A New P-Chiral Aminophosphine Ligand Containing a 2,2′-Coupled Pyrrolidine–Phospholane Ring System. Synthesis and Coordination Properties with Rhodium(I) and Iridium(I) Fragments

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A new approach to the synthesis of chiral P,N-ligands containing a stereogenic phosphorus atom is reported; the synthesis, characterization and coordination properties of (*PR*, 2*R*, 3*R*, 2′*R*, 3′*S*, 4′*S*) 2[2′(3′,4′-di-*tert*-butoxy-1′-methyltetrahydropyrrolyl)]-3-methoxy-1-phenyltetrahydrophosphole (**P*-N-1**), which contains a stereogenic phosphorus in addition to five contiguous stereocentres in the ligand backbone; compound **P*-N-1** represents the first example of a new class of chiral P,N-ligands with the heteroatoms incorporated in two 2,2′-coupled pyrrolidine–phospholane rings.

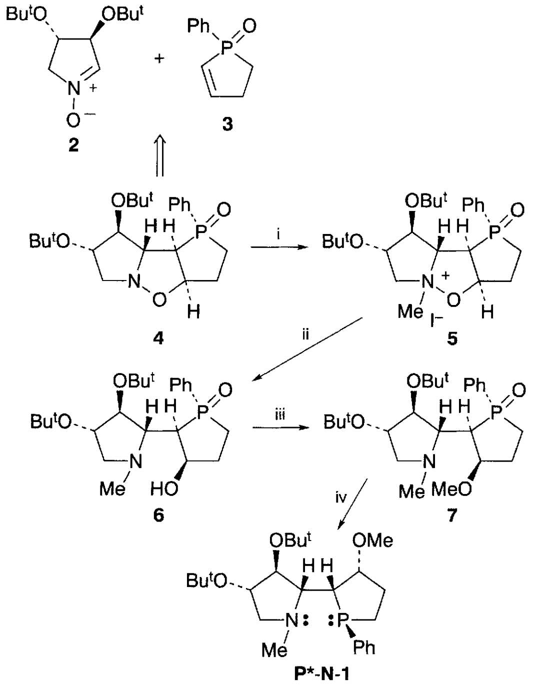
The design and development of chiral aminophosphine ligands is being actively pursued for applications in transition metal asymmetric catalysis.[1] So far, however, very few P,N-ligands are known which contain a stereogenic phosphorus atom in addition to stereocentres in the ligand backbone.[2] This report details our endeavours to design, synthesize and characterize a new class of optically pure P,N-ligands in which the phosphorus donor is a stereocentre and the heteroatoms are incorporated in two 2,2′-connected five-membered rings.

A structural arrangement of this type is expected to favour the formation of metal complexes in which the five-membered chelate ring is forced into a specific conformation, as is often the case for some widely used chiral diphosphine ligands, such as those adopting binaphthyl-like chelate rings.

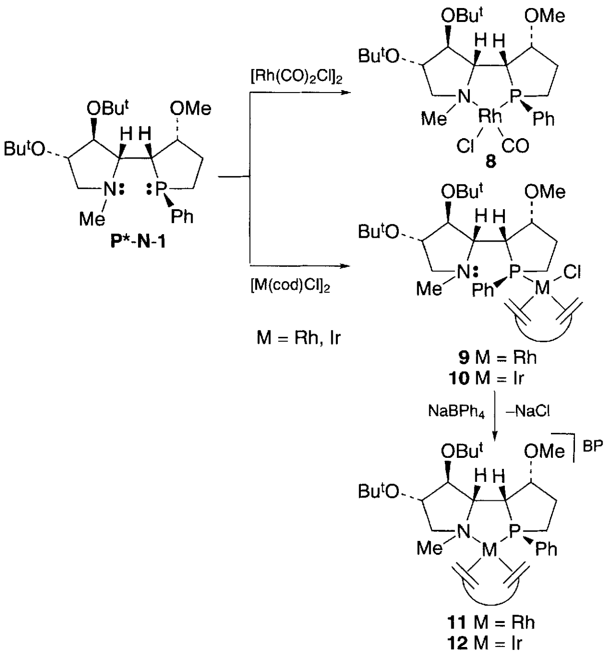
We also report some preliminary results on the bonding capabilities of **P*-N-1** with selected organorhodium(I) and organoiridium(I) fragments, which are widely used in a variety of homogeneous catalytic reactions.

The synthesis of **P*-N-1** was carried out as illustrated in Scheme 1. The isoxazolidine **4**,[3] obtained as the major isomer of the 1,3-dipolar cycloaddition of the nitrone **2**[4] with the phosphole **3**,[5] was treated with MeI in CH_2Cl_2 to give the isoxazolinium salt **5** in quantitative yield. The salt **5** was reduced to the amino alcohol **6** with Zn–$MeCO_2H$,[6] and after treatment with NaH in THF, was alkylated with MeI to afford the protected phosphine oxide **7**. The key step of the synthesis of **P*-N-1** is thus the stereoselective reduction of **7**. This reaction was carried out in refluxing benzene for 12 h with $HSiCl_3$ which, in the presence of NEt_3, is known to bring about the reduction of the P=O functionality with retention of configuration.[2,7]† In this way, the optically pure aminophosphine ligand (*PR*, 2*R*, 3*R*, 2′*R*, 3′*S*, 4′*S*) 2[2′(3′,4′-di-*tert*-butoxy-1′-methyltetrahydropyrrolyl)]-3-methoxy-1-phenyltetrahydrophosphole (**P*-N-1**)‡ was obtained in 55% yield (based on **4**) as a single stereoisomer [$^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −15.22 (s)] with a known absolute configuration at all six stereogenic centres. This methodology is suitable for the synthesis of a class of P,N-ligands bearing different substituents and in either enantiomeric form.

The ligand **P*-N-1** reacts in deaerated CH_2Cl_2 with an equivalent amount of $[Rh(CO)_2Cl]_2$, $[Rh(cod)Cl]_2$ or $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) to give brown to orange microcrystals of the square-planar complexes (**P*-N-1**)Rh(CO)Cl **8**,‡ (η^1-*P*-**P*-N-1**)Rh(cod)Cl **9**,‡ and (η^1-*P*-**P*-N-1**)Ir(cod)Cl **10**,‡ respectively (Scheme 2). The $^{31}P\{^1H\}$ NMR spectra of **8** and **9** show the expected doublet multiplicity with coupling constants within the range for Rh^I square-planar complexes containing phosphorus donor ligands[8] [**8**, δ 76.51 (d,



Scheme 1 *Reagents and conditions*: i, MeI; ii, $MeCO_2H$, Zn; iii, MeI, NaH; iv, $HSiCl_3$



Scheme 2

J_{PRh} 171.2 Hz); **9**, δ 25.82 (d, J_{PRh} 146.2 Hz); **10**, δ 19.26 (s)]. The coordination of the nitrogen donor, demonstrated by the low-field shift of the N–*Me* signal,[9] occurs only for the carbonyl complex **8**, which thus contains a bidentate **P*-N-1** ligand. The carbonyl ligand in **8** lies *trans* to the nitrogen atom as inferred from the $^{13}C\{^1H\}$ NMR spectrum, which shows the CO resonance as a doublet of doublets at δ 189.12 (J_{CRh} 70.9, J_{CP} 19.0 Hz).[10]

Unlike **8**, the two diene complexes **9** and **10** do not exhibit a bonding interaction of the pyrrolidine N atom with the metal as shown by the chemical shifts of both the N–*Me* group[9] (**9**, δ 2.51; **10**, δ 2.75) and the P nucleus (**9**, δ 29.49; **10**, δ 19.26). Thus, a chloride, a bidentate cod ligand and a phosphorus atom complete the square-planar geometry about the metal centre in both **9** and **10**. The coordination of the nitrogen donor atoms can readily be achieved by treatment of **9** and **10** in THF with a chloride scavenger such as $NaBPh_4$ in ethanol. As a result, the complexes [(**P*-N-1**)Rh(cod)]BPh_4 **11**‡ and [(**P*-N-1**)Ir(cod)]BPh_4 **12**‡ are quantitatively obtained, in which the presence of a chelating P,N-ligand ring is shown by the highfield shift of the phosphorus resonance (**11**, δ 58.50; **12**, δ 54.14).[8]

The potential of **P*-N-1** and related ligands bearing different substituents on the pyrrolidine and phospholane rings in asymmetric catalysis is currently under investigation in our laboratories.

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Footnotes

† The retention of configuration at the phosphorus atom has been confirmed by reoxidation of the **P*-N-1** ligand to the starting product **7** by reaction with hydrogen peroxide, which is known to proceed with complete retention of configuration (L. Horner, *Pure Appl. Chem.*, 1964, **9**, 225).

‡ Satisfactory spectroscopic and analytical data were obtained for all compounds.

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