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Perfect complementarity in the fitting of two homochiral heterodonor ligands around a nickel(II) centre: an 'intramolecular embrace'

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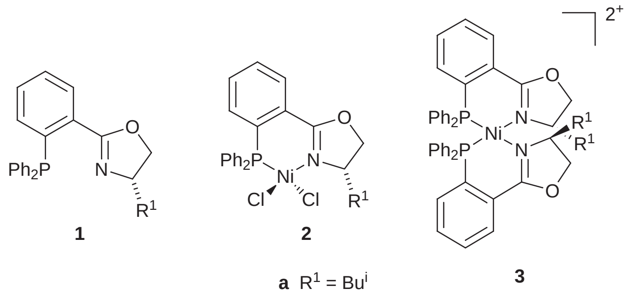
The homochiral form of the complex $[(\text{'P,N'})_2\text{Ni}]^{2+}$ ('P,N' is a phosphino–heteroatom bidentate ligand) has been found to be more stable than its heterochiral analogue due to a 'fitting' of the two 'P,N' ligands about the Ni that is reminiscent of an 'intramolecular embrace'.

Chiral ligand self-recognition phenomena have been reported for transition-metal complexes of the type $[(\text{P,P})_2\text{M(L)}_n]$ where 'P,P' is a bidentate chiral diphosphine ligand.[1] However, there have been no reports of such phenomena with phosphinoaryl oxazolines **1** (Fig. 1). These have been the subject of much recent attention[2] along with other[3] phosphino–heteroatom bidentate ligand systems ('P,X ligands'; X = N, O or S). Complexes of **1**, which can function as highly enantioselective catalysts, all show remarkable similarity in ligand conformation which therefore appears to be independent of the other ligands at the transition-metal centre as well as the metal geometry itself.[4]

Herein we report on the Ni^{II} complex **3a** in which there is homochiral self recognition of ligand **1a**. Reaction of the purple-black coloured paramagnetic Ni^{II} complex (4*S*)-**2a** (0.082 mmol) in THF (2.5 ml) with 2 equivalents of AgO_3SCF_3 in the presence of 1 equivalent of (4*S*)-**1a** affords, after work-up, [(4*S*),(4′*S*)]-**3a** as a bright orange crystalline solid in 97% yield.[4e] Diamagnetic ^{1}H and ^{31}P NMR spectra, indicate that the complex is symmetrical with a geometry close to square planar or a highly distorted octahedron. Two arrangements of the P,N ligand allow for a square planar geometry, Fig. 2. Although at first glance, arrangement *T* appears less sterically demanding than *C*, the two ligands **1a** in arrangement *C* fit surprisingly well (see below) and additionally this arrangement may be preferred since the π-accepting P centres are *trans* to the σ-donating N centres. To study the geometry of [(4*S*),(4′*S*)]-**3a** in solution we obtained 500 MHz ^{1}H NOESY spectra in CDCl_3 (*ca.* 0.01 M, 25 °C). The resonance arising from the proton attached to C(3A/B) in **3a** is readily identified.‡ There are two key negative-phase cross-peaks: the first between C(3A/B)H and one of the two diastereotopic CH_3 groups [δ 0.81; C(24A/B)] and the second between C(20A/B)H_{anti} and the other diastereotopic CH_3 group [δ 0.82 C(25A/B)]. Importantly, these cross-peaks are not observed in the NOESY spectrum of **1a** and thus the NOE cross-peaks observed in **3a** are interligand and not intraligand.§ Only arrangement *C* accounts for all of the solution phase NMR data.

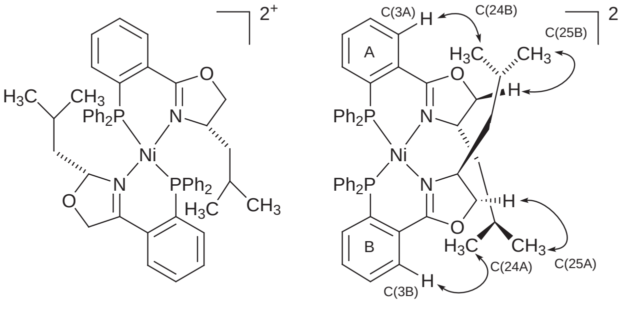
A single octahedral shaped crystal of [(4*S*),(4′*S*)]-**3a** was selected and studied by X-ray diffraction.¶ Two views of the structure are presented in Fig. 3. The preferred structure for **3a** is thus arrangement *C* both in the solid state and in solution. The ligand substructures of **1a** in **2a** and **3a** are almost superimposable and thus the two ligands (**1a**) in **3a** influence each other surprisingly little. This arises by a near-perfect complementarity in the fitting of the two ligands about the Ni^{II} centre and it is the homochirality of the complex which allows this fitting. The conformational preference of **1** in its metal complexes arises from the placement of the substituent at the stereogenic carbon of the oxazoline ring in a pseudo-axial position relative to the P–M–N plane. This reduces steric clashing in the equatorial space about the co-ordination sphere and as a consequence of the rigidity of the aryl ring that connects the oxazoline and diphenylphosphino moieties a helical chirality is induced in the triaryl phosphine donor. The prevailing conformational bias in **1a** allows the two triaryl phosphine units to engage in the 'double phenyl embrace' described by Dance and Scudder[5] and the stereogenic substituents to occupy opposite faces of the square plane. In the heterochiral assembly there would be at



1 **2** **3**

a $\text{R}^1 = \text{Bu}^{\text{i}}$

Fig. 1 Phosphinoaryl oxazoline ligands **1** and Ni^{II} complexes **2** and **3**



3a (*T*) **3a** (*C*)

Fig. 2 Two arrangements of **1a** in complex **3a** with key interligand NOE in **3a** (*C*)

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‡ In both **1a** and **3a** this will be the only aromatic ^{1}H NMR signal approximating a doublet, all other *ortho* protons have a $^3J_{\text{HP}}$ coupling. In **3a** this doublet is significantly downfield (δ 8.1) and well separated from the bulk of the aromatic region.

§ The NOE systems are thus [C(3A)H; C(24B)H_3]/[C(3B)H; C(24A)H_3] and [C(25A)H_3; C(20B)H_{anti}]/[C(25B)H_3; C(20A)H_{anti}]. In the NOESY spectrum of a mixture of **3a** and **1a** there were no intermolecular positive-phase cross-peaks and thus no evidence for ligand exchange on the NMR time-scale.

¶ Crystal data for complex $\mathbf{3a}[\text{O}_3\text{SCF}_3]_2\cdot\text{H}_2\text{O}$: $\text{C}_{52}\text{H}_{52}\text{F}_6\text{N}_2\text{NiO}_9\text{P}_2\text{S}_2$, *M* = 1147.73, orthorhombic, space group $P2_12_12_1$, *a* = 12.6377(5), *b* = 15.6545(6), *c* = 28.4325(11) Å, *U* = 5625.0(4) Å^3, *Z* = 4, μ = 0.549 mm^{-1}, *T* = 173(2) K. Data: 36 176 total, 12 884 unique, $R_{\text{int}} = 0.1124$. Final *R*1 = 0.0647 for all 6540 data with $F^2 > 2\sigma(F^2)$. CCDC reference number 186/942. See http://www.rsc.org/suppdata/dt/1998/1421/ for crystallographic files in .cif format.

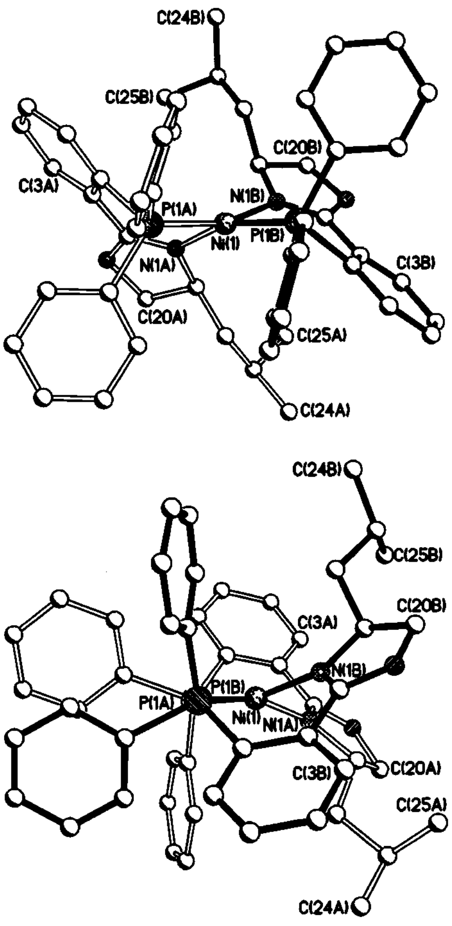

Fig. 3 Two views of the molecular structure of dication [(4*S*),(4′*S*)]-**3a**. Triflate counter ions and the single water of crystallisation are not shown. For clarity, the bonding in ligand **1a** (A) is white and in ligand **1a** (B) it is black. Selected bond lengths (Å) and angles (°): Ni(1)–N(1A) 1.918(4), Ni(1)–N(1B) 1.924(4), Ni(1)–P(1A) 2.172(2), Ni(1)–P(1B) 2.179(0); N(1A)–Ni(1)–N(1B) 90.0(2), N(1A)–Ni(1)–P(1A) 86.27(13), N(1B)–Ni(1)–O(1A) 161.76(13), N(1A)–Ni(1)–P(1B) 161.02(13), N(1B)–Ni(1)–P(1B) 87.66(12), P(1A)–Ni(1)–P(1B) 101.49(6). Dihedral angle between P_2Ni/N_2Ni planes: 24°

least two points of severe steric clashing, one between the two pseudo-equatorial phenyl rings and one between the two isobutyl chains (Fig. 4). In stark contrast homochiral [(4*S*),(4′*S*)]-**3a** has a 'fully staggered' conformation along the P–P axis.

To test whether homochiral **3a** would be kinetically favoured over heterochiral **3a** from a reaction that could produce either complex, (4*S*)-**2a** (0.13 mmol) was reacted with 2 equivalents of AgO_3SCF_3 and (±)-**1a** in THF (5 ml). This reaction afforded solely the homochiral form of **3a** (>95%) in a high state of purity (as judged by ^1H and ^{31}P NMR spectroscopy) but in 30% enantiomeric excess (e.e.).‖ A survey of the CSD[6] indicates that [(4*S*),(4′*S*)]-**3a** is the first example of a crystal structure in which there is homochiral fitting of two bidentate nitrogen–triaryl phosphine donor ligands forming a six-membered chelate about a square planar metal centre. Notably, a few tetradentate systems have been reported.[7] However, in these cases the relative configurations of the two halves of the tetradentate ligand unit are pre-set and hence matching or mismatching is enforced.

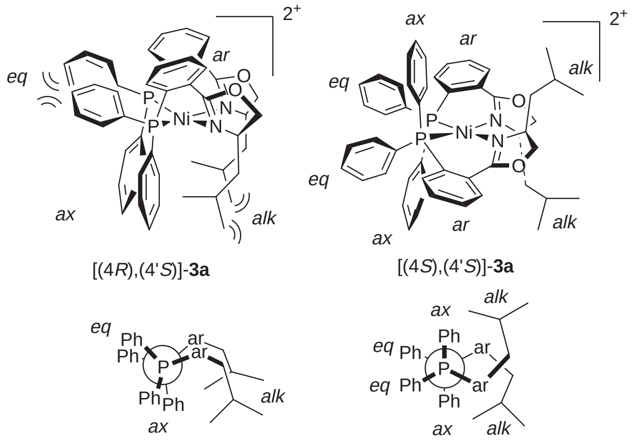

Fig. 4 Schematic representations of heterochiral and homochiral forms of complex **3a**

Acknowledgements

Complex **3a** was first synthesised (by G. C. L.-J.) in the laboratories of Professor Andreas Pfaltz, University of Basel. G. C. L.-J. thanks the Zeneca Strategic Research Fund for generous support and Professor A. Guy Orpen for helpful discussions.

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Received 10*th February* 1998; *Communication* 8/01170B

‖ The e.e. value indicates thermodynamic equilibration. In further experiments, zero rotation (α) was observed immediately after mixing equal volumes of solutions of [(4*S*),(4′*S*)]-**3a** (2.0 mM) and (4*R*)-**1a** (4.0 mM) in CH_2Cl_2 in the cell of a polarimeter and pure homochiral but racemic (±)-**3a** was recovered in 57% yield from reaction of [(4*S*),(4′*S*)]-**3a** (0.043 mmol) with 2 equivalents of (4*R*)-**1a** in CH_2Cl_2 (5 ml). Thus, ligand exchange occurs rapidly.