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Constrained coordination through atropisomerism: Synthesis and structure of an η^5 : κN -bidentate N,N-dimethylaniline-functionalised indenylruthenium(II) complex

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Abstract

Reaction of 1-(2-*N*,*N*-dimethylaminophenyl)-2-methylindenyllithium with (Ph₃P)₃RuCl₂ affords the chloro(indenyl)bis(triphenylphosphine)ruthenium(II) complex **5**, where the nitrogen is not coordinated to the metal. The corresponding reaction of 1-(2-*N*,*N*-dimethylamino-6-methylphenyl)-2-methylindenyllithium affords the chloro(η^5 : κ *N*-indenyl)(triphenylphosphine)ruthenium(II) complex **6**, which has been characterised by single crystal X-ray analysis. © 2005 Elsevier B.V. All rights reserved.

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The chemistry of cyclopentadienyl ligands bearing pendant donor atoms is a rapidly growing area, with the potential to produce metal complexes of unique structure and reactivity compared with conventional cyclopentadienyl ligands [1]. When the side-chain donor is a hard atom such as nitrogen, hemilabile interactions are usually observed with transition metals in a low oxidation state, while isolable complexes showing a nitrogen-metal bond are normally observed only for transition metals in their higher oxidation states [1b]. While the vast majority of cyclopentadienyl ligands bearing pendant donor atoms employ flexible bridging units [1], Enders et al. [2] have been exploring the chemistry of 2-N,N-dimethylaminophenyl and 8-quinolylfunctionalised cyclopentadienyl and indenyl ligands,¹ with the geometric constraints present in such ligands enhancing interactions between the nitrogen and π -complexed metals. We have also been examining the preparation of indenyl and fluorenyl ligands containing an aromatic bridge to a second coordination site, with the initial purpose of our design being the enantiospecific synthesis of planar chiral complexes using axial chirality in the ligands [5]. It occurred to us that the atropisomerism of our ligands could also be used as an additional constraint to favour the coordination of a hard donor atom to metals in lower oxidation states, rendering the metal more electron-rich. Here, we describe the preparation of two closely related N,N-dimethylaniline-funtionalised indenvlruthenium(II) complexes designed to demonstrate this constrained coordination.

We sort to prepare a pair of ligands as alike as possible electronically, differing only in the degree of steric demand around the bond between the cyclopentadienyl moiety and the aromatic bridge. The ligands were prepared from methyl 2-*N*,*N*-dimethylaminobenzoate **1**

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¹ Bergman and co-workers [3] have also described the preparation of some Ir and Zr complexes of an N,N-dimethylaniline-substituted cyclopentadienyl ligand, and Djukic and co-workers [4] have described the preparation of cymantrenes, benzocymatrenes and dibenzocymantrenes containing a 1,2-phenylidene bridge to pendant azaheterocylic ligands.

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Scheme 1. Synthesis of complexes **5** and **6**: (i) o-[CH₃CH(MgBr) CH₂]C₆H₄MgBr (3 equiv.), THF, -78 to 25 °C, 48 h; (ii) conc. HCl, ethanol, reflux, 48 h; (iii) BuLi (1.2 equiv.), ether, 25 °C, 10 min, then (Ph₃P)₃RuCl₂ (0.9 equiv.), benzene, 70 °C, 16 h.

and methyl 2-*N*,*N*-dimethylamino-6-methylbenzoate **2** (Scheme 1) through reaction with an excess of the di-Grignard reagent derived from *o*-bromo(2-bromo-propyl)benzene followed by acid-catalysed dehydration of the intermediate 1-indanols [6]; ligands **3** and **4** were isolated in overall yields of 79% and 67%, respectively.

Indene **3** was treated with BuLi (1.2 equiv.) in ether solution during 10 min at RT, the solvent replaced with benzene, and (Ph₃P)₃RuCl₂ (0.9 equiv.) then added. After stirring for 16 h at 70 °C, the reaction mixture was subjected to flash chromatography under an atmosphere of argon eluting with dichloromethane; complex **5**,² obtained in 75% yield (based on ruthenium), crystallised from benzene–hexane solution as orange microcrystals.³ The ³¹P{¹H} NMR (CD₂Cl₂) spectrum⁴ of complex **5** at 300 K shows the two inequivalent phosphorus signals (due to the planar chirality of the complex) at δ_P 35.8 and 48.5, with ²J_{PP} = 39 Hz. In the ¹H NMR (CD₂Cl₂) spectrum⁴ the indenyl 3-H and 2-Me appear as broadened singlets at δ_H 4.35 and 1.51, respectively, and the *N*,*N*-dimethylamino signal appears as a sharp singlet at $\delta_{\rm H}$ 2.00, upfield compared with the signal for the *N*,*N*-dimethylamino group in the starting ligand **3** at $\delta_{\rm H}$ 2.60. This indicates that the nitrogen is not coordinated to the metal and is located on the opposite face of the indenyl ring. Consistent with this, the phenyl 6-H experiences a strong downfield shift ($\delta_{\rm H}$ 9.03, ${}^{3}J_{6,5} = 7.6$ Hz, ${}^{4}J_{6,3} = 1.5$ Hz) owing to a large steric interaction with the metal; similar deshielding effects have been observed in chromium tricarbonyl complexes of axially chiral biaryls [7].

In the ${}^{31}P{}^{1}H{}$ NMR spectrum of complex 5, the lower field phosphorus signal exhibits substantial broadening. Variable temperature NMR spectra (d_8 -toluene) were obtained to determine the nature of the fluxional behaviour responsible for this.⁴ At 194 K the ${}^{31}P{}^{1}H{}$ NMR spectrum displays two pairs of doublets at δ_P 59.5 and 35.5, with ${}^{2}J_{\rm PP} = 48$ Hz, and $\delta_{\rm P}$ 40.1 and 29.9, with ${}^{2}J_{PP} = 33$ Hz, in a ratio of ca. 3:2, respectively. The ¹H NMR spectrum at this temperature shows the N,N-dimethylamino signal as a broad singlet at $\delta_{\rm H}$ 1.90, similar to the chemical shift at 300 K ($\delta_{\rm H}$ 1.96), and the phenyl 6-H as two signals at $\delta_{\rm H}$ 10.26 and 9.43, in a ratio of ca. 3:2, respectively. This indicates that the two species observed at 194 K both have the N,Ndimethylamino group on the opposite face of the indenyl ring to the metal. Simulation⁵ of a series of ${}^{31}P{}^{1}H{}$ NMR spectra obtained between 194 and 349 K provided kinetic data for the conversion of the major to the minor conformer observed at 194 K. An Eyring plot for the kinetic data and a linear least-squares analysis gave values of $\Delta G_{272}^{\ddagger} = 43.5 \pm 2.2 \text{ kJ mol}^{-1}$, $\Delta H^{\ddagger} = 45.4 \pm 1.0 \text{ kJ mol}^{-1}$ and $\Delta S^{\ddagger} = 6.9 \pm 4.0 \text{ J mol}^{-1} \text{ K}^{-1}$ (95% confidence limits). These values are consistent with the fluxional behaviour arising from hindered rotation around the metal-indenvl bond [10].

Indene 4 was metallated under identical conditions to 3; following flash chromatography under an atmosphere of argon eluting with 5% ethyl acetate–dichloromethane, complex 6^2 was obtained in 44% yield, crystallising from benzene–hexane solution as black prisms.³ The ³¹P{¹H} NMR (CD₂Cl₂) spectrum⁴ of complex 6 at 300 K shows two singlets at δ_P 44.2 and 39.6 in a ratio of ca. 2:1, respectively; these signals derive from the presence of two diasteroisomers, (p R^*, R^*_{Ru})-6 and (p R^*, S^*_{Ru})-6, respectively (Fig. 1). The ¹H NMR (CD₂Cl₂) spectrum⁴ of the complex confirms the coordination of the nitrogen to the metal and allows the assignment of relative configurations through the differential shielding effects produced by

 $^{^2}$ Complexes **5** and **6** are prepared here as racemic mixtures, however, for simplicity only one enantiomer is illustrated.

³ Analytical data for complexes **5** and **6**. Complex **5**: Found C, 71.5; H, 5.6; N, 1.55. $C_{54}H_{48}CINP_2Ru$ requires C, 71.3; H, 5.3; N, 1.55%. Complex **6**: Found C, 70.05; H, 5.65; N, 1.95. $C_{37}H_{35}CINPRu \cdot C_6H_6$ requires C, 69.85; H, 5.6; N, 1.9%.

⁴ The ¹H and ³¹P{¹H} NMR spectra for complexes **5** and **6**, and the variable temperature ${}^{31}P{^{1}H}$ NMR spectra for complex **5** are available as online supplementary data.

⁵ Simulations were carried out using the DNMR3 [8] utility within Spinworks Ver. 2.4 [9] using a two site exchange model with independent ${}^{2}J_{PP}$ values. Triphenylphosphine oxide was added as an internal standard for signal intensities and chemical shifts. Temperature calibration was based on the chemical shift dependence of methanol.



Fig. 1. Diastereoisomers of complex 6.

the proximity of the triphenylphosphine ligand. Thus, for (pR^*, R_{Ru}^*) -6 the indenyl 3-H appears as a singlet at δ_H 4.18 and the indenyl 2-Me a doublet at δ_H 1.93, with ${}^4J_{HP} = 3.0$ Hz; the phenyl 6-Me appears as a singlet at δ_H 2.27; and the *N*-methyl signals appear as two broadened singlets at δ_H 2.46 and 2.82. In the case of (pR^*, S_{Ru}^*) -6 the proximity of the triphenylphosphine ligand produces a shielding effect on the indenyl 3-H and 2-Me signals; the indenyl 3-H appears as a doublet at δ_H 3.54, with ${}^3J_{HP} = 2.9$ Hz, and the indenyl 2-Me a singlet at δ_H 0.32; the phenyl 6-Me appears as a singlet at δ_H 2.17; and the *N*-methyl signals appear as two broad singlets at δ_H 2.71 and 2.87.

Complex 6 crystallised from benzene-hexane solution in a centrosymmetric space group, with X-ray structure analysis revealing the presence of only the (pR^*, R_{Ru}^*) -6 diasteroisomer (Fig. 2).⁶ However, the ³¹P{¹H} and ¹H NMR spectra obtained within a few minutes of re-dissolving (pR^*, R_{Ru}^*) -6 in CD_2Cl_2 at ambient temperatures again show a ca. 2:1 equilibrium mixture of (pR^*, R_{Ru}^*) -6 and (pR^*, S_{Ru}^*) -6, respectively. Equilibration also occurred rapidly in C₆D₆ solution, however, in this case the equilibrium ratio was ca. 4:1 of (pR^*, R_{Ru}^*) -6 and (pR^*, S_{Ru}^*) -6, respectively. Facile racemisation or epimerisation of chiral-at-metal halfsandwich complexes has been previously observed for a number of systems [11]. The indenyl ligand shows typical slip-fold distortions in the solid state, with a slip distortion $\Delta = 0.091(2)$ Å, hinge angle = 6.6° and fold angle = 11.5° [12]. These values are within the range classified as distorted η^5 -coordination [12]. In addition, the metal is displaced towards the pendant amine



Fig. 2. ORTEP plot of (pR^*, R_{Ru}^*) -6, with crystallographic numbering [the (pS, S_{Ru}) -enantiomer is shown]; 50% thermal ellipsoids are shown for non-hydrogen atoms. Selected distances (Å) and angles (°): Ru(1)–C(1) 2.1179(9), Ru(1)–C(2) 2.1750(9), Ru(1)–C(3) 2.1674(10), Ru(1)–C(4) 2.2410(9), Ru(1)–C(9) 2.2250(9), Ru(1)–Cl(1) 2.4217(2), Ru(1)–P(1) 2.3347(3), Ru(1)–N(1) 2.3052(8) and Cl(1)–Ru(1)–P(1) 85.353(9), Cl(1)–Ru(1)–N(1) 92.37(2), P(1)–Ru(1)–N(1) 105.87(2).

ligand, with the Ru(1)–C(1) bond 0.0495(20) Å shorter than the Ru(1)–C(3) bond, and the Ru(1)–C(9) bond 0.016(2) Å shorter than the Ru(1)–C(4) bond.

There have been relatively few cyclopentadienylruthenium half-sandwich complexes functionalised with a pendant donor nitrogen described in the literature [2g,13]. Only in those cases of cationic ruthenium(II) complexes has a bond between the metal and the pendant nitrogen been observed; thus, the failure of the pendant amine to displace triphenylphosphine in the case of complex 5 was not unexpected. The formation of the η^5 : κN -bidentate complex 6 demonstrates how appropriate steric constraints can be introduced into aromatic-bridged chelating cyclopentadienyl ligands to favour the coordination of a hard donor atom. In future work, we will be exploring the scope of this approach and its effect on metal reactivity.

Appendix A. Supplementary data

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (Deposition No. 267612). Copies of the information can be obtained from The Director, CCDC, 12 Union Road, Cambridge, CD2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2005.06.002.

⁶ Crystal data for (p*R**, *R*^{*}_{Ru})-**6** · C₆H₆ : C₄₃H₄₁ClNPRu, *M* = 739.26, monoclinic, space group *P*₂₁/*n* (no. 14), *a* = 9.8130(3), *b* = 14.1066(4), *c* = 24.8746(8) Å, β = 91.699(2), *V* = 3441.83(18) Å³, *T* = 150(2) K, *Z* = 4, μ(Mo-Kα) = 0.612 mm⁻¹, *N* = 110,903, *N*(unique) = 16,455 (*R*_{int} = 0.0219), *N*_{obs} = 14,401 [*I* > 2σ(*I*)]. The asymmetric unit contains the complex molecule and a benzene solvate molecule disordered over three orientations with occupancies refined and then fixed at 0.4, 0.4 and 0.2, respectively. In general, the non-hydrogen sites were modelled with anisotropic displacement parameters and a riding atom model with group displacement parameters was used for the hydrogen atoms. The partially occupied non-hydrogen sites were modelled with isotropic displacement parameters. Final *R*₁(*F*) = 0.0259, *wR*₂(*F*²; all data) = 0.0728.

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