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Iridium complexes with aliphatic, non-innocent pincer ligands

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This review is dedicated to Prof. Irina Beletskaya in recognition of her brilliant work in organometallic chemistry and catalysis

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ABSTRACT

Pincer complexes attract considerable attention both as interesting objects for fundamental studies and efficient catalysts. This review describes a relatively new offshoot of the field – namely, the chemistry of iridium complexes with aliphatic PC_{sp3}P non-innocent pincer ligands. High flexibility, often combined with possibility to activate internal C–H bonds, offers several new patterns of metal–ligand cooperation; some of them were successfully used in catalysis of acceptorless alcohol dehydrogenation, olefin hydroformylation and deuterium exchange, others opened up for remarkable stoichiometric reactions.

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Contents

1. Introduction	00
2. Pincer ligands operating through carbene species	00
3. Dehydrogenation of a pincer ligand and related processes	00
4. Demetallation and related processes	00
5. Ligands with a fourth, labile point of coordination	00
6. Conclusions and outlook	00
Acknowledgements	00
References	00

1. Introduction

The chemistry of pincer complexes, i.e. complexes of transition metals with tridentate, typically meridional ligands (Chart 1) has experienced an explosive growth in the past several decades. The basic idea of a pincer complex is to strongly clamp a metal atom into a pair of chelating metallacycles and to vary the reactivity of the remaining coordination sites or ancillary ligands via

modification of the pincer backbone. This design provides thermal robustness and virtually limitless possibilities to fine tune the electronic or steric properties of a pincer ligand, and thus its reactivity. Pincer complexes have found applications in catalysis, small molecule activation, stabilization of elusive particles and studies of reaction mechanisms. The pincer complexes topic has been extensively reviewed [1,2], and in this review we will focus only on a small part of the area – iridium complexes with aliphatic pincer ligands, specifically those that demonstrate non-innocent behaviour, i.e. are chemically modified as a result of bond breaking/bond formation or other impact on a metal centre. Since

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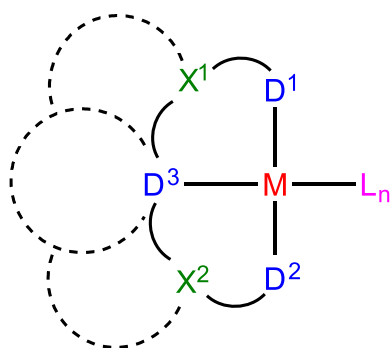


Chart 1. The generalized structure of a pincer complex. M – metal atom, D¹, D² and D³ – neutral or charged donating groups (typically PCP, PSI_P, NCN, PNP, PCN, OCO, CCC etc.), X¹ and X² – linkers of the pincer arms (typically -CH₂-, -O-, -NH- etc.), L_n – ancillary ligands or free coordination sites. The dashed line indicates possible ring or condensed rings structures of various types.

their initial synthesis by Shaw in the late 1970s [3], aliphatic pincer complexes experienced relatively little development compared to their arene-based counterparts, due to their inferior stability and the lower availability of precursors, at least when it comes to the archetypical compounds of that time. However, the lability and fluxionality of aliphatic ligands also has advantages. A growing interest in systems capable of metal-ligand cooperation [4], in the pincer field primarily driven by the success of Milstein's catalysts [5], as well as an increased attention to the generation and study of new carbene complexes, perhaps not the least due to the success of olefin metathesis catalysts [6–8], led to a renaissance in the area in 2010s and to an increased number of publications, since these are features for which aliphatic pincer complexes appeared to be suitable. The systems described below (Chart 2) will be grouped according to the type of the non-innocent behaviour they demonstrate. Sections 2–4 describe compounds with an α -C–H bond or species derived from them; Section 5 deals with frameworks where the α -C position was exploited to introduce a hemilabile coordinating group.

2. Pincer ligands operating through carbene species

In this section, processes involving formation of carbene complexes will be described. As a preface, we would like to remind the reader about two important reactions (Chart 3), that will accompany us here and in some places further in this review, namely β - and α -eliminations. Both reactions transfer an X group to the metal

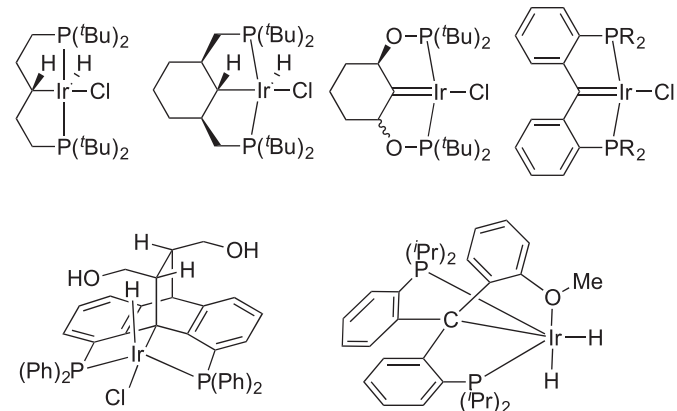


Chart 2. Some of the pincer complexes described in this review.

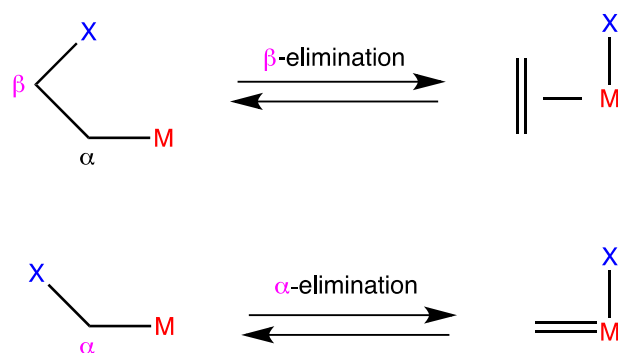
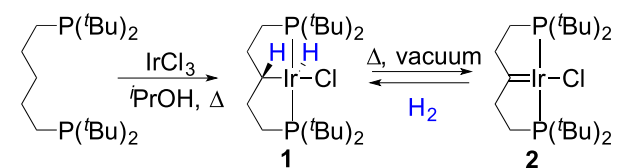


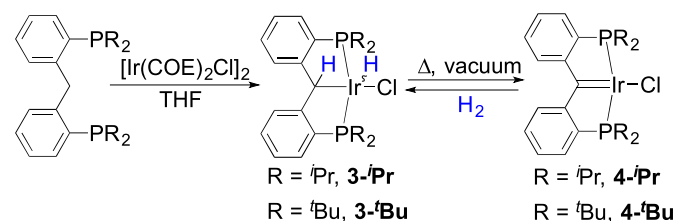
Chart 3. β - and α -elimination reactions.

and result in olefin and carbene complexes, respectively. It should be noted that not only hydrogen can hide behind the symbol X. It should also be kept in mind, that, while in principle β -elimination does not change the oxidation state of the metal, a significant contribution from the metallacyclopropane form may make it difficult to distinguish from an oxidative addition. As for α -elimination, it may lead to a Schrock or a Fischer type carbene, so it may or may not change the oxidation state of the metal.

In his early studies Shaw made double C–H activation of a ligand (^tBu)₂P[CH₂]₅P(^tBu)₂ and obtained carbene complex **2** (Scheme 1) [3,9]. The reaction likely consisted of oxidative addition of a reduced Ir species to the ligand C–H bond to give hydrido-chloride **1**, followed by the aforementioned α -elimination of hydrogen. The reverse reaction, hydrogenation of **2** to **1**, was the first example (in the field of pincer complexes) of what we now call metal-ligand cooperation, where both the metal and ligand are involved in the activation of the incoming substrate. Based on the quite strange low-field chemical shift of the α -C of 66.6 ppm Shaw described compound **2** as an ylide rather than a carbene. It has been noted, however [10], that a comparison of the reported spectral data with those for related compounds shows that it is probable that the true carbene resonance remained unobserved in compound **2**. Also note the mutual trans arrangement of the hydrogens in **1**, indicating a complex mechanism for hydrogen addition (*vide infra* for a discussion). Low yields of **2** and various side reactions, especially β -elimination from the saturated alkyl chains, prevented studies of these and related compounds for many years. Similar side reactions were reported by Gusev in his studies of related Ru and Os carbenes



Scheme 1. Pioneer experiments of Shaw with aliphatic iridium pincer complex.



Scheme 2. Synthesis of the diarylmethane-based (PCP)Ir carbene complex.

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