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Synthesis and Structures of Ruthenium and Iron Complexes Bearing an Unsymmetrical Pincer-type Ligand with Protic Pyrazole and Tertiary Aminoalkyl Arms

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Dedicated to Professor F. Ekkehardt Hahn on the Occasion of His 60th Birthday

Keywords: Iron; Ruthenium; N ligands; Tridentate ligands; Hydrogen bonds

Abstract. A protic pyrazole-armed NNN-type pincer ligand 2-(5-*tert*-butylpyrazol-3-yl)-6-(diethylaminomethyl)pyridine (**LH**) with a tertiary aminomethyl tether was synthesized as a new template for metal-ligand bifunctional catalysts furnished with proton-responsive pyrazole and hemilabile amine as the cooperating units. Treatment of **LH** with *trans*-[$RuCl_2(Me_2SO)_4$] and anhydrous $FeCl_2$ led to the formation of the pincer-type ruthenium complex [$RuCl_2(Me_2SO$-*S*)(**LH**)] (**2**) and iron complex [$FeCl_2$(**LH**)] (**3**), respectively. Detailed structures of **2**·CH_2Cl_2 and **3** were determined by X-ray crystallography. The Brønsted acidic pyrazole NH group proved to be engaged in intra- or intermolecular hydrogen bonding. Catalytic hydrogenation of acetophenone with the protic pincer-type complexes **2** and **3** was also investigated.

Introduction

The meridional, tridentate pincer-type ligands have been used as scaffolds for rational construction of rigid coordination environments with thermal stability. The modular nature of the ligand design has led to the development of structurally diversified pincer-type complexes, which have been applied successfully to bond activation and catalytic processes.[1] As an extension of our continuing study on metal-ligand bifunctional catalysts,[2] we have recently been interested in pincer-type ligands furnished with two proton-delivering pyrazole arms, because such ligands would offer a platform for long-range metal-ligand cooperation by the pyrazole NH groups at the position β to the metal.[3–6] A particularly demonstrative example is provided by a 2,6-bis(pyrazol-3-yl)pyridine iron complex, which catalyzes disproportionation of hydrazine through intramolecular multiproton-coupled electron transfer between the ligated substrates.[3] On the other hand, *Milstein* and coworkers revealed that ruthenium complexes bearing a PNN-type pincer ligand with a diethylaminomethyl arm catalyze dehydrogenative couplings of alcohols and amines,[7] and also mediates water splitting.[8] It is notable that, in some cases, dissociation of the amino group to create a vacant coordination site during the reactions was proposed in addition to the metal-ligand cooperation triggered by reversible dearomatization of the pincer ligand.

In this context, the ligand design to allow appropriate location of both protic pyrazole and hemilabile tertiary amine arms appears an attractive strategy to realize effective metal-igand bifunctional catalysis. We report herein the synthesis of a (protic pyrazole)-aminoalkyl hybrid pincer-type ligand **LH** and its complexation to ruthenium and iron. The catalytic performance of these protic pincer-type complexes for hydrogenation of a ketone was also evaluated.

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Results and Discussion

Synthesis of a Protic Pincer-Type Ligand with an Aminomethyl Arm

We have recently demonstrated that the desymmetrized pyridinedicarboxylic acid derivative **1**[9] can be converted to an unsymmetrical pincer-type complex bearing a protic N-heterocyclic carbene arm in addition to a pyrazole arm.[4] The procedure was applied to the designed pincer-type ligand **LH**; amination of **1** and subsequent construction of the pyrazole ring successfully afforded **LH** in good yield, as summarized in Scheme 1.

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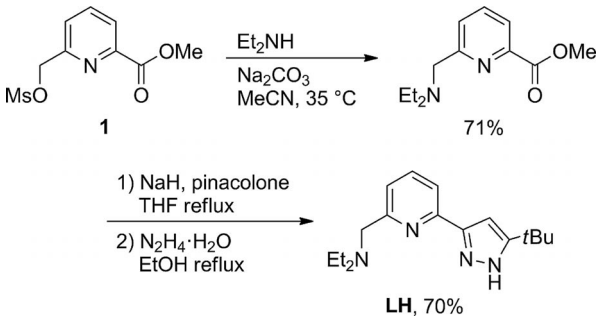
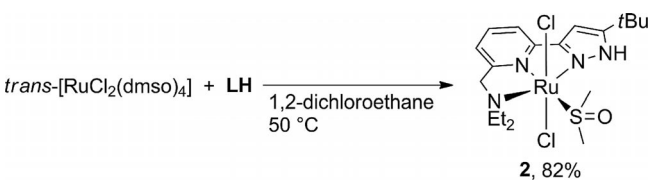


Scheme 1. Preparation of the unsymmetrical pincer-type ligand **LH**.

Synthesis and Structure of the Ruthenium Complex

When *trans*-[$RuCl_2$(dmso)$_4$] (dmso = Me_2SO) was treated with a slight excess of **LH** at 50 °C, the dichloridoruthenium(II) complex [$RuCl_2$(dmso)(**LH**)] (**2**) was obtained in good yield (Scheme 2). The ^{1}H NMR spectroscopy indicates the approximate C_s symmetry of **2** as well as the presence of the Brønsted acidic NH group (δ = 13.04 ppm). Unlike for the free ligand **LH**, the methylene resonances for the diethylamino group appear diastereotopic, which substantiates the chelation of the aminomethyl arm in solution. X-ray analysis of **2** definitely revealed that the pincer-type tridentate ligation of **LH**, as depicted in Figure 1 (selected bond lengths and angles are listed in Table 1). An S-bound dimethylsulfoxide ligand *trans* to the pyridine moiety is engaged in an intramolecular hydrogen bonding interaction with a short NH···O contact (N1···O1: 2.719(8) Å). The hemilabile nature of the aminomethyl arm may be suggested by the Ru–N4 distance (2.216(6) Å), which is much longer than those of the rest Ru–N bonds (2.012(6) and 2.029(5) Å) and comparable with that in the related PNN-type pincer complex [RuHCl(CO)(PNN)] (PNN = (tBu$_2$PCH$_2$)(Et$_2$NCH$_2$)C$_5$H$_3$N, 2.260(2) Å).[10] In spite of the relatively long Ru–N distance, however, dissociation of the tertiary amine arm was not observed in the ^{1}H NMR spectroscopy criteria (vide supra) even at 60 °C.



Scheme 2. Preparation of ruthenium complex **2**.

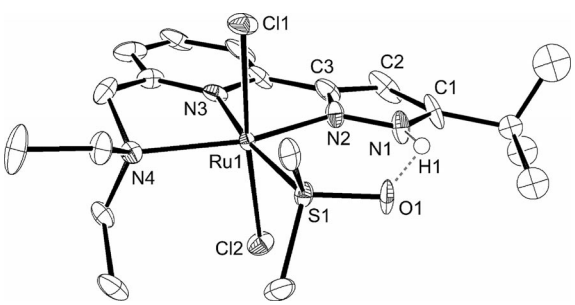


Figure 1. Crystal structure of **2**·CH_2Cl_2. The hydrogen atoms except for the pyrazole NH hydrogen as well as the solvating molecule and a minor component of the disordered tBu group are omitted for clarity. Ellipsoids are drawn at the 30% probability level.

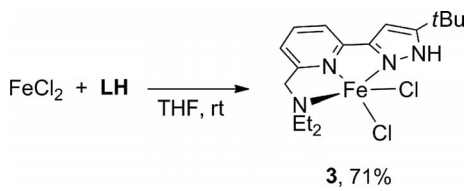
Table 1. Selected bond lengths /Å and angles /° for **2** and **3**.

	2·CH_2Cl_2	**3**
M–Cl1 [a]	2.417(2)	2.3431(6)
M–Cl2 [a]	2.403(2)	2.2838(5)
Ru1–S1	2.236(2)	
M–N2[a]	2.029(5)	2.1734(12)
M–N3[a]	2.012(6)	2.1178(11)
M–N4[a]	2.216(6)	2.3192(12)
N1–N2	1.320(8)	1.353(2)
N1–C1	1.352(9)	1.357(2)
C1–C2	1.421(11)	1.385(2)
C2–C3	1.357(11)	1.399(2)
N2–C3	1.342(10)	1.345(2)
H1···*X*[b]	1.980	2.269
N2–N1–C1	112.4(6)	112.18(11)
N1–N2–C3	106.2(6)	104.97(11)

a) *M* = Ru1 (**2**) or Fe1 (**3**). b) *X* = O1 (**2**) or Cl1* (**3**).

Synthesis and Structure of Iron Complex

Iron complexes bearing a pincer-type ligand with tertiary aminoalkyl arms have been less explored in comparison with the ruthenium congeners.[11,12] Reaction of the unsymmetrical pincer-type ligand **LH** with anhydrous iron(II) chloride led to the formation of the dichloridoiron(II) complex [$FeCl_2$(**LH**)] (**3**) as shown in Scheme 3. Figure 2 shows the crystal structure of **3**. Complex **3** forms a C_i-symmetric dimer by two hydrogen bonds (NH···Cl1* = 3.1902(12) Å), which suggests the Brønsted acidity of the pyrazole arm. The preservation of the NH group is further supported by the large N2–N1–C1 angle of 112.18(11)°.[13] In contrast to the ruthenium complex **2**,



Scheme 3. Preparation of iron complex **3**.

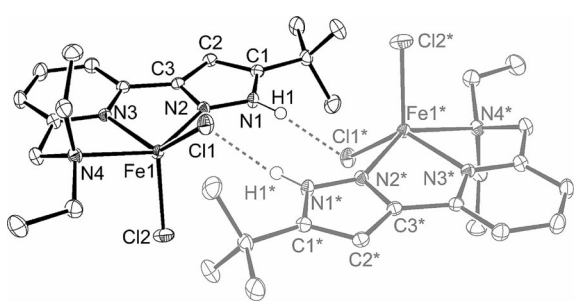


Figure 2. Crystal structure of **3**. The hydrogen atoms except for the pyrazole NH hydrogen are omitted for clarity. Asterisks denote atoms generated by a symmetry operation (–x, 1–y, –z). Ellipsoids are drawn at the 30% probability level.

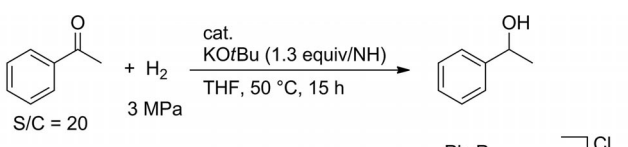
Dedicated Cluster

complex **3** is pentacoordinate, and the arrangement around the metal is a distorted square-pyramid with the axial position occupied by the Cl2 atom; the τ value[14] is 0.18. The pincer ligand **LH** is again bound to the metal through the three nitrogen atoms with a weaker coordination of the amino group (Table 1). The Fe–N distances more than 2.1 Å suggested the high-spin state of the iron[15] as in the symmetrical bis(pyrazolyl)pyridine complex,[3] in agreement with the observed μ_{eff} value of 5.0μ_B. The Fe–N(sp^3) distance of 2.3192(12) Å in **3** is comparable with that in the PNN-type iron pincer complex [$FeCl_2$(PNN)] [2.288(4) Å].[11]

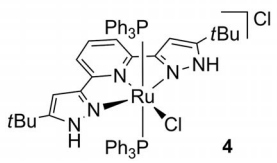
Catalytic Hydrogenation of a Ketone with Protic Pincer-type Complexes

Considering the potential role of the hemilabile arm to promote hydrogen transfer with the substrate,[7] we investigated the pincer-type complexes **2** and **3** as catalysts for hydrogenation of a ketone. The reaction was carried out at 50 °C under 3 MPa of H_2 in the presence of a base (Table 2).[16] Use of the ruthenium complex **2** as the catalyst led to the formation of the hydrogenation product in 36% yield (entry 1). The positive effect of the tertiary amino group to the catalysis is not evident because the product yield was much increased when the bis(pyrazolyl)pyridine complex **4** without tertiary aminomethyl arm[5] was employed under the same conditions (entry 2).[17] The iron complex **3** exhibited no catalytic activity (entry 3) despite that efficient hydrogenation catalysis of metal-ligand bifunctional iron complexes has recently been emerging.[18]

Table 2. Catalytic hydrogenation of acetophenone.[a)]



Entry	Cat.	Yield /%[b)]
1	**2**	36
2	**4**	86
3	**3**	0



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a) Reaction conditions: acetophenone:cat = 20:1, [acetophenone] = 0.1 M. b) Determined by GC using durene as internal standard.

Conclusions

In this study, we have developed an unsymmetrical pincer-type ligand **LH** having a protic pyrazole and tertiary aminomethyl arms as a new entry of pincer-type metal-ligand bifunctional catalysts. The ligand **LH** proved to be a useful precursor for the pincer-type ruthenium and iron complexes of **2** and **3**. The Brønsted acidity of the pincer ligand, which may be a key to the ligand cooperation to the catalysis, was demonstrated. Further work would be directed to the synthesis of complexes having this class of ligands as well as the catalytic application, which still remains in its infancy.

Experimental Section

General: All manipulations were performed in an atmosphere of argon using standard Schlenk technique unless otherwise specified. Solvents were dried by refluxing over sodium benzophenone ketyl (THF, diethyl ether, and hexane), CaH_2 (dichloromethane, 1,2-dichloroethane), and distilled before use. $CDCl_3$ was dried with MS4A. Reagents were commercially obtained and used as received. ^{1}H (398.78 MHz) NMR spectra were obtained with a JEOL JNM-ECX-400 spectrometer. ^{1}H NMR shifts are relative to the signal of the residual $CHCl_3$ (δ = 7.26 ppm). Magnetic susceptibility was measured on a Sherwood Scientific MSB-AUTO at room temperature. The diamagnetic correction was estimated from Pascal's constants[19]. ESI-MS spectra were obtained with a JEOL JMS-T 100LC (methanol was used as a solvent). GC analyses were performed with a Shimazu GC-17A with an INNOWAX column. Electrochemical measurements were made with a VersaSTAT 4 electrochemical analyzer using a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. Potentials were measured in dichloromethane–0.1 M nBu$_4$NPF$_6$. Elemental analyses were performed with a Perkin-Elmer 2400II CHN analyzer.

Preparation of Methyl 6-(Diethylaminomethyl)pyridine-2-carboxylate: To a solution of methyl 6-(methylsulfonyloxymethyl)pyridine-2-carboxylate[9] (**1**) (6.08 g, 24.8 mmol) in acetonitrile (200 mL) in an open flask was added diethylamine (2.56 mL, 24.8 mmol) and sodium carbonate (5.34 g, 50.4 mmol). The mixture was stirred for 16 h at 35 °C. After evaporation of the solvent, water (100 mL) and dichloromethane (100 mL) were added. The aqueous layer was extracted with dichloromethane (100 mL × 2), and the combined organic layer was dried with $MgSO_4$. Removal of the solvent under reduced pressure afforded the title compound as pale brown oil (3.90 g, 17.5 mmol, 71%), which was used for the subsequent reaction without further purification. **^{1}H NMR** ($CDCl_3$): δ = 7.97–8.00 (m, 1 H, pyridine CH), 7.78–7.82 (m, 2 H, pyridine CH), 3.99 (s, 3 H, CO_2CH_3), 3.84 (s, 2 H, benzyl-CH_2), 2.59 (q, ^3J(H,H) = 7.1 Hz, 4 H, CH_2CH_3), 1.05 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH_2CH_3).

Preparation of 2-(5-*tert*-Butylpyrazol-3-yl)-6-(diethylaminomethyl)pyridine (LH): To a suspension of NaH (60 wt% in mineral oil, 0.950 g, 23.8 mmol) in THF (30 mL) was added 3,3-dimethyl-2-butanone (2.42 mL, 19.4 mmol). The mixture was stirred for 20 min at room temperature and heated to reflux. To the boiling mixture was added methyl 6-(diethylaminomethyl)pyridine-2-carboxylate (3.90 g, 17.5 mmol) in THF (30 mL) over the course of 20 min, and the mixture was allowed to reflux for additional 30 min. After cooling, the mixture was treated with 1 M HCl solution at 0 °C until pH 7 in open air, and extracted with diethyl ether (20 mL × 4). The combined organic layer was washed with brine (30 mL) and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure afforded 2-(1,3-dioxo-4,4-dimethylbutyl)-6-(diethylaminomethyl)pyridine as brown oil (3.94 g). To a boiling solution of the crude diketone in ethanol (30 mL) in an open flask was added hydrazine monohydrate (1.98 mL, 40.7 mmol) over the course of 10 min. The mixture was allowed to reflux for additional 2 h. After removal of the solvent in vacuo, the residue was dissolved in diethyl ether (30 mL), washed with brine (10 mL × 3), and dried with $MgSO_4$. Evaporation of the solvent in vacuo afforded **LH** as brown oil (3.50 g, 12.2 mmol, 70% over 2 steps). **^{1}H NMR** ($CDCl_3$): δ = 7.66 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, pyridine CH), 7.52 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, pyridine CH), 7.34 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, pyridine CH), 6.59 (s, 1 H, pyrazole CH), 3.78 (s, 2 H, benzyl CH_2), 2.62 (q, $^3J_{H,H}$ = 7.0 Hz, 4 H, CH_2CH_3), 1.37 (s, 9 H, *t*Bu), 1.09 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH_2CH_3). $C_{17}H_{26}N_4$

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(286.42 g·mol^{-1}): C 71.26 (calcd. 71.29); H 9.31 (9.15), N 19.45 (19.56) %.

Preparation of [RuCl$_2$(Me$_2$SO-*S*)(LH)] (2): A mixture of *trans*-RuCl$_2$(dmso)$_4$[20] (634.8 mg, 1.310 mmol) and **LH** (409.0 mg, 1.428 mmol) in 1,2-dichloroethane (30 mL) was stirred at 50 °C for 17 h. After removal of a small amount of insoluble materials, the filtrate was evaporated to dryness. The residue was washed with diethyl ether (10 mL × 2). Recrystallization from dichloromethane/hexane (10 mL/70 mL) afforded **2**·CH$_2$Cl$_2$ as red black crystals. The thoroughly dried sample was found to lose the solvating molecule on the basis of ^{1}H NMR spectroscopy and combustion analysis. Yield: 574.1 mg (1.070 mol, 82 %). **^{1}H NMR** (CDCl$_3$): δ = 13.04 (br. s, 1 H, NH), 7.81–7.89 (m, 2 H, pyridine CH), 7.37 (dd, $^3J_{H,H}$ = 7.3, $^4J_{H,H}$ = 1.2 Hz, 1 H, pyridine CH), 6.64 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, pyrazole CH), 4.33 (s, 2 H, benzyl CH$_2$), 3.72 (s, 6 H, CH$_3$SOCH$_3$), 3.076, 3.081 (q, $^3J_{H,H}$ = 7.0 Hz, 2H each, C*H*$_2$CH$_3$), 1.35 (s, 9 H, *t*Bu), 1.07 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH$_2$C*H*$_3$). $E_{1/2}$ = +0.05 V (vs. Fc$^{0/+}$). C$_{19}$H$_{32}$N$_4$OCl$_2$SRu (536.53 g·mol^{-1}): C 42.30 (calcd. 42.53); H 6.08 (6.01), N 10.29 (10.44) %.

Preparation of [FeCl$_2$(LH)] (3): To a solution of **LH** (346.2 mg, 1.209 mmol) in THF (20 mL) was added FeCl$_2$ (anhydrous, beads; 150.6 mg, 1.188 mmol) and stirred at room temperature for 1 h. Slow addition of hexane (60 mL) afforded **3** as orange crystals (346.9 mg, 0.8396 mmol, 71 %). μ_{eff} = 5.0 μ_B. **^{1}H NMR** (CDCl$_3$): δ = 8.60, 3.65 1.92, 1.37, 0.29, –9.30, –11.93 (br). **ESI-MS**: *m*/*z* = 377.21 ([FeCl(**LH**)]$^+$). E_{pa} = +0.08 V (vs. Fc$^{0/+}$). C$_{17}$H$_{26}$N$_4$Cl$_2$Fe (413.17 g·mol^{-1}): C 49.78 (calcd. 49.42); H 6.44 (6.34), N 13.38 (13.56) %.

Catalytic Hydrogenation of Acetophenone: In a typical experiment, a 50-mL stainless steel autoclave equipped with a pressure gauge and a magnetic stirrer was charged with durene (28.9 mg, 0.215 mmol) as an internal standard. A mixture of **2** (6.10 mg, 0.0114 mmol), potassium *tert*-butoxide (0.5 M in THF, 30.0 µL, 0.0150 mmol) in THF (2.3 mL) and acetophenone (27.0 µL, 0.232 mmol) was added in an argon atmosphere. The autoclave was flushed with H$_2$ and then pressurized to 3 MPa. The reaction mixture was stirred at 50 °C for 15 h. After venting hydrogen, the mixture was filtered through a small amount of florisil (magnesium silicate), and subjected to GC analysis.

X-ray Diffraction Studies: Diffraction experiments were performed with a Rigaku Saturn CCD area detector with graphite monochromated Mo-K_α radiation (λ = 0.710 70 Å). Single crystals suitable for X-ray analyses were mounted on a fiber loop. Intensity data were corrected for Lorentz polarization effects and for absorption. Details of crystal and data collection parameters are summarized in Table 3. Structure solution and refinements were carried out by using the CrystalStructure program package[21]. The heavy-atom positions were determined by a direct methods program (SIR92[22]) and remaining non-hydrogen atoms were found by subsequent Fourier syntheses. The *tert*-butyl group and solvating dichloromethane molecule in **2**·CH$_2$Cl$_2$ were located at two disordered positions with 0.6/0.4 and 0.55/0.45 occupancies, respectively. For these disordered moieties, the carbon atoms were refined isotropically and the hydrogen atoms were not included in the refinements; the disordered *tert*-butyl groups were refined with restraint geometries. The rest non-hydrogen atoms were refined anisopropically by full-matrix least-squares techniques based on F^2. The rest hydrogen atoms were placed at calculated positions and included in the refinements with a riding model. The absolute structure of **2**·CH$_2$Cl$_2$ was determined on the basis of the Flack absolute structure parameter.[23]

Table 3. X-ray crystallographic data for **2** and **3**.

	2·CH$_2$Cl$_2$	**3**
Chemical formula	C$_{20}$H$_{34}$Cl$_4$N$_4$ORuS	C$_{17}$H$_{26}$Cl$_2$FeN$_4$
Formula weight	621.46	413.17
Crystal size /mm^3	0.44 × 0.28 × 0.22	0.20 × 0.16 × 0.07
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a /Å	12.478(5)	8.4951(14)
b /Å	13.021(5)	12.197(2)
c /Å	16.583(6)	19.617(4)
β /°	90	93.445(3)
V /Å^3	2694.3(17)	2028.9(6)
Z	4	4
T /K	93	93
$\rho_{calcd.}$ /g·cm^{-3}	1.532	1.353
F(000)	1272	864
μ /mm^{-1}	1.075	1.012
Transmission factors	0.702–0.789	0.794–0.932
No. reflns measured	21372	16274
Independent reflns (R_{int})	6070 (0.0377)	4629 (0.0412)
Parameters	318	243
R_1 [$I > 2\sigma(I)$]	0.0511	0.0264
wR_2 (all data)	0.1450	0.0866
Goodness-of-fit	1.000	1.000
Max. diff. peak and hole /e·Å^{-3}	1.41/–1.41	0.525/–0.308

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1409447 and CCDC-1409448 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra of **LH** and compounds **2** and **3**.

Acknowledgements

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