Available online at www.sciencedirect.com
ScienceDirect
Coordination Chemistry Reviews 251 (2007) 2266–2279
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

Recent developments in the coordination and organometallic chemistry of Kläui oxygen tripodal ligands

Wa-Hung Leung[a,*], Qian-Feng Zhang[b], Xiao-Yi Yi[a]

[a] Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR China
[b] Department of Applied Chemistry, Anhui University of Technology, Maanshan, Anhui 243002, PR China

Received 13 October 2006; accepted 30 November 2006
Available online 8 December 2006

Contents

Abstract

The Kläui oxygen tripodal ligands $[(\eta^5\text{-}C_5H_5)Co\{P(O)(OR)_2\}_3]^-$ (L_{OR}^- where R = alkyl group), which have been recognized as oxygen analogues of cyclopentadienyl, can form stable complexes with a range of main group and transition metal ions. This review reports on the recent developments in the coordination and organometallic chemistry of the Kläui tripodal ligands. Special attention will be paid to polynuclear M-L_{OEt} (M = Ti, Zr) oxo and hydroxo compounds that may serve as models for group 4 metal aqua ions.

Keywords: Oxygen ligand; Tripodal ligand; Metal complex; Cluster

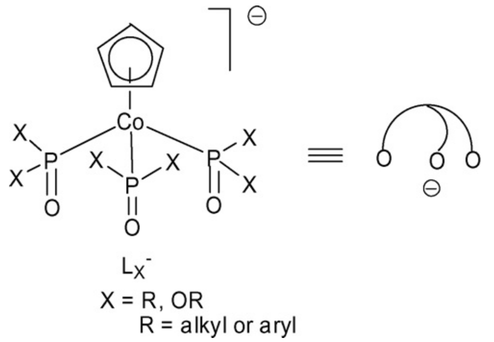
1. Introduction

The mono-anionic oxygen tripodal ligands of the general formula $[CpCo(P(O)(X)_2)_3]^-$ (L_x^-), where Cp = cyclopentadienyl; X = alkyl, aryl, alkoxy or aryloxy (Scheme 1), developed by Kläui and co-workers [1–4] have been recognized as oxygen analogues of cyclopentadienyl. The

---

[*] Corresponding author. Tel.: +852 2358 7360; fax: +852 2358 1594.
E-mail address: chleung@ust.hk (W.-H. Leung).

0010-8545/$ – see front matter
doi:10.1016/j.ccr.2006.11.019



Scheme 1. Structure of the Kläui oxygen tripodal ligands.

Kläui tripodal ligands can form stable complexes with various main group and transition metal ions [1,5–10]. Owing to their hydrolytic stability, they have been used as models of facially coordinated aqua ligands in organometallic compounds [11]. Despite their hardness and strong π-donor strength, L_x^- are compatible with both hard and soft metal ions, exhibiting interesting organometallic chemistry. The use of M-L_x complexes in homogeneous catalysis has been reported [12].

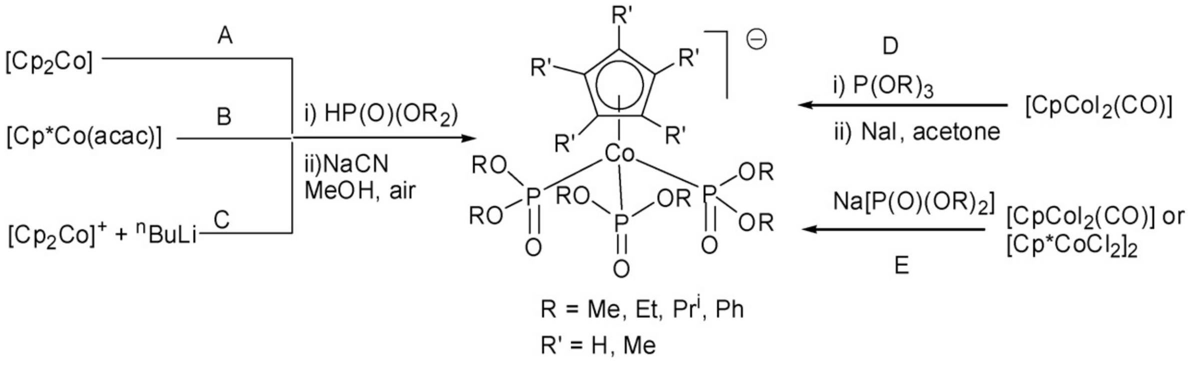
This review summarizes the recent developments in the coordination and organometallic chemistry of the Co(III)-based Kläui tripodal ligands $[CpCo\{P(O)(OR)_2\}_3]^-$, denoted as L_{OR}^-. In particular, the studies on polynuclear Ti(IV)- and Zr(IV)-L_{OEt} oxo and hydroxo complexes that are relevant to group 4 aqua ions will be highlighted. The review is organized into three sections: (i) Ligand syntheses, (ii) Survey of metal complexes, and (iii) Applications. The survey of complexes, which is organized by groups, will cover the works published after 1990. A detailed account on metal complexes with L_{OR}^- prepared prior to 1990 can be found in Kläui's review [1].

2. Ligand syntheses

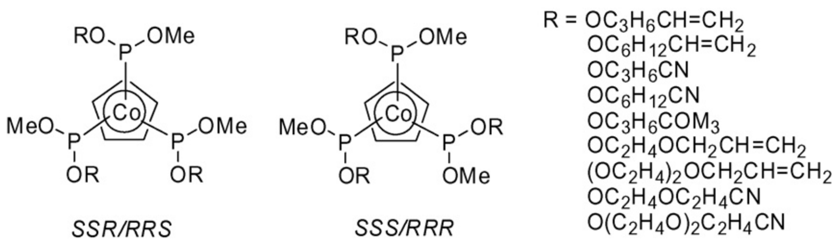
L_{OR}^- are generally synthesized by (i) reaction of $[CP_2Co]$ (method A), $[Cp^*Co(acac)]$ ($Cp^* = \eta^5$-C_5Me_5, $acac^-$ = acetylacetonate) (method B), or $[Cp_2Co]^{+/n}BuLi$ (method C) with $HP(O)(OR)_2$ followed by demetallation with NaCN in air; (ii) reaction of $[CpCoI_2(CO)_2]$ with $P(OR)_3$ followed by Arbuzov dealkylation with NaI (method D); or (iii) reaction of $[CpCoI_2(CO)_2]$ or $[Cp^*CoCl_2]_2$ with $NaP(O)(OR)_2$ (method E) (Scheme 2) [2–4,12–14].

The analogous Ir(III)-based tripodal ligand $[Cp^*Ir\{P(O)(OMe)_2\}_3]^-$ has been prepared by reaction of $[Cp^*IrCl_2]_2$ with $Ag(ClO_4)$ and $P(OMe)_3$ followed by NaI/acetone [15]. Di-anionic Ru(II)-based tripodal ligands $[Cp^*Ru\{P(O)(OR)_2\}_3]^{2-}$ ($L_{Ru,OR}{}^{2-}$), where R = Me, Et, Pr^i, have been synthesized by either (i) treatment of $[Cp^*Ru(OMe)]_2$ with $HP(O)(OR)_2$ (R = Me, Ph) followed by dealkylation with NaI, or (ii) direct reaction of $[Cp^*RuCl]_2$ with $NaP(O)(OEt)_2$. Similar to mono-anionic L_{OR}^-, $L_{Ru,OR}{}^{2-}$ reacted with metal halides to give stable complexes of the types $[M(L_{Ru,OR})_2]^{n-}$ (M = Si^{IV}, Ti^{IV}, Nb^{IV}, $n = 0$; Cr^{III}, Fe^{III}, $n = 1$; Co^{II}, $n = 2$) and $[MX(L_{Ru,OR})]$ (MX = BPh or $V^{IV}(O)$) [16,17].

Kläui tripodal ligands bearing functional groups in pendant side chains $[CpCo\{P(O)(OMe)(OR')_3\}]^-$, where R = $(C_2H_4O)_nCH_2CH{=}CH_2$, $(C_2H_4O)_nC_2H_4CN$, $(C_3H_6)CN$, $C_3H_6C(O)CH_3$, $(CH_2)_5CO_2Me$; $n = 1$ or 2, have been synthesized by reaction of $[CpCoI_2(CO)P(OMe)(OR')$ with $P(OMe)_2(OR)$ followed by dealkylation with NaI, and iso-



Scheme 2. Synthetic routes to L_{OR}^-.



Scheme 3. Newman projections of the *RRR*/*SSS* and *RRS*/*SSR* diasteromers of $L_{OMe,OR}^-$ (*R* and *S* refer to the configurations of the phosphorus centers).