Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2017, **46**, 15865

Half-sandwich complexes of Ir(III), Rh(III) and Ru(II) with the MaxPhos ligand: metal centred chirality and cyclometallation†

Juan Téllez,[a] Albert Gallen, [b] Joaquina Ferrer, *[a] Fernando J. Lahoz, [a] Pilar García-Orduña, [a] Antoni Riera, [c,d] Xavier Verdaguer, [c,d] Daniel Carmona *[a] and Arnald Grabulosa *[b]

Received 7th September 2017,
Accepted 25th October 2017

DOI: 10.1039/c7dt03327c

rsc.li/dalton

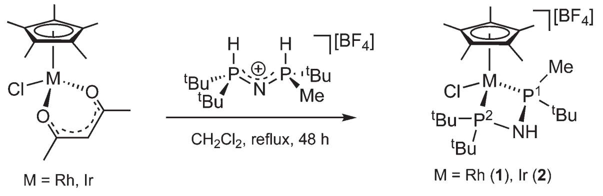
The reaction of the acetylacetonates [(η^5-C_5Me_5)M(acac)Cl] with (S_P)-[HMaxPhos][BF_4] afforded cationic complexes with the formula (S_M,R_P)-[(η^5-C_5Me_5)MCl(MaxPhos)][BF_4] (M = Rh (**1**), Ir (**2**)). The reaction of (S_P)-MaxPhos with [RuCl(μ-Cl)(η^6-*p*-$MeC_6H_4{}^iPr$)]$_2$ and NH_4X afforded (S_{Ru},R_P)-[(η^6-*p*-$MeC_6H_4{}^iPr$)RuCl(MaxPhos)][X] (X = BF_4 (**3**), PF_6 (**3′**)). The complexes have been completely characterized by analytical and spectroscopic means, including the determination of the crystal structures of **1**, **2** and **3′**. Treatment of the iridium complex **2** with $AgBF_4$, at 253 K, resulted in the intramolecular cyclometallation of one of the *tert*-butyl substituents of the MaxPhos diphosphane ligand, affording a mixture of isomers of (S_{Ir},R_{P1},S_{P2} and R_{Ir},R_{P1},R_{P2})-[(η^5-C_5Me_5)Ir(MaxPhos)][BF_4] (**4a** and **4b**). However, rhodium complex **1** and ruthenium complex **3** reacted with $AgBF_4$ forming the expected unsaturated intermediates "(η^n-ring)M(MaxPhos)" which were trapped by MeCN, affording the cationic adducts (S_M,R_P)-[(η^n-ring)M(MaxPhos)(MeCN)][BF_4]$_2$ (M = Rh (**5**), Ru (**6**)). Only one epimer at the metal was isolated in high yield for the complexes **1**, **2**, **3**, **3′**, **5** and **6** and the metallation of **2** to give **4** occurs with high diastereoselectivity.

Introduction

Since the origins of asymmetric homogeneous catalysis with transition metals, chiral phosphanes and their derivatives have been the preferred type of ligand.[1–3] The synthesis of new phosphane ligands is still an extremely active area, fostered by a continuous need for new ligands that lead to faster and more selective processes, operating under milder conditions. This research is leading to new families of chiral phosphanes, exploiting all possible sources of diversity including stereogenic carbon and phosphorus atoms, axes and planes.[4,5] A particularly appealing family is that of *P*-stereogenic phosphanes, a ligand type that, despite being linked to the origins of asymmetric catalysis, was neglected for a long time[6] and is now experiencing an intense renaissance.[7–10]

A few years ago, some of us reported on the MaxPhos ligand (see Scheme 1), which is a rare example of a *P*-stereogenic, C_1-symmetric ligand with a short bridge between the phosphorus atoms.[11,12] In addition, thanks to a tautomeric equilibrium involving the P atoms and the NH bridge, it was obtained as its bench-stable crystalline tetrafluoroborate salt, in contrast to many of the new generation highly basic and air-sensitive *P*-stereogenic ligands with alkyl substituents.[13]

The coordination chemistry of this ligand was initially explored with Rh(I) diene complexes,[11] which were found to be



Scheme 1 Reaction of (S_P)-[HMaxPhos][BF_4] with Rh- and Ir-acac precursors.

---

[a] Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC – Universidad de Zaragoza, Departamento de Química Inorgánica, Pedro Cerbuna 12, Zaragoza 50009, Spain. E-mail: dcarmona@unizar.es

[b] Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, Barcelona 08028, Spain. E-mail: arnald.grabulosa@qi.ub.es

[c] Institute for Research in Biomedicine (IRB-Barcelona), The Barcelona Institute of Science and Technology, Baldiri i Reixac 10, Barcelona 08028, Spain

[d] Departament de Química Inorgànica i Orgànica, Secció de Química Orgànica, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

† Electronic supplementary information (ESI) available: Selected NMR, MS, IR and CD spectra of the compounds. X-ray crystallographic information files containing full details of the structural analysis of complexes 1, 2 and 3′. CCDC 1573023–1573025. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt03327c