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Synthesis and coordination chemistry of enantiopure *t*-BuMeP(O)H†

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Both enantiomers of the optically pure Secondary Phosphine Oxide (SPO) *t*-BuMeP(O)H (**1**) have been obtained by deboronation of phosphinous acid-borane *t*-BuMeP(O)H·BH_3 (**3**) with HBF_4 followed by hydrolysis of the intermediate adduct *t*-BuMeP(O)H·BF_3 (**1·BF₃**), which has been isolated and crystallographically characterised. Complexes [MCl(COD)(κ*P*-(***R***)-**1**)] (M = Ir, Rh; **4** and **7** respectively) have been detected in solution but could not be isolated while *trans*-[RhCl(CO)(κ*P*-(***S***)-**1**)$_2$] (**9**) has been successfully obtained in good yield. Gold complex [AuCl(κ*P*-(***S***)-**1**)] (**10**) has been prepared and its crystal structure shows the presence of aurophilic interactions. Three new ruthenium complexes ([$RuCl_2$(η^6-*p*-cymene)(κ*P*-(***R***)-**1**)], **12**), ([$RuCl_2(CO)_3$(κ*O*-(***S***)-**1**)], **13**) and *trans*-([$RuCl_2(CO)_2$(κ*P*-(***S***)-**1**)$_2$], **14**) have been synthesised and fully characterised, including the crystal structure of **12**. Four palladium coordination compounds have been prepared: *trans*-[$PdCl_2$(κ*P*-(***S***)-**1**)$_2$] (***trans*-15**), [Pd(μ-Cl)(κ*P*-(***S***)-**1**)$_2$]$_2$ (**16·OH** and **16·BF₂**) and [Pd(μ-OAc)(κ*P*-(***S***)-**1**)$_2$] (**17**) and the crystal structure of complex **16·OH** proves the pseudobidentate coordination of the two molecules of **1**. Three organometallic allylpalladium complexes have been prepared namely [Pd(η^3-$Ph_2C_2H_3$)Cl(κ*P*-(***S***)-**1**)] (**18**) and [Pd(η^3-$Ph_2C_2H_3$)(κ*P*-(***S***)-**1**)$_2$] (**19·OH** and **19·BF₂**). The crystal structure of **19·BF₂** constitutes the first allylpalladium-SPO complex reported to date.

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Introduction

In the field of organometallic chemistry and homogeneous catalysis, P(III)-based ligands can be considered the most important type ligands due to their ability to stabilize transition metal centres.[1,2]

Secondary Phosphine Oxides (SPOs), described more than 50 years ago, present a tautomeric equilibrium between the pentavalent oxide form and the trivalent phosphinous acid form. This equilibrium is completely shifted towards the oxide form except for phosphines with extremely electron-withdrawing groups[3–5] but the presence of a transition metal cation can shift the equilibrium to the trivalent form, forming a metallic complex with the phosphinous acid (Scheme 1).[6]

As shown in Scheme 1, SPOs can act as ambidentate ligands by using the soft phosphorus atom in the phosphinous acid tautomer or the hard oxygen atom in the phosphine oxide tautomer. The coordinative behaviour depends on the affinity of the metal for one site or the other. Examples of *P*-coordinated complexes can be found for Fe, Pd, Ir, Au, Pt, Rh and Ru whereas the *O*-coordination has been described for example with Cr, Mo, W, Ru and Rh.[6–8]

Interestingly, two SPO units attached to a metal centre can form an intramolecular hydrogen bond, acting as a pseudobidentate ligand (Scheme 1) with a negative formal charge. This moiety can be formally considered as formed by combination of a neutral phosphinous acid and an anionic phosphinito unit. This process often requires an external base and leads to a stable six-membered ring. Although the formation of such species is both thermodynamically and kinetically favoured, the required *cis* geometry can not always be achieved and sometimes the *trans* isomers with two monodentate SPOs are obtained instead.[9,10]

SPOs are appealing because they are air-stable in contrast to many phosphines and derivatives, which require inert atmosphere techniques for their manipulation, limiting their practical use. This has spurred interest into the study of the applications of SPOs in catalysis[8,11] and it has been found, for example, that dialkyl SPOs are excellent ligands for cross-coupling reactions.[12] Interestingly, in the case of enantiopure

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