Account

Bis(*ortho*-)chelated Monoanionic Bisphosphinoaryl Ruthenium(II) Complexes: Synthesis, Characterization and Reactivity†

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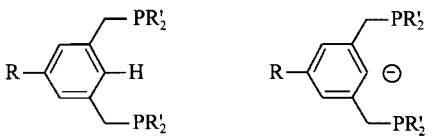
Bisphosphinoaryl ruthenium(II) compounds are synthesized using two distinct synthetic routes. One route, direct cycloruthenation, consists of the reaction of the parent arene compound R-PCHP with [$RuCl_2(PPh_3)_3$] in chlorinated solvents. However, this route suffers from major drawbacks because HCl is formed as well as free triphenylphoshine. The other route, the transcyclometalation reaction, involves the interconversion of one cyclometalated ligand metal complex, [RuCl(NCN)(PPh_3)], into another complex, [RuCl(R-PCP)(PPh_3)], with concomitant consumption and formation of the corresponding arenes R-PCHP and NCHN, respectively.

Keywords ruthenium, transcyclometalation reaction, monoanionic terdentate P,C,P'-bisphosphinoaryl, hydrogen transfer reaction

Introduction

The interaction of bisphosphines with (transition) metals is a fascinating field from the coordination chemist's point of view. A wide array of mono- and multi-metallic *cis*-η^2-*P*, *P'* coordinated complexes are formed in which a variety of coordination modes is encountered. The chelating properties of bisphosphines are greatly affected by the length and rigidity of the chain linking both phosphorus donor groups, and by the type of substituents present either on the phosphorus donor atoms or in the organic backbone linking the two phosphorus centers.[1] Linking both donor atoms by a chain of at least five preferential carbon atoms results in a bisphosphine complex capable of forming *trans*-spanning complexes with concomitant alternative binding modes. An example of such potential *trans*-spanning ligand is the monoanionic η^3-*P*, *C*, *P'*-coordinating PCP ligand (Fig. 1) commonly abbreviated as 'pincer' ligand (PCP is the abbreviation of the monoanionic, terdentate ligand [$C_6H_3(CH_2PR_2)_2$-2,6]$^-$).



R-PCHP R-PCP$^-$

R'=alkyl or aryl R=H, alkyl, halogen, Me_3Si

Fig. 1 R-PCHP-type ligands and their respective monoanionic [R-PCP]$^-$ derivatives.

Here, we report our recent studies on the synthesis and use of the bis (*ortho*-) chelated complex [RuCl(PCP)(PPh_3)]. In addition, the formation of species with an η^1-*P*-monodentate or μ-bridging η^1-*P*, η^1-*P'* bonded neutral arene R-PCHP ligand and their involvement as cyclometalation reaction intermediates will be

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briefly commented on.

Synthesis of bisphosphinoaryl ruthenium(II) complexes

The synthetic methods used for the formation of PCP containing organometallic complexes can be divided into three categories: (i) transmetalation with a [(PCP)Li] compound, (ii) direct activation of a ligand C—X bond (X = H, C, O, or Br), and (iii) cycloruthenation of a PCHP ligand with a cyclometalated Ru(II) complex, *i.e.*, [RuCl(NCN)(PPh_3)], NCN = [C_6H_3-(CH_2NMe_2)$_2$-2, 6]$^-$, a process known as transcyclometalation (TCM).

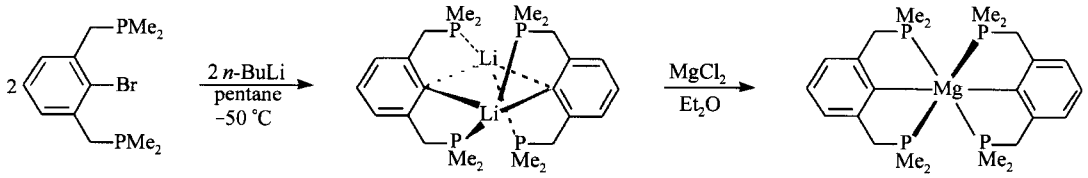
Synthesis of the ruthenium complexes via transmetalation

Transmetalation of a [Li(PCP)] complex with ruthenium is commonly used in the chemistry of the corresponding nitrogen-based NCN ligands.[2] In these ligands, the lithium atom is generally introduced by either one of the two following methods: (i) a halide-lithium exchange reaction or, (ii) direct deprotonation of the target C—H bond by an organolithium reagent. For PCP ligands, only one case was reported in which a transmetalation reaction is used. Reaction of PCBrP (P = PMe_2) with *n*-BuLi followed by the addition of $MgCl_2$ resulted in the formation of [Mg(PCP)$_2$] complex **1** (Scheme 1).[3]

Synthesis of the ruthenium complexes via direct metalation

The synthesis of [Ru(PCP)]-type complexes comprises the reaction of a 1∶1 molar mixture of the *meta*-bisphosphinoarene ligand with [$RuCl_2(PPh_3)_3$] in 1,2-dichloroethane at reflux temperature (Scheme 2).[4]

Scheme 1 Synthesis of [Mg(PCP)$_2$] complex **1**



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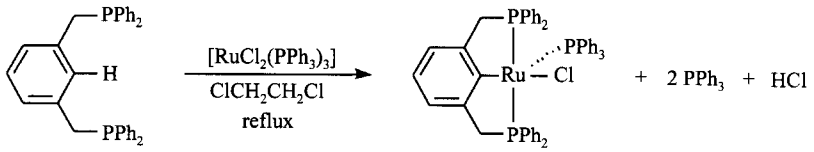
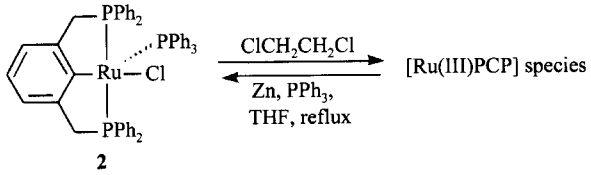
Scheme 2 Direct cyclometalation of PCHP affording [RuCl(PCP)(PPh_3)]



PCHP [RuCl(PCP)(PPh_3)] (**2**)

Reflux in 1,2-dichloroethane for 15 h afforded a green solution, from which, after workup, **2** was obtained in 58% yield.[5] However, this method has several drawbacks. Firstly, the cycloruthenated complex could not be obtained free from uncoordinated PPh_3 due to their similar solubility properties in common organic solvents. Secondly, synthesis of **2** is accompanied with the formation of a red, paramagnetic material (*e.g.*, a Ru(III) species) The long reaction time and the use of a chlorinated solvent can be responsible for this oxidation. Accordingly, reflux of a solution of pure **2** in 1, 2-dichloroethane led to slow formation of a similar red material (^{31}P NMR). Reductive treatment of the red solid with an excess of zinc and PPh_3 in refluxing THF (Scheme 3) again afforded **2**. Thirdly, the direct ruthenation method is not compatible with certain substituents. Reaction of *para*-trimethylsilyl-substituted compound, **4** (Scheme 4, R = Me_3Si), under the conditions of direct cyclometalation led to the formation of **2** (*vide infra*). Metathesis of the Me_3Si—C bond with the

Scheme 3 Equilibrium between different cycloruthenated species

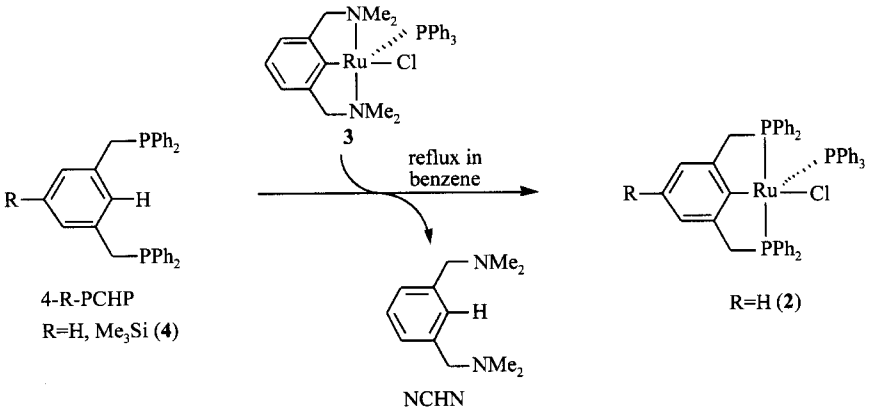


HCl formed during the ruthenation process is most likely the reason for the observed Si—C bond cleavage.[4] Addition of NEt_3 to the reaction mixture could only partially prevent this cleavage.[4]

Synthesis of the ruthenium complexes via a transcyclometalation reaction

Recently, cyclometalated Ru(II) complexes, *i.e.*, [RuCl(NCN)(PPh_3)] (**3**), have been successfully used as metal precursors for cycloruthenation of a PCHP ligand.[6] In analogy to transesterification reactions, we introduced the term transcyclometalation (TCM) reaction to describe the overall process of this reaction.[4,7,8] Reaction of PCHP ligand with **3** in a 1∶1 molar reaction in refluxing benzene afforded **2** with NCHN as the only other product (Scheme 4).[4]

Scheme 4 Transcyclometalation (TCM) reaction to prepare [RuCl(PCP)(PPh_3)] complexes (and NCHN) from [RuCl(NCN)(PPh_3)] and PCHP



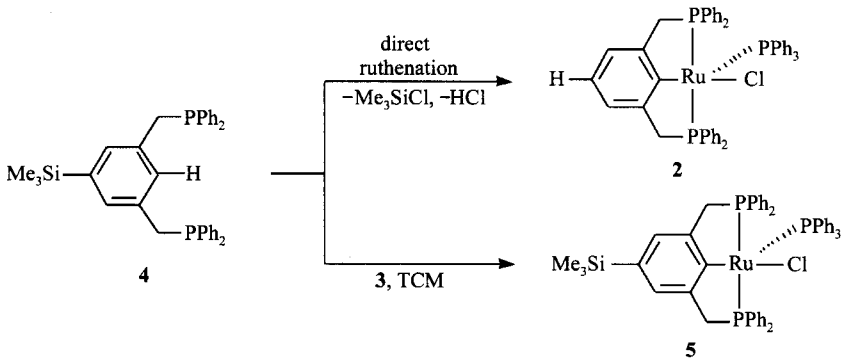
This process has been reported to occur in palladium(II)[8a] and platinum(II)[7,8] complexes as well. Unlike in the case of Pd (or Pt) complexes, transcycloruthenation occurred without the presence of any added activating reagent such as acetic or trifluoroacetic acid.[4,7] In contrast to the direct ruthenation, transcyclometalation is fully compatible with a trimethylsilyl substituent. The synthesis of Me_3Si-PCHP ligand **4** can be seen as a model route for the grafting of a PCP ligand to a carbosilane dendrimer. Reaction of **4** under direct ruthenation conditions led to the formation of known **2** (Scheme 5) in 90% yield instead of the expected *para*-trimethylsilyl-substituted complex **5**.[4-6] The mild conditions characteristic for the TCM reaction, addition of **3** to **4** in refluxing benzene, resulted in the formation of **5** (Scheme 5).[4]

The *meta*-bisaminoarene compound also formed during the reaction was isolated and characterized as H-NCHN. As chlorinated solvents are not used and HCl is not generated during the transcyclometalation reaction, this reaction procedure suppresses undesired side reactions such as formation of Ru(III) compounds or Si—C bond cleavage.

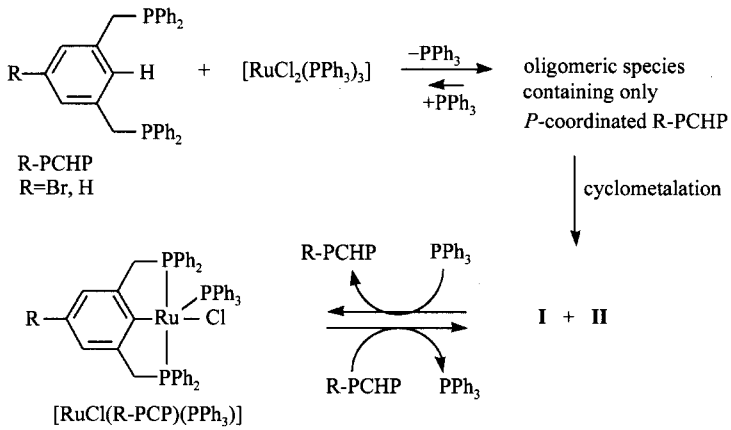
Structural characterization of bisphosphinoaryl ruthenium(II) complexes

When equimolar amounts of [$RuCl_2(PPh_3)_3$] and R-PCHP ligands are mixed, a chemo- and regio-selective reaction with the intra-annular C—H bond of the *m*-xylylenediyl ligand occurs leading to the exclusive formation of [RuCl(R-PCP)(PPh_3)] complexes. In the early stages of the reaction between [$RuCl_2(PPh_3)_3$] and R-PCHP, the PCP ligand readily displaces the PPh_3 ligands coordinated at the ruthenium center forming a mixture of oligomeric species (Scheme 6).[9] This process is likely to be dictated by the chelate-coordinating properties of the R-PCHP ligand as compared to PPh_3.

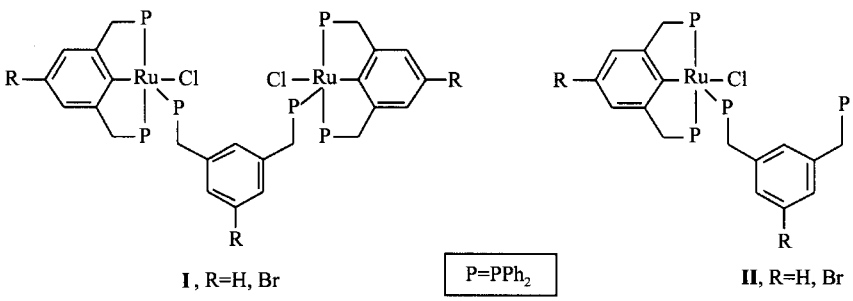
Scheme 5 Reaction of **4** under direct ruthenation and transcyclometalation conditions



Scheme 6 Formation of $[RuCl(R\text{-}PCP)(PPh_3)]$ complexes by reaction between $[RuCl_2(PPh_3)_3]$ and R-PCHP ligands



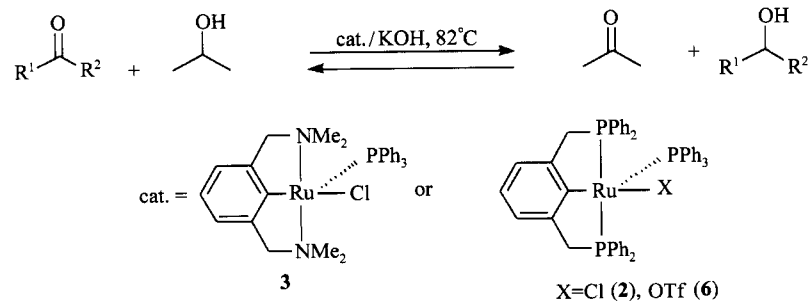
Scheme 7 Observed μ-η^1-P,η^1-P' (**I**) and η^1-P-coordinated (**II**) intermediates in cyclometalation of bisphosphinoaryl ligands



A fast irreversible cyclometalation leads to the formation of intermediate complexes **I** and **II**. ^1H and ^{31}P NMR spectroscopy showed the intermediacy of these monomeric (**II**) and dimeric (**I**) ruthenium complexes containing an η^3-P, C, P' R-PCP ligand and an η^1-P R-PCHP ligand bonded to the same metal center (Scheme 7).

The excess free PPh_3 present slowly displaces the coordinated R-PCHP ligands (in **I** or **II**), which are subsequently trapped by ruthenium centers lacking a cyclometalated R-PCP ligand. The displacement of the R-PCHP ligand constitutes the rate-determining step in the

Scheme 8 Reduction of ketones by ruthenium(II) complexes



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cyclometalation reaction. Thus, the observed intermediates operate as reservoirs, slowly releasing R-PCHP fragments during the course of the reaction.[9]

Catalysis with bisphosphinoaryl ruthenium (II) complexes

Organometallic pincer complexes have been used in a number of metal-mediated organic transformations such as dehydrogenation,[10] asymmetric allylic alkylation,[11] Michael reaction,[12] asymmetric aldol condensation,[13] Heck reaction,[14] atom-transfer radical polymerization (ATRP),[15] and Kharasch addition (ATRA).[16] Arylruthenium(II) complexes are highly active catalysts for the reduction of various ketones to the corresponding alcohols with *i*-PrOH as the hydrogen source and KOH as the promoter (Scheme 8).[17]

Representative ketones were chosen to examine the performance of **2**, **3**, and **6** as catalyst in hydrogen-transfer reactions. Dialkyl (aliphatic and cyclic), alkyl aryl, and diaryl ketones were all reduced in good to high yield.[17] In case of cyclohexanone, more than 98% conversion and a turn-over-frequency (TOF) of 1100 h^{-1} were attained by using **3** (0.1 mol%) without removal of the acetone formed in the reaction. The use of only 0.01 mol% of **2** or **6** under the same conditions resulted in higher TOF of up to 10.0×10^3 h^{-1} and 27.0×10^4 h^{-1}.[17] These values are superior to those obtained with ruthenium(II) complexes containing only monodentate phoshino ligands, such as $[RuCl_2(PPh_3)_3]$,[18] $[RuCl(H)\text{-}(PPh_3)_3]$, and $[Ru(H)_2(PPh_3)_4]$.[19,20] *In situ* monitoring under catalytic conditions indicated: (i) the structural unit $[Ru(PCP)PPh_3]$ was retained in the course of the catalytic cycle, (ii) a ruthenium hydride was most probably the true catalyst in this process, and (iii) the ruthenium hydrido complex $K[Ru(H)(i\text{-}PrO)\text{-}(PCP)PPh_3]$ represented a resting state of the catalyst before the addition of the substrate.[17]

Conclusion

A new synthetic approach is described, *i.e.*, a transcyclometalation reaction, in which a *meta*-bisaminoaryl terdentate NCN ligand is quantitatively replaced by a corresponding *meta*-bisphosphinoaryl ligand leading to the formation of $[RuCl(R\text{-}PCP)(PPh_3)]$ complexes. Synthesis of bisphosphinoaryl ruthenium(II) complexes via direct ruthenation suffers from problems such as the presence of free phosphine or free HCl or the need for the use of chlorinated solvents, which give rise to secondary products. These problems were overcome by the transcyclometalation procedure. The bisphosphinoaryl ruthenium(II) complexes form active catalysts in the reduction of ketones by hydrogen transfer in *i*-PrOH. Under these conditions, the σ Ru—C bond is stable and the $[Ru(PCP)PPh_3]$ fragment is preserved.

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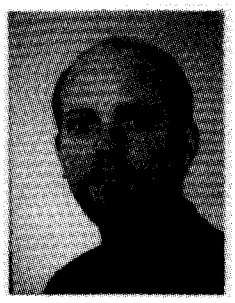
van KLINK, Gerard obtained his Ph.D. from the Vrije Universiteit, Amsterdam, under supervision of Prof. Bickelhaupt on the mechanism of formation of organomagnesium compounds. He worked as a post-doctoral fellow on the design and synthesis of co-catalysts for Ziegler-Natta polymerization processes and on low-valent catalysts for olefin polymerization in the group of Prof. Eisch at the State University of New York at Binghamton, both in cooperation with DSM Research. In 1998, he joined the group of Prof. van Koten at the Utrecht University where he currently is working as a lecturer.



DANI Paulo studied Chemistry at the Universidade Federal do Rio Grande do Sul, Brazil, under the supervision of Prof. Dupont. In 1995, he was awarded a fellowship from the Conselho Nacional de Desenvolvimento Científico e Tecnológioco (CNPq), Brazil, which enabled him to join the group of Prof. van Koten at the Utrecht University. In 2000, he received his Ph.D. from the Utrecht University on the development of ruthenium complexes of (a)chiral monoanionic bisphosphinoaryl ligands. Presently, he is project leader at Avantium Technologies.

van KOTEN Gerard studied Chemistry at the Utrecht University (Master of Science, 1967). In 1967, he joined the Institute for Organic Chemistry, TNO, where he obtained his Ph.D. (1974). In 1977, he moved to the University of Amsterdam where he was appointed to professor (personal chair) in Organometallic Chemistry. He has been Professor of Organic Synthesis at the Debye Institute of the Utrecht University since 1986. He is Scientific Director of the Netherlands Institute for Catalysis Research (NIOK), and has served on many national and international boards of scientific journals and committees. His research interests comprise the study of fundamental processes in organometallic chemistry, the application of organometallic complexes as catalysts for homogeneous catalysis, in particular for fine-chemical synthesis, and as material with special physicochemical properties (molecular wires and switches). The preparation and use of the first example of homogeneous metallodendrimer catalysts demonstrate his interest for supramolecular systems with (organometallic) catalytically active functionalities.

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