



Review

Homo- and heterometallic polynuclear transition metal catalysts for alkane C–H bonds oxidative functionalization: Recent advances



Dmytro S. Nesterov*, Oksana V. Nesterova*, Armando J.L. Pombeiro*

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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ABSTRACT

Polynuclear homo- and heterometallic complexes of transition metals constitute a broad class of coordination compounds with recognized applications in catalysis, and polymetallic active sites in enzymes inspire their significance as bio-mimicking catalysts. The current interest of synthetic chemistry in the mild functionalization of alkanes demands a rapid progress in the field of metal-catalysed alkane oxidation. This review covers the synthesis of homo- and heterometallic polynuclear complexes of 3d metals with N,O-donor ligands and their application in homogeneous catalytic alkane hydroxylation and hydrocarboxylation, mainly during the last six years. The synthetic approaches used for the preparation of the polynuclear compounds and their structural features are discussed, as well as their use as catalysts in that field, effects of oxidants and promoters, and main reaction mechanisms.

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* Corresponding authors.

E-mail addresses: dmytro.nesterov@tecnico.ulisboa.pt (D.S. Nesterov), oksana.nesterova@tecnico.ulisboa.pt (O.V. Nesterova), pombeiro@tecnico.ulisboa.pt (A.J.L. Pombeiro).

Abbreviations

General terms

CSD	Cambridge Structural Database
SMM	single molecule magnetism
MOF	metal–organic framework
MMO	methane monooxygenase
sMMO	soluble methane monooxygenase
pMMO	particulate methane monooxygenase
PDB	protein data bank
IL	ionic liquid
TON	turnover number, moles of product per mol of catalyst
TOF	turnover frequency, moles of product produced per mol of catalyst per a certain period of time
A/K	alcohol to ketone ratio
ESI-MS	electrospray mass spectroscopy
GCMS	gas chromatography–mass spectroscopy
KIE	kinetic isotope effect

Amino- and aminoalcohol (pro-)ligands

H ₂ dea	diethanolamine
H ₃ tea	triethanolamine
H ₂ tBuDea	<i>N</i> - <i>tert</i> -butyldiethanolamine
Hbz	benzoic acid
H ₂ hxbz	4-hydroxybenzoic acid
Hnbz	<i>p</i> -nitrobenzoic acid
Hbea	<i>N</i> -benzylethanolamine
H ₃ tipa	triisopropanolamine
H ₅ bistris	bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane
H ₄ edte	<i>N,N,N',N'</i> -tetrakis(2-hydroxyethyl)ethylenediamine
tpa	tris(2-pyridylmethyl)amine
H ₄ L ^{1e}	bis(2-hydroxybenzylidene)terephthalohydrazide
H ₃ L ²	<i>N</i> -acetylsalicylhydrazidate
L ³	1,4,7-trimethyl-1,4,7-triazacyclononane
H ₃ L ^{4k}	<i>keto</i> form of (3,5-di- <i>tert</i> -butyl-2-hydroxybenzylidene)-2-hydroxybenzohydrazide
H ₃ L ^{4e}	<i>enol</i> form of (3,5-di- <i>tert</i> -butyl-2-hydroxybenzylidene)-2-hydroxybenzohydrazide
Na ₂ L ⁵	sodium 2-[2-(2,4-dioxopentan-3-ylidene)hydrazinyl]terephthalate
H ₂ L ⁶	3,3'-(1,4-diazepane-1,4-diyl)bis[1-(4-ethylpiperazine-1-yl)propan-2-ol]
HL ⁷	2-(2-pyridylmethyleneamino)benzenesulfonic acid

H ₄ L ⁸	2-[(5-bromo-2-hydroxybenzylidene)amino]-2-(hydroxymethyl)propane-1,3-diol
H ₄ L ⁹	2-[(2-hydroxybenzylidene)amino]-2-(hydroxymethyl)propane-1,3-diol
H ₃ L ¹⁰	salicylidene-2-ethanolamine
L ¹¹	<i>N,N</i> -dimethyl- <i>N'</i> -(pyrid-2-ylmethyl)ethylenediamine
H ₂ L ^{13k}	(2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide
H ₃ L ^{14k}	2-amino-(2,3-dihydroxybenzylidene)benzohydrazide
H ₃ L ^{15k}	(2,3-dihydroxybenzylidene)benzohydrazide

Carboxylic acids

H ₄ pma	pyromellitic acid
H ₂ hpa	homophthalic acid
H ₄ cdc	cyclohexane-1,4-dicarboxylic acid
H ₂ pmal	phenylmalonic acid
HOAc	acetic acid
HPiv	pivalic acid
Ph ₂ AcOH	diphenylacetic acid
Ph ₃ AcOH	triphenylacetic acid
TFA	trifluoroacetic acid
PCA	pyrazinecarboxylic acid
H ₂ Ox	oxalic acid

Other reagents and solvents

im	imidazole
Et ₃ N	triethylamine
Py	pyridine
Ph ₃ P	triphenylphosphine
Ph ₃ P=O	triphenylphosphine oxide
TEMPO	2,2,6,6-tetramethylpiperidin-1-oxyl
BHT	2,6-di- <i>tert</i> -butyl-4-methylphenol
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
<i>m</i> -CPBA	<i>m</i> -chloroperoxybenzoic acid
<i>m</i> -CBA	<i>m</i> -chlorobenzoic acid
Oxone [®]	2KHSO ₅ ·KHSO ₄ ·K ₂ SO ₄
TBHP	<i>tert</i> -butylhydroperoxide
DMCH	dimethylcyclohexane
DMPO	5,5-dimethyl-pyrroline <i>N</i> -oxide
benzil	1,2-diphenylethane-1,2-dione

1. Introduction

1.1. Historical remarks and development of the field

According to the Cambridge Structural Database (CSD) [1], the oldest crystal structures of polynuclear compounds concern bi- and tetranuclear complexes of copper and palladium described in the thirties of the XX century [2–4]. However, only in the eighties, with the perfection of small-molecule X-ray analysis, the number of crystallographically characterized polynuclear complexes started to exhibit an acute growth (Fig. 1.1). Often possessing beautiful, highly-symmetrical structures, polynuclear coordination compounds were also found to reveal some other specific features. The discovery of slow magnetic relaxation in the dodecanuclear manganese complex [Mn₁₂(OAc)₁₂(H₂O)₄O₁₂].2HOAc·4H₂O [5] by Gatteschi in 1993 [6] facilitated the progress in the scientific field known as “single-molecule magnetism” (SMM) [7]. The SMM effect caused an extreme interest in the polynuclear complexes chemistry with the number of metals of twelve and more (the so-

called “high-nuclear complexes”). In fact, the number of M₁₂₊ structures started to grow in the middle of the nineties (Fig. 1.1, inset). The brilliant works by Winpenny, Christou, Powell and many other scientists brought the field of polynuclear compounds into a new level, where complex physical effects arose from the interactions between numerous closely located paramagnetic centres [8–12]. The high-nuclear complexes with more than 40 metal centres within one molecule can be considered as nanoscale objects (nanoclusters), with the size being compatible to those of nanoparticles area (2 nm and more) [13–16]. However, in contrast to nanoparticles, the high-nuclear complexes constitute reproducible, atomically precise materials. The large size and potential porosity of such nanoobjects, in combination with their molecular nature, provides properties which until recently were attributable to solid state chemistry only (e.g., metal–organic frameworks, MOFs [17,18]), such as host–guest exchange or surface catalysis [16,19–21].

A special part of polynuclear complexes concerns those containing atoms of different metals within one molecule (heterometallic

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