

Review

Metal complexes with ‘pincer’-type ligands incorporating *N*-heterocyclic carbene functionalities

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Abstract

The coordination and organometallic chemistry of linear, rigid, tridentate ligands, which incorporate at least one *N*-heterocyclic carbene and other ‘classical’ donors, is reviewed across the periodic table with emphasis on unique features due to the presence of the *N*-heterocyclic carbene donor. © 2006 Elsevier B.V. All rights reserved.

Keywords: Carbenes; Pincer; Tridentate; Rigid; Crystal structures; Transition metals

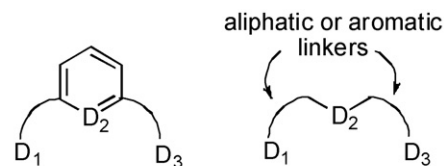
Abbreviations: Bu, butyl; Bz, benzyl; COD, 1,5-cyclooctadiene; DBA, dibenzylidene acetone; DCM, dichloromethane; DiPP, diisopropylphenyl; DMAc, *N,N*-dimethylacetamide; DME, 1,2-dimethoxyethane; DMF, *N,N*-dimethylformamide; DMS, dimethylsulfide; Et, ethyl; HMDS, hexamethyldisilazide; Me, methyl; Mes, mesityl(2,4,6-trimethylphenyl); Nbd, norbornadiene; NHC, *N*-heterocyclic carbene; NMO, *N*-methylmorpholine-*N*-oxide; NMR, nuclear magnetic resonance; OAc, acetate; OTf, trifluoromethanesulfonate; Ph, phenyl; ppm, parts per million; Pr, propyl; py, pyridine; RT, room temperature; TEA, triethylamine; TMS, trimethylsilyl; TON, turnover number; Xy, Xylyl(2,6-dimethylphenyl); tmeda, *N,N,N',N'*-tetramethylethylenediamine

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1. Introduction

The isolation of thermally stable *N*-heterocyclic carbenes by Arduengo in 1991 initiated intense research activity into the organometallic chemistry of these versatile ligands. Furthermore, the ease of functionalisation of the imidazolium salt proligands led to the incorporation of *N*-heterocyclic carbene donors in polydentate ligand structures, usually in combination with other classical donors. The aim of this approach has been the development of functional complexes and the precise tailoring of the metal coordination sphere since dissociation–association reactions, which are important for the generation of active species in homogeneous catalysis, are not possible in the kinetically formed NHC complexes due to the strength of the metal–NHC bonding [1]. The first classical donor functionalised *N*-heterocyclic carbene complexes were described by Lappert and comprised saturated imidazolin-2-ylidene donor groups linked to alkenes or phosphines by C3 linkers [2]. The complexation reactions involved cleavage of electron rich olefins by low oxidation state transition metals. The introduction of the silver transmetallation route [3] and the ‘bottleable’ functionalised *N*-heterocyclic carbenes [4–6] opened up further possibilities for the synthesis of well defined functionalised carbene complexes. Among the polydentate ligand structures with carbene donors, tripodal [7,8] and ‘pincer’ systems [9–11] have attracted a lot of attention. The rigid linear tridentate and ‘pincer’ ligands support meridional (in octahedral geometries) or pseudo-meridional (in trigonal bipyramidal, square pyramidal or square planar geometries)



At least one of the donors is an *N*-heterocyclic carbene

Fig. 1. Generic structures of the ligands featured in this review.

tries) coordination. Seminal work with ‘pincer’ ligands bearing phosphine and amine donors was carried out by Shaw, van der Boom and Milstein [12], Albrecht and van Koten [13] and others. Linear rigid tridentate ligands are being investigated by various groups with metals from across the periodic table [14,15]. In this paper, we review the use of rigid linear tridentate ligands with at least one *N*-heterocyclic carbene donor as shown schematically below (Fig. 1).

In most cases the above ligands adopt meridional coordination modes with the majority of the transition metals, except group 11 metals. However, complexes with less rigid, long aliphatic linkers may adopt distorted facial coordination modes and therefore have been excluded from this review. A list of the ligand structures discussed is shown below (Fig. 2).

Substantial work with preorganised rigid tridentate ligands incorporating non-cyclic carbene donors of P-heteroatom stabilized carbenes has been described by Cavell, recently reviewed [16,17] and will not be covered any further here. The literature has been covered systematically until March 2006.

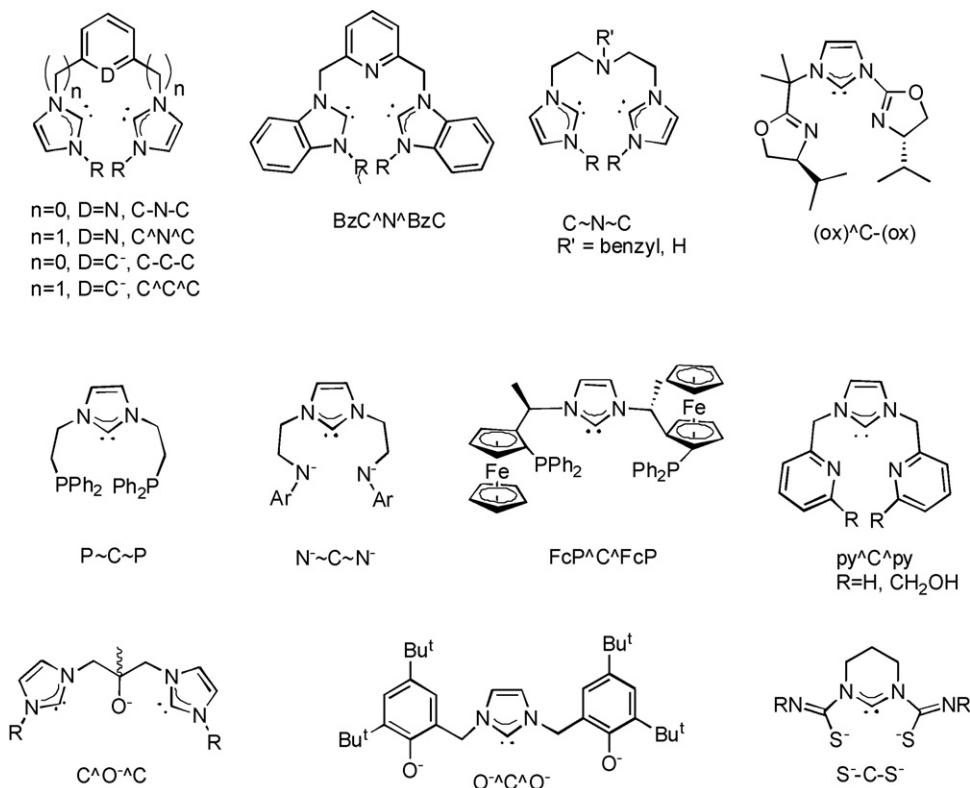


Fig. 2. Structures of the ligands discussed in this review.

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