

Functionalised dien ligands of the type $(\text{ArNHCH}_2\text{CH}_2)_2\text{NR}$ [$\text{R} = \text{Me}, (2\text{-C}_5\text{H}_4\text{N})\text{CH}_2$] and their complexes with iron and cobalt halides

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Abstract

The alkylation of $(\text{ArHNCH}_2\text{CH}_2)_2\text{NH}$ with RX [$\text{RX} = \text{MeI}, (2\text{-C}_5\text{H}_4\text{N})\text{CH}_2\text{Cl}$] under basic conditions gives $(\text{ArHNCH}_2\text{CH}_2)_2\text{NMe}$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ **L1a**, $2,4\text{-Me}_2\text{C}_6\text{H}_3$ **L1b**) and $(\text{ArHNCH}_2\text{CH}_2)_2\{(2\text{-C}_5\text{H}_4\text{N})\text{CH}_2\}\text{N}$ ($\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ **L2a**, $2,4\text{-Me}_2\text{C}_6\text{H}_3$ **L2b**) in moderate yield, respectively. Alternatively, **L1a** and **L1b** can be accessed by the arylation (with Ar-Br) of $(\text{H}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$ in the presence of a catalytic quantity of $\text{Pd}_2(\text{dba})_3$. Treatment of **L1** with CoCl_2 in *n*-BuOH gave high-spin $[(\text{ArHNCH}_2\text{CH}_2)_2\text{NMe}\{\text{CoCl}_2\}]$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ **1a**, $2,4\text{-Me}_2\text{C}_6\text{H}_3$ **1b**) in good yield; no reaction occurred with FeCl_2 . The molecular structure of **1a** reveals a distorted trigonal bipyramidal geometry with the **L1a** adopting a *mer*-configuration. Reaction of **L2** with MCl_2 affords the cobalt and iron complexes, $[(\text{ArHNCH}_2\text{CH}_2)_2\{(2\text{-C}_5\text{H}_4\text{N})\text{CH}_2\}\text{NMCl}_2]$ ($\text{M} = \text{Co}$, $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ **2a**, $2,4\text{-Me}_2\text{C}_6\text{H}_3$ **2b**; $\text{M} = \text{Fe}$, $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ **3a**, $2,4\text{-Me}_2\text{C}_6\text{H}_3$ **3b**); the octahedral frameworks in **2a** and **3a** are found to be considerably distorted with one of the two M-N (mesityl-substituted) distances noticeably elongated [M-N 2.597(4)–2.795(2) Å]; no such inequivalence is observed in solution at room temperature. On activation with methylaluminoxane, complexes **1a** and **1b** display some activity for the oligomerisation of ethylene.

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1. Introduction

Dianionic ligands derived from functionalised diethylenetriamines (dien) have been the subject of considerable interest in recent years due, in part, to the ability of the tridentate diamido unit to act as an inert spectator ligand for main group [1] and transition metals [2–8] during a variety of chemical transformations. The amenability of the dien manifold towards structural varia-

tion and, in particular, towards the incorporation of steric bulk has allowed access to a wide range of substituted dien compounds of the type, $\text{R}_2\text{-dien}$ ($\text{R} = \text{silyl}$ [2], aryl [3]) and $\text{R}'\text{R}_2\text{-dien}$ ($\text{R}' = \text{R} = \text{silyl}$ [2,4]; $\text{R}' = \text{alkyl}$, $\text{R} = \text{silyl}$ [5]; $\text{R}' = \text{vinyl}$, $\text{R} = \text{alkyl}$ [6]; $\text{R}' = \text{alkyl}$, $\text{R} = \text{aryl}$ [7]; $\text{R}' = \text{picolyl}$, $\text{R} = \text{silyl}$ [8]) (Fig. 1). In many cases, ligand synthesis necessitates firstly the introduction of two R groups to the terminal nitrogen atoms in dien to give $\text{R}_2\text{-dien}$ and then, in a second step, addition of R' group at the central secondary amine to afford $\text{R}'\text{R}_2\text{-dien}$.

Recently, we have been interested in employing the functionalised dien ligands as neutral supports for late transition metals and have prepared a series of

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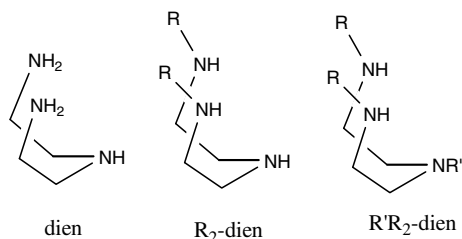


Fig. 1. Diethylenetriamine and derivatives (R or R' = alkyl, aryl, silyl or a combination).

Ar₂-dien-supported metal halide complexes. Notably, the cobalt-containing examples exhibit, on activation with methylaluminoxane (MAO), some activity for the oligomerisation of ethylene [9]. In this article we are concerned with derivatising the central amine in Ar₂-dien with an alkyl group or with a potential donor group, 2-pyridylmethyl (2-picoly), and examining the resultant coordination chemistry with divalent iron and cobalt halide precursors.

2. Results and discussion

2.1. Synthesis of the ligands

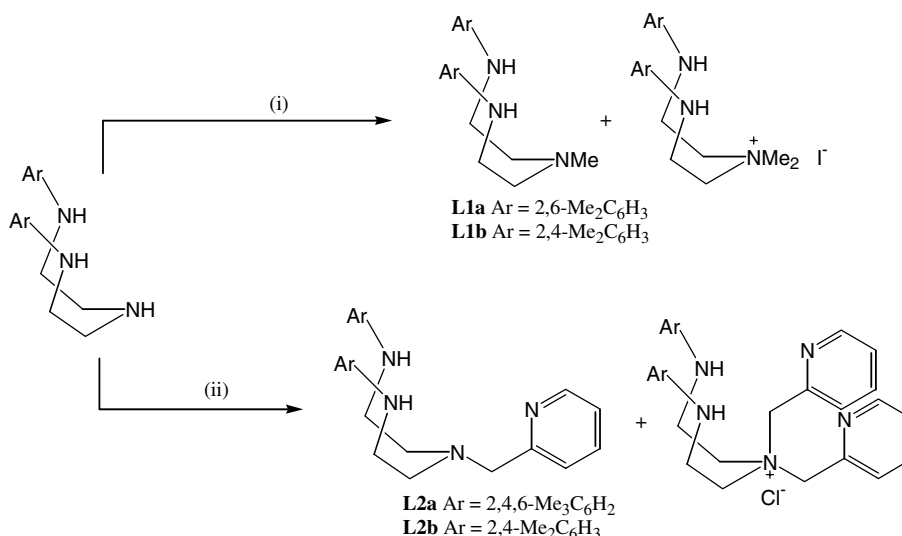
The ligands, (ArHNCH₂CH₂)₂NMe (Ar = 2,6-Me₂C₆H₃ **L1a**, 2,4-Me₂C₆H₃ **L1b**), could be prepared in modest yield by treating (ArHNCH₂CH₂)₂NH with MeI under conditions established by Schrock et al. for the preparation of (MeHNCH₂CH₂)₂NMe [7a]. However, we have found this approach for the synthesis of **L1a** and **L1b** to be hampered by the ready formation of ammonium salts of the type ((ArHNCH₂CH₂)₂-NMe₂)I[−] (Scheme 1).

To circumvent this problem, we have employed a palladium catalysed N-C(aryl) coupling reaction of *N*-methyldiethylenetriamine (prepared from *N*-methyldiethanolamine [10]) with two equivalents of the corresponding aryl bromide using experimental conditions established by Buchwald and Hartwig [11]. Following work-up **L1a** and **L1b** could be isolated as the sole product in high yield (Scheme 2).

The picolyl-substituted ligands, (ArHNCH₂CH₂)₂-{(2-C₅H₄N)CH₂}N (Ar = 2,4,6-Me₃C₆H₂ **L2a** [12], 2,4-Me₂C₆H₃ **L2b**) could be prepared in modest yield from (ArHNCH₂CH₂)₂NH (Ar = 2,4,6-Me₃C₆H₂, 2,4-Me₂C₆H₃) by treating them with 2-picoly chloride hydrochloride in acetonitrile at 55 °C in the presence of potassium carbonate (Scheme 1). Following purification on an alumina column, **L2a** and **L2b** could be isolated as yellow oils. All the new ligands have been characterised by IR, ¹H and ¹³C NMR spectroscopy, mass spectrometry (see Section 4).

2.2. Synthesis of the complexes

The reaction of **L1a** and **L1b** with CoCl₂ in *n*-butanol at elevated temperatures gave complexes [{(ArHNCH₂CH₂)₂NMe}CoCl₂] (Ar = 2,6-Me₂C₆H₃ **1a**, 2,4-Me₂C₆H₃ **1b**) in high yield (Scheme 3), respectively. The corresponding reactions of **L1** with FeCl₂ in *n*-butanol at elevated temperature or with FeCl₂(THF)_{1.5} in tetrahydrofuran at ambient temperature gave only unreacted starting materials. Complexes **1a** and **1b** have been characterised by FAB mass spectrometry, infrared spectroscopy, magnetic susceptibility and by elemental analysis (see Table 1). In addition, a crystal of **1a** has been the subject of a single crystal X-ray diffraction study.



Scheme 1. Reagents and conditions: (i) K₂CO₃, 0 °C, MeI; (ii) K₂CO₃, 55 °C, C₅H₄NCH₂Cl · HCl.

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