

# A Critical Study of Diimines and Related Ligands



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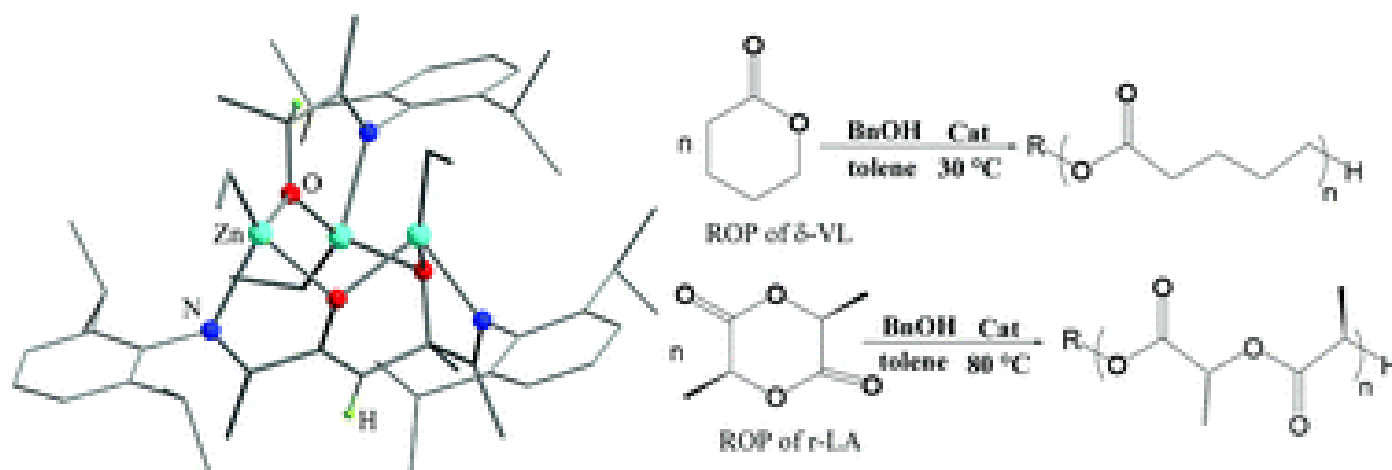
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The basic iron (II)  $\alpha$ -diimine five-membered unsaturated chelate ring (35) is a key unit in iron chemistry. In this review the classic ligands important in the early development of the area have been allocated separated section: 2, 2'-bipyridine and 1, 10-phenanthroline and 2, 2':6,6''-terpyridine. The closely related dioxides are discussed in another section, while the many macro cyclic system containing such linkages are covered in later sections. Once it was appreciated that only the basics structure rather than a fully aromatic legends is necessary to obtain stable, highly colored (metal-to-legends charge transfer<sup>136</sup> complexes, many legends containing this moiety were synthesized and  $\alpha$ -Diimine are among the most robust and versatile legends available in synthetic coordination chemistry, possessing finely tunable streak and electronic properties. A series of novel cationic ruthenium (II) *p*-cymene complexes bearing simple  $\alpha$ -diimine ligands,  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}\{\kappa^2N\text{-(HCNR)}_2\}]\text{NO}_3$  (R = Cy, [1] $\text{NO}_3$ ; R = 4-C<sub>6</sub>H<sub>10</sub>OH, [2] $\text{NO}_3$ ; R = 4-C<sub>6</sub>H<sub>4</sub>OH, [3] $\text{NO}_3$ ), were prepared in near-quantitative yields as their nitrate salts. [2] $\text{NO}_3$  displays high water solubility. The potential of the  $\alpha$ -diimine ligand in [3] $\text{NO}_3$  as a carrier of bioactive molecules was investigated via esterification reactions with the hydroxyl groups. Thus, the double-functionalized derivatives  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}\{\kappa^2N\text{-(HCN(4-C}_6\text{H}_4\text{OCO-R))}_2\}]\text{NO}_3$  (R = aspirinate, [5] $\text{NO}_3$ ; valproate, [6] $\text{NO}_3$ ) and also [4]Cl (R = Me) were obtained in good-to-high yields. UV-vis and multinuclear NMR spectroscopy and cyclic voltammetric studies in aqueous solution revealed only minor ruthenium chloride hydrolytic cleavage, biologically accessible reduction potentials, and pH-dependent behavior of [3] $\text{NO}_3$ . Density functional theory analysis was performed in order to compare the Ru-Cl bond strength in [1]<sup>+</sup> with the analogous ethylenediamine complex, showing that the higher stability observed in the former is related to the electron-withdrawing properties of the  $\alpha$ -diimine ligand. In vitro cytotoxicity studies were performed against tumorigenic (A2780 and A2780cisR) and nontumorigenic (HEK-293) cell lines, with the complexes bearing simple  $\alpha$ -diimine ligands ranging from inactive to IC<sub>50</sub> values in the low micromolar range. The complexes functionalized with bioactive components, i.e., [5] $\text{NO}_3$  and [6] $\text{NO}_3$ , exhibited a marked increase in the cytotoxicity with respect to the precursor [3] $\text{NO}_3$ .

Four heteroleptic cationic iridium(III) complexes containing cyclometalating 2-{3-[7-(benzothiazol-2-yl)fluoren-2-yl]phenyl}pyridine ligand and different diimine ( $N^<^>N$ ) ligands ( $N^<^>N$  = 2-(pyridin-2-yl)quinoline (1), 1,10-phenanthroline (2), 2,2'-biquinoline (3), and 1,1'-biisoquinoline (4)) and a reference complex bearing 2-(pyridin-2-yl)quinoline and 2-phenylpyridine ligands (5) were synthesized and characterized. The influence of the diimine ( $N^<^>N$ ) ligand on the photophysics of these complexes has been systematically investigated via spectroscopic methods and by time-dependent density functional theory (TDDFT). All complexes exhibit  $N^<^>N$  or  $C^<^>N$  ligand localized (1) $\pi,\pi^*$  transitions below 400 nm, and broad and structureless metal-to-ligand and ligand-to-ligand charge transfer ((MLCT)-M-1/(LLCT)-L-1) absorption bands between 400 and 450 nm, and weak (MLCT)-M-3/(LLCT)-L-3 absorption above 450 nm. Increasing the  $\pi$ -conjugation of the  $N^<^>N$  ligand causes enhanced molar extinction coefficients of the absorption bands and a bathochromic shift of the (MLCT)-M-3/(LLCT)-L-3 band. All complexes show orange to red phosphorescence at room temperature, with the emitting state being predominantly assigned to (MLCT)-M-3/(LLCT)-L-3 states for 15, but with some (3) $\pi,\pi^*$  contributions for 3 and 5. Extending the  $\pi$ -conjugation of the  $N^<^>N$  ligand induces a pronounced red-shift of the emission band and decreases the emission lifetime and quantum yield. Complexes 15 exhibit relatively strong singlet and triplet transient absorption from 450 to 800 nm, where the reverse saturable absorption (RSA) could occur. Nonlinear transmission experiments at 532 nm using nanosecond laser pulses demonstrate that complexes 15 are strong reverse saturable absorbers at 532 nm.

A series of organoaluminium imino-amido complexes of the type  $\{[ArNC(Me)_2C(Me)=NAr]AlMe_2\}$  ( $Ar$  = 2,6- $iPr_2C_6H_3$  (1),  $Ar$  = 2,6- $Et_2C_6H_3$  (2);  $Ar$  = 2,6- $Me_2C_6H_3$  (3) have been prepared *via* reaction of  $AlR_3$  and the respective  $\alpha$ -diimine. Similar reaction of the bis( $\alpha$ -diimine)  $[ArN=C(Me)C(Me)=N-]_2$  ( $Ar$  = 2,6- $iPr_2C_6H_3$ ) with  $AlMe_3$  afforded the bimetallic complex  $[ArN-C(Me)_2C(Me)=NAlMe_2]_2$  (4), whilst reaction of the acetyl-imino compound  $[O=C(Me)C(Me)=NAr]$  ( $Ar$  = 2,6- $Et_2C_6H_3$ ) with  $AlMe_3$  afforded the bimetallic complex  $\{[OCMe_2CH(Me)=NAr]AlMe_2\}_2$  (5). In related organozinc chemistry, we have isolated  $\{[ArNC(Me)(Et)C(Me)=NAr]ZnEt\}$  ( $Ar$  = 2,6- $iPr_2C_6H_3$ , 6) and the trinuclear complex  $\{[ArN=C(Me)COCHCO(Me)C(Me)=NAr][OCH(Me)C(Me)=NAr](ZnEt)_3\}$  ( $Ar$  = 2,6- $iPr_2C_6H_3$ , 7) from reactions of  $ZnEt_2$  with  $ArN=C(Me)C(Me)=NAr$  or  $[O=C(Me)C(Me)=NAr]$ , respectively. Reaction of the bis( $\alpha$ -diimine),  $L^{iPr-N_2}-ArCH_2Ar-N_2$ , derived from 4,4'-methylenebis(2,6-diisopropylaniline), with  $ZnCl_2$  affords  $[L^{iPr-N_2}-ArCH_2Ar-N_2(ZnCl_2)_2]$  (8). The molecular structures of complexes 1–8 are reported. Preliminary results of the ability of 1–8, along with the previously reported metal–metal bonded complex  $\{[ArN=C(Me)C(Me)=NAr]Al(THF)\}_2$  (9), to act as catalysts for the ring

opening polymerization (ROP) of the cyclic esters  $\epsilon$ -caprolactone ( $\epsilon$ -CL),  $\delta$ -valerolactone ( $\delta$ -VL) and *rac*-lactide (*r*-LA) are presented. For  $\epsilon$ -CL and  $\delta$ -VL, best results were obtained using the metal–metal bonded complex **9**. For *r*-LA, the Al-based systems exhibited moderate activity affording only liquid oligomers, whilst the Zn-based systems performed better affording at 80 °C isotactic PLA with *M<sub>n</sub>*ca. 10 kea with conversions of up to 66%. The co-polymerization of  $\epsilon$ -CL with  $\delta$ -VL was also examined, and differing preferences were noted for monomer incorporation.



Aluminum complexes, the bimetallic complexes outperformed their monometallic counterparts for the ROP of  $\epsilon$ -CL, which suggested the presence of beneficial cooperative effects.<sup>7g</sup> Also relevant to the work herein is the report by Bachmann et al.,<sup>7b</sup> who reported that zinc captions bearing the  $\alpha$ -dimming (diazadiene) ligand (MeCvNC6H3Pri-2-2,6)<sub>2</sub>, are active for the ROP of  $\epsilon$ -caprolactone under mild conditions (60 °C,  $\alpha$ -diimine ligation have been shown to be active catalysts for  $\epsilon$ -caprolactone polymerization, and were found to be highly active, which was proposed to be due to the cooperative role between the two Al(II) centers.<sup>8j</sup> The molecular structures and ROP capability towards the cyclic esters  $\epsilon$ -caprolactone ( $\epsilon$ -CL),  $\delta$ -valerolactone ( $\delta$ -VL) and *rac*-lactide (*r*-LA) of the complexes **1–9** (Chart 3), which are prepared from the pre-ligands LiPr, LEt, LMe, LEt–NO, LiPr–NO, LiPr–N<sub>4</sub> and LiPr–N<sub>2</sub>–ArCH<sub>2</sub>Ar–N<sub>2</sub>, are reported herein. The effect of the presence of these reduced  $\alpha$ -diimines on the ROP process has also been evaluated herein. The interest in the area is stimulated by the application of poly(caprolactone)/poly(lactide) type biodegradable polymers in the packaging and medical arenas. based complexes prepared herein were tested as catalysts for the ROP of  $\epsilon$ -CL (Table 2). At 30 °C, good conversions were achieved in the presence of complexes **1–3** over 60 min (runs 1–4), with the R = iPr (**1**) and Me

(3) systems outperforming the R = Et (2) system in terms of both conversion and control. The bimetallic system 4 (which is an iPr derivative) afforded only slightly higher conversion than 1 (91 vs. 89%, cf. runs 1 and 4), but with far less control (2.10 vs. 1.20). On the other hand, longer reaction times were required by the bimetallic species 5 (an ethyl derivative) in order to obtain complete conversion (480 min versus 60 min, runs 5 and 6). In the case of the Zn-based catalysts 6 and 7 (runs 7 and 8), mono-metallic 6 (an i-Pr derivative) afforded 84% conversion (run 7) with good control (1.20), whilst tri-metallic 7 (also an i-Pr derivative) afforded near quantitative conversion (99%) but with slightly less control (1.70). Interestingly, almost no activity was observed in the presence of the Zn species 8 (run 9). We ascribe this inactivity to the inefficient formation of the required catalytically active alkoxide species from this chloride pre-catalyst. Indeed, we note that in reports by other groups, the formation of M-OR species from parent a chloride complex required salt metathesis via the use of Na (or K) alkoxides, rather than by direct reaction with alcohols.<sup>24</sup> Concerning the effect of the metal center (zinc versus aluminium), slightly lower conversions and polymer Mn were observed in the presence of the Zn-species 6 at 30 °C, compared to the values obtained when using the Al-derivative 1 (cf. runs 7 and 1). Notably, the Al–Al bonded complex 9 outperformed all the other systems tested herein, allowing for complete monomer conversion within 5 minutes (run 10).

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