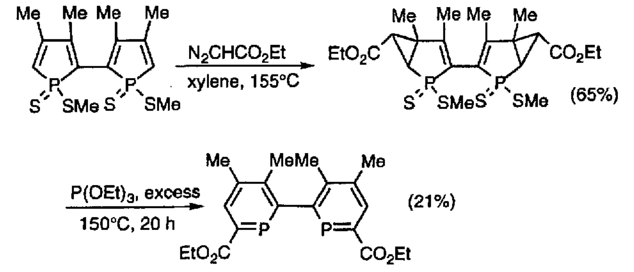
Scheme 9



It is interesting that the X-ray crystal structure analysis of the 3,3′-dimethyl-2,2′-biphosphinine suggests that the methyl groups are able to block the free rotation of the two rings around the C-2−C-2′ bridge, thus allowing atropisomerism.

Finally, a completely different approach relies on the double ring expansion of a 2,2′-biphosphole (Scheme 10)[19].

Scheme 10

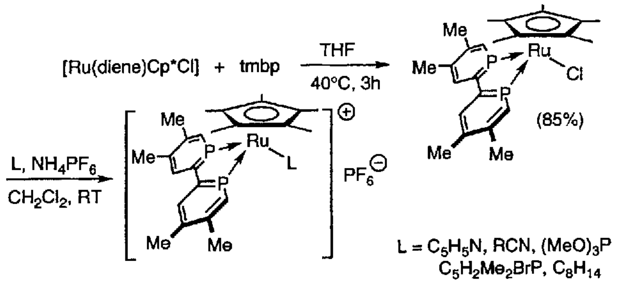


Evidently, the two ethoxycarbonyl substituents migrate unexpectedly from the β to the α carbons, thus forming the only known 6,6′-bifunctional-2,2′-biphosphinine. This product could be an interesting starting point for the building of polyphosphinine macrocycles.

Coordination Chemistry

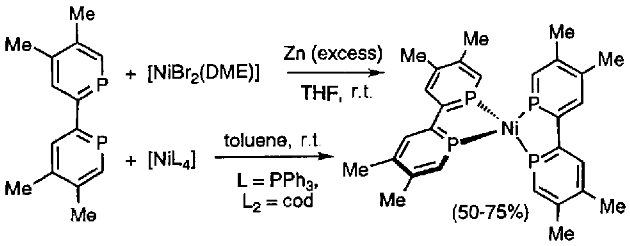
So far all the reactivity studies have been performed with the 4,4′,5,5′-tetramethyl derivative prepared according to either Scheme 6 or 8. The first monoelectronic reduction wave of the free ligand occurs at −1.85 V (vs SCE in DMF) as compared to −2.20 V for the 4,4′-dimethyl-2,2′-bipyridine[20]. Another interesting preliminary finding concerns the almost quantitative displacement of the bipyridine from its $Cr(CO)_4$ chelate by the biphosphinine in refluxing toluene[20]. Apparently, biphosphinine is a far better acceptor and a far better ligand for low-valent metals than bipyridine; this was fully confirmed by subsequent studies. Of course, the opposite is true for high-valent metals, and the study of the $[Ru(bpy)_3]^{2+}$ analogs underlines this point. The direct reaction of biphosphinine (tmbp) with *cis*-$[RuCl_2(dmso)_4]$ in THF at 20 °C leads to the monochelate *cis*-$[RuCl_2(dmso)_2(tmbp)]$. In refluxing chloroform, the reaction gives the bis-chelate *cis*-$[RuCl_2(tmbp)_2]$[21]. It has been imossible to prepare the tris-chelate$[Ru(tmbp)_3]^{2+}$ probably because the central metal becomes excessively electron-deficient. However, the mixed cationic complex $[Ru(bpy)_2(tmbp)]^{2+}$ is accessible from the reaction of tmbp with $[Ru(bpy)_2(Me_2CO)_2]^{2+}$[29]. Obviously, the preparation of stable Ru(II) complexes of biphosphinine requires a proper balance of the electron-withdrawing capacity of tmbp by electron-releasing ligands. This point is nicely illustrated by the extraordinary stability of the biphosphinine-RuCp* complexes (Scheme 11).

Scheme 11



The group of Elschenbroich has shown that the parent phosphinine can give a series of stable homoleptic complexes of Cr(0)[22], Fe(0)[23] and Ni(0)[24]. In line with these observations, biphosphinine is also able to give stable homoleptic complexes with Cr(0), Mo(0), W(0) and Ni(0). The nickel complex is prepared as shown in Scheme 12[25].

Scheme 12



The X-ray crystal structure analysis shows a distorted tetrahedron with a PNiP/PNiP angle of 74.4°. The electrochemistry is particularly interesting (Scheme 13).

Two monoelectronic reduction waves are observed. The 19-electron species is stable. The corresponding bipyridine species is formed at a more negative potential and is unstable. Thus biphosphinine is superior to bipyridine for the stabilization of low-valent highly reduced transition metal complexes. An additional confirmation of this statement can be found in the high stability of the homoleptic derivatives of Cr(0), Mo(0) and W(0), prepared as shown in Scheme 14[29].

Scheme 13

$$Ni(tmbp)_2 + e^- \rightleftharpoons [Ni(tmbp)_2]^{-\bullet} \quad \text{(stable in THF)}$$

$$E_1^0 = -1.64\text{V } (\underline{vs}\text{ SCE})$$

$$[Ni(tmbp)_2]^{-\bullet} + e^- \rightleftharpoons [Ni(tmbp)_2]^{2-} \quad \text{(half-life >15sec.)}$$

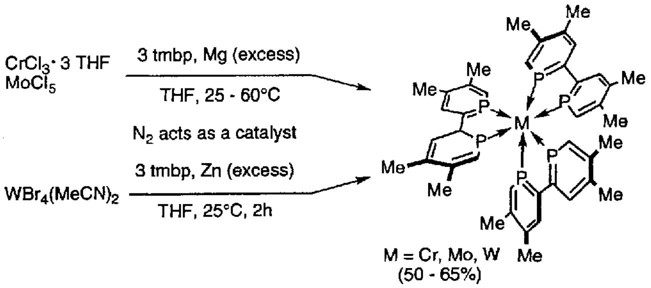
$$E_2^0 = -1.89\text{V } (\underline{vs}\text{ SCE})$$

For comparison:

$$Ni(bpy)_2 + e^- \rightleftharpoons [Ni(bpy)_2]^{-\bullet} \quad \text{(unstable in MeCN)}$$

$$E_1^0 = -1.97\text{V } (\underline{vs}\text{ SCE})$$

Scheme 14



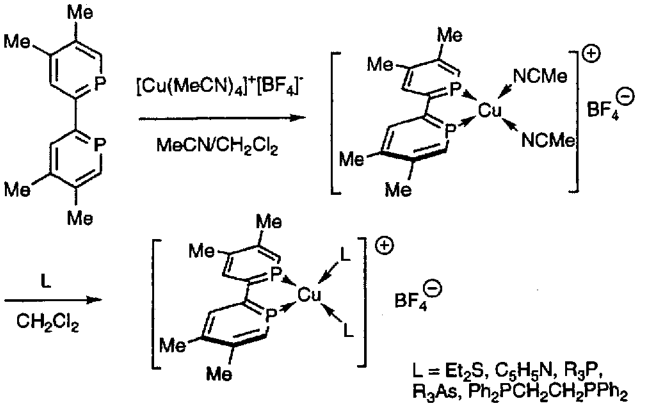
The deep purple W(0) complex displays a strong absorption at 280 nm ($\varepsilon = 4.38 \cdot 10^4$). The geometry is trigonal prismatic. Some delocalization within the WP_2C_2 five-membered heterocyclic units is evident. The P–W bonds are found in the range 2.35–2.36 Å and are shorter than in a phosphinine $P-W(CO)_5$ complex [2.457(2) Å][15b]. The internal P–C bonds are abnormally long at 1.742(3) Å as compared to 1.726(3) Å for the external ones and the C–C bridge at 1.442(7) Å is shorter than in the free cisoid biphosphinine [1.490(8) Å][20]. The photochemistry of this complex is currently under investigation.

The biphosphinines are not only able to act as [2+2] electron chelating ligands but can also act as bridging ligands. This complexing mode was first found during an investigation of the copper(I) complexes. A wide range of Cu(I) chelates can be prepared as shown in Scheme 15.

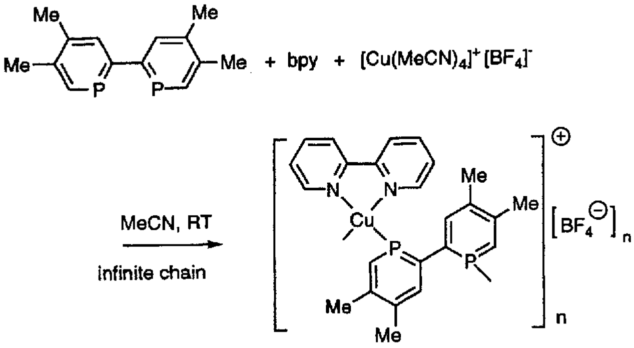
The picture changes completely in the presence of bipyridine. In that case, an infinite chain is obtained (X-ray crystal structure analysis) where each biphosphinine bridges two [Cu(bpy)] units Scheme 16[28].

Still another coordination mode was found during an investigation of reactivity towards manganese and rhenium

Scheme 15

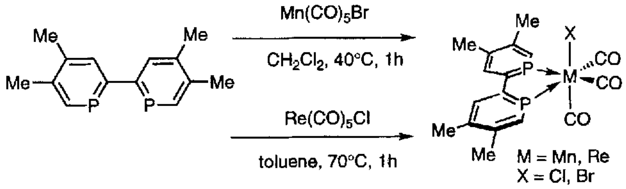


Scheme 16



carbonyl complexes. The reaction with mononuclear carbonyl halides gives the expected chelates Scheme 17[29].

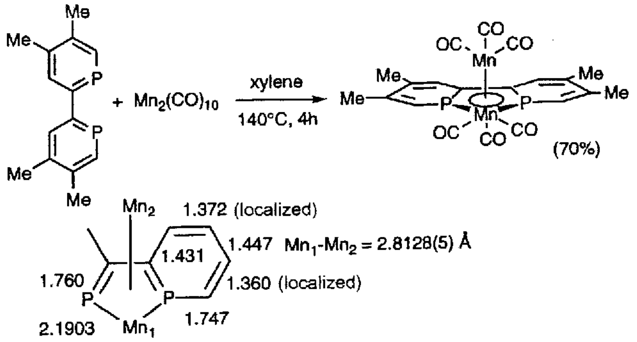
Scheme 17



The reaction pathway is strikingly different with the binuclear manganese carbonyl Scheme 18[26]. In the product, an $Mn_2(CO)_6$ complex, the biphosphinine chelates one of the $Mn(CO)_3$ units to give a planar tricyclic system. The second $Mn(CO)_3$ unit lies above the plane on the top of the five-membered ring. Each phosphinine acts as a four electron donor through its P lone pair and its P=C internal bond. As a consequence of the π-coordination, the aromaticity of the two phosphinine rings is destroyed, and the C–C bonds show the expected alternation. A somewhat related four electron coordination mode has been found in a phosphinine-Os_3 complex[27].

This short survey clearly demonstrates that 2,2′-biphosphinines have a tremendous potential as stabilizers for low oxidation states of transition metals. New redox and photochemical catalysts may be found in this new field of coordination chemistry. A prerequisite for the full development of this area is a better and more versatile access to these ligands and the possibility to graft functional groups onto them.

Scheme 18



Most of the work described in this review was done in the laboratory of the authors. The help of many dedicated coworkers and colleagues, whose names are cited in the references, is acknowledged. The unpublished X-ray crystal structure analyses were performed by our colleague Dr. *Louis Ricard*. Over the years, this program has been supported by CNRS, SNPE and Ecole Polytechnique.

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