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Aminooxazolinate; a chiral amidinate analogue[†]

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High levels of diastereoselection with respect to chirality-atmetal are achieved at equilibrium for complexes containing a new and available range of diazaallyl ligands.

Complexes of the amidinate ligand I have an extensive stoichiometric¹ and now a considerable catalytic chemistry.^{2,3} In particular for the latter aspect, Sita and co-workers have developed a class of cyclopentadienyl complexes *e.g.* II that are capable of highly stereocontrolled α -olefin polymerisation⁴ and have potential for the development of reagents for asymmetric hydrozirconation.⁵ Also of interest is the development by Nagashima *et al.* of Kharasch cyclisation catalysed by III.⁶ These results and others indicate that chiral diazaallyl ligands have many potential applications in enantioselective synthesis using their metal complexes. However, while ligands with chiral alkyl substituents such as IV are readily prepared, free rotation about the N–C single bond(s) limits the degree to which the ligand-centred chirality is expressed in the structure of the complex. For chiral-at-metal systems⁷ this leads to modest diastereoselectivity.⁸ We thus sought cyclic analogues of IV.



Using Kim and co-workers' synthesis of 2-phenylamino-2oxazolines⁹ we prepared a range of proligands HL^{n} in two steps from commercially available isothiocyanates and optically-pure (*S*)-aminoalcohols in *ca*. 60% overall yield.[†] Treatment of HL^{1} with NaH in THF led to quantitative conversion to Na(THF)_mL¹ which may be isolated by filtration and evaporation or used directly as a ligand transfer agent. Subsequent treatment of Na(THF)_mL¹ with [{Ru(η -arene)Cl}₂- μ -Cl}₂] (arene = C₆H₆, *p*-¹PrMeC₆H₄) in THF gave crystalline [Ru(η -arene)L¹Cl] in good yield. [Ru(η -C₆H₆)L²Cl] was prepared similarly. ¹H NMR spectra of crude reaction mixtures indicate that single diastereomers are formed (d.e. > 95%, *vide infra*).

$$HL^{1} [R^{1} = Ph, R^{2} = {}^{t}Bu, R^{3} = H]$$

$$HL^{2} [R^{1} = R^{2} = Ph, R^{3} = H]$$

$$HL^{3} [R^{1} = Ph, R^{2} = R^{3} = Me]$$

$$HL^{4} [R^{1} = 3,5-Me_{2}C_{6}H_{3}, R^{2} = {}^{t}Bu, R^{3} = H]$$

$$HL^{5} [R^{1} = adamantvl, R^{2} = {}^{t}Bu, R^{3} = H]$$

The molecular structure of $(S_{\text{Ru}}, S_{\text{C}})$ -[Ru $(\eta$ -C₆H₆)L¹Cl] is shown in Fig. 1.‡ The two N–Ru bond lengths are very similar (*ca.* 2.15 Å) as are the N–Ru–Cl angles (*ca.* 85°), but there is a 17.5° fold in the

† Electronic supplementary information (ESI) available: synthesis and characterisation data for all complexes; crystal data and structure files for $(S_{\text{Ru}}, S_{\text{C}})$ - $[\text{Ru}(\eta$ - $C_6H_6)$ L¹Cl], (Δ, S_{C}) - $[\text{ZrL}^4_2(\text{CH}_2\text{Ph})_2]$ and $[\text{Ru}(\eta$ -p-iPr-MeC₆H₄)L³Cl]; DFT calculated structure files for eight diastereomers of $[\text{ZrL}^4_2(\text{CH}_2\text{Ph})_2]$. See http://www.rsc.org/suppdata/cc/b4/b409113b/



Fig. 1 Molecular structure of (S_{Ru}, S_C) -[Ru(η -C₆H₆)L¹Cl]. Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 2.150(3), Ru(1)–N(2) 2.154(3), Ru(1)–C(arene) 2.16–2.20, Ru(1)–Cl(1) 2.3997(11), N(1)–Ru(1)–N(2) 62.71(12), N(1)–Ru(1)–Cl(1) 85.74(8), N(2)–Ru(1)–Cl(1) 84.83(8).

4-membered chelate unit at the N–N vector such that O(1) is tilted slightly toward the RuCl unit.

In order to probe the possibility of metal-centred epimerisation processes and the issue of thermodynamic diastereoselection⁷ in these compounds we have synthesised chiral racemic [Ru(η -*p*-^{*i*}PrMeC₆H₄)L³Cl] [Scheme 1(a)]. The ¹H NMR spectrum of this complex at 298 K in d₈-toluene contains two resonances separated by *ca.* 0.03 ppm for the oxazolinyl 4-methyl groups, these being rendered inequivalent on complexation. As a result of this small chemical shift difference we were able to observe coalescence at 373 K. This corresponds (at 400 MHz) to a ΔG^{\ddagger} of *ca.* 95 kJ mol⁻¹ for interconversion of enantiomers.

The pure diastereomers $(S_{\text{Ru}},S_{\text{C}})$ -[Ru(η -arene)L¹Cl] were also studied by variable temperature NMR spectroscopy. The ¹H spectra in d₈-toluene did not alter significantly up to 373 K, and were identical to the starting spectra on returning to 298 K. Storage at 323 K for 14 days had no noticeable effect; no new diastereomers were observed.

Hence an epimerisation process for optically pure (S_{Ru}, S_C) -



Scheme 1 (a) Inversion of chirality-at-metal observed for racemic $[Ru(\eta-p-^iPrMeC_6H_4)L^3Cl];$ (b) only $(S_{Ru},S_C)-[Ru(\eta-arene)L^1Cl]$ (A) detected under equilibrium conditions.

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Fig. 2 Molecular structure of (Δ, S_C) -[ZrL⁴₂(CH₂Ph)₂]; most H atoms have been removed and benzyl ligands hatched for clarity. Selected bond lengths (Å) and angles (°): Zr(1)–N(1) 2.319(6), Zr(1)–N(2) 2.233(5), Zr(1)–N(3) 2.244(6), Zr(1)–N(4) 2.259(5), Zr(1)–C(38) 2.276(7), Zr(1)–C(31) 2.278(7), N(1)–C(3) 1.305(8), N(2)–C(3) 1.321(9), N(3)–C(18) 1.319(8), N(4)–C(18) 1.316(9), N(3)–Zr(1)–N(4) 59.6(2), C(38)–Zr(1)–C(31) 94.2(3), N(2)–Zr(1)–N(1) 59.3(2).

[Ru(η -arene)L¹Cl] [Scheme 1(b)] and related chiral ligand complexes is kinetically feasible on the chemical timescale, but the *thermodynamic* diastereoselection for the observed ($S_{Rus}S_C$) isomers is very high. Examination of molecular models of the unobserved ($R_{Rus}S_C$) diastereomers reveals a strong steric interaction between the oxazolinyl 4-alkyl substituent and the Ru–Cl unit [Scheme 1(b)].§[

We were interested to investigate the synthesis and stereochemical behaviour of aminooxazolinate complexes of earlier transition metals. Direct reactions of two equivalents of HL^{*n*} ($n \neq 3$) with [Zr(CH₂R)₄] (R = Ph, ^{*t*}Bu) gave a range of chiral zirconium complexes [ZrL^{*n*}₂(CH₂R)₂] in *ca.* 90% yield. Good control over metal/ligand stoichiometry is evident in these reactions, in contrast to the related (achiral) aminopyridinates.¹⁰

The molecular structure of $[ZrL_2^4(CH_2Ph)_2]$ determined by X-ray diffraction is shown in Fig. 2. The overall structure is closely related to achiral bis(benzamidinate) complexes of zirconium^{11,12} and our achiral ligand bis(aminopyridinate) complexes.¹³ The zirconium-bound benzyl methylene groups in $[ZrL_2^4(CH_2Ph)_2]$ occupy mutually *cis* positions and the *C*₂-symmetry is apparent from Fig. 2; the metal is stereogenic with Δ configuration (*vide infra*). The conformation of the benzyl ligands serves to minimise steric interactions between their phenyl groups and the oxazolinyl units, which project over the open face of the metal centre. The chelate units are folded at the N–N vectors in the same sense as in (*S*_{Ru},*S*_C)-[Ru(η -C₆H₆)L¹Cl] above, by 26.2 and 22.4°.

Investigation of metal-centred epimerisation of these zirconium compounds was hampered by the inaccessibility of complexes containing achiral L³, presumably for steric reasons.§ ¹H NMR spectra of (Δ, S_C) -[ZrL⁴₂(CH₂Ph)₂] in d⁸-toluene varied little in appearance from 363 K to the onset of viscosity broadening. Only one set of signals was evident throughout. While we expect inversion of chirality-at-metal to be rapid relative to that in the ruthenium compounds above, we have previously reported chiral-at-zirconium systems which exhibit slow exchange at ambient temperature on the NMR chemical shift timescale.¹⁴ We thus turned to computational methods as a probe of the relative stability of possible diastereomers.

 $[ZrL_{2}^{4}(CH_{2}Ph)_{2}]$ has eight possible six-coordinate S_{C} -diastereomers. DFT calculations† on the Δ -*cis,trans,cis* isomer led to an optimised structure which was indistinguishable from that observed in the solid state (Fig. 2). The remaining seven isomers were found to be 45–111 kJ mol⁻¹ less stable; only in the observed isomer are the oxazolinyl alkyl substituents able to point into regions of steric space. In other words, the same effects dominate the stereochemical preference here as in the ruthenium compounds above.

Hence in complexes of aminooxazolinate with zirconium and ruthenium the chirality of the ligand is expressed very efficiently in the structure of the complex. The thermodynamic diastereoselection is excellent. We are currently investigating stereoselective catalytic applications of this type of complex guided by the chemistry of the functionally related amidinates.

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Notes and references

[‡] Crystal data: (*S*_{Ru},*S*_C)-[Ru(η-C₆H₆)L¹Cl]: C₁₉H₂₃ClN₂ORu, *M* = 431.91, orthorhombic, *a* = 10.1427(4), *b* = 11.1134(4), *c* = 16.1543(6) Å, *U* = 1820.91(12) Å³, *T* = 180 K, space group *P*2₁2₁2₁, *Z* = 4, μ(Mo-Kα) = 1.015 mm⁻¹, 4368 independent reflections (*R*_{int} = 0.0574). Final *R*1 = 0.0368 [*I* > 2σ(*I*)] CCDC 246168. [ZrL⁴₂(CH₂Ph)₂]: C₄₄H₅₆N₄O₂Zr, *M* = 764.15, orthorhombic, *a* = 10.1903(2), *b* = 17.3251(4), *c* = 25.7931(4) Å, *U* = 4553.72(16) Å³, *T* = 180 K, space group *P*2₁2₁2₁, *Z* = 4, μ(Mo-Kα) = 0.277 mm⁻¹, 11289 independent reflections (*R*_{int} = 0.1133). Final *R*1 = 0.0892 [*I* > 2σ(*I*)]. CCDC 246169. [Ru(η-*p*^{-*i*}PrMeC₆H₄)L³Cl]: CCDC 246170. See http://www.rsc.org/supp-data/cc/b4/b409113b/ for crystallographic data in .cif or other electronic format.

§ The molecular structure of racemic $[Ru(\eta-p-iPrMeC_6H_4)L^3Cl]$ (see ESI†) provides evidence of this type of steric compression. We suggest that the low synthetic yield of this compound (17%) is a direct result of this unfavourable interaction.

¶ In Brunner *et al.*¹⁵ and Davies *et al.*¹⁶ related ruthenium salicyloxazoline complexes the opposite situation prevailed, *i.e.* the major (or exclusive) product was in most cases the equivalent of isomer **B** [Scheme 1(b)]. Examination of molecular structures for both series indicates that this disparity arises from the variance in chelate ring size. For the 6-membered chelate salicyloxazolines, avoidance of steric compression between the alkyl group and the η -arene dominates. For the present system with 4-membered chelates, this potential steric interaction with the η -arene is minimised, but that with the Ru–Cl unit depicted in Scheme 1(b) is exacerbated. See also ref. 17.

- F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403; J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.
- 2 E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2000, 497.
- 3 V. Volkis, M. Schmulinson, C. Averbuj, A. Livovskii, F. T. Edelmann and M. S. Eisen, *Organometallics*, 1998, **17**, 3155; C. Averbuj, E. Tish and M. S. Eisen, *J. Am. Chem. Soc.*, 1998, **120**, 8640; D. Herskovics-Korine and M. S. Eisen, *J. Organomet. Chem.*, 1998, **503**, 307.
- 4 L. R. Sita, R. J. Keaton, K. C. Jayaratne, D. A. Henningsen and L. A. Koterwas, *J. Am. Chem. Soc.*, 2001, **123**, 6197; L. R. Sita and K. C. Jayaratne, *J. Am. Chem. Soc.*, 2000, **122**, 958; L. R. Sita and Y. Zhang, *Chem. Commun.*, 2003, 2358.
- 5 L. R. Sita, R. J. Keaton and Y. Zhang, J. Am. Chem. Soc., 2003, 125, 8746.
- 6 H. Nagashima, M. Gondo, S. Masuda, H. Kondo, Y. Yamaguchi and K. Matsubara, *Chem. Commun.*, 2003, 442.
- 7 (a) H. Brunner, Eur. J. Inorg. Chem., 2001, 905; (b) C. Ganter, Chem. Soc. Rev., 2003, 32, 130; (c) J. W. Faller and A. R. Lavoie, New J. Chem., 2003, 27, 899.
- 8 For example, the two diastereomers of [CpTi(IV)Me₂] are observed in approximately equal quantities (L. A. Koterwas, J. C. Fettinger and L. R. Sita, *Organometallics*, 1999, 18, 4183), and diastereoselection in similar molybdenum cyclopentadienyls is relatively low (M. Draux and I. Bernal, *Inorg. Chim. Acta*, 1986, 114, 75 and references therein).
- 9 T. H. Kim, N. Lee, G.-J. Lee and J. N. Kim, Tetrahedron, 2001, 57, 7137.
- 10 R. Kempe, Eur. J. Inorg. Chem., 2003, 5, 791.
- 11 J. R. Hagdahorn and J. Arnold, J. Chem. Soc., Dalton Trans., 1997, 3087.
- 12 D. Herskovics-Korine and M. S. Eisen, J. Organomet. Chem., 1998, 503, 307.
- 13 C. Morton, P. O'Shaughnessy and P. Scott, Chem. Commun., 2000, 2099.
- 14 I. J. Munslow, A. J. Clarke, R. J. Deeth, I. Westmoreland and P. Scott, *Chem. Commun.*, 2002, 1868.
- 15 H. Brunner, B. Nuber and M. Prommesberger, *Tetrahedron: Asymmetry*, 1998, 9, 3223.
- 16 A. J. Davenport, D. L. Davies, J. Fawcett and D. R. Russell, *Dalton Trans.*, 2004, 1481.
- H. Brunner, R. Oeschey and B. Nuber, *Organometallics*, 1996, 15, 3616;
 H. Brunner, R. Oeschey and B. Nuber, *Dalton Trans.*, 1996, 1499.