Synthesis, structure and reactivity of new solvent (MeOH or Me_2SO) coordinated Rh(III) complexes: a cyclic series of chemical transformations involving $RhCl_3$-mediated azo cleavage

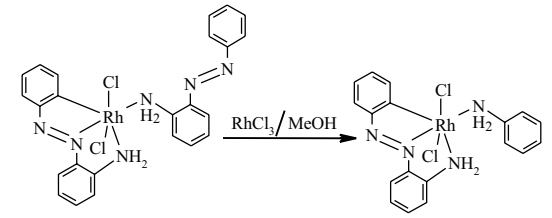
Jahar lal Pratihar, Poulami Pattanayak and Surajit Chattopadhyay*

Department of Chemistry, University of Kalyani, Kalyani-741235, India

Reaction of $RhCl_3.3H_2O$ with 2-(phenylazo) aniline, HL–NH_2, in boiling methanol afforded three products [$RhCl_2$(L–NH_2)(HL–NH_2)], **1**, [$RhCl_2$(L–NH_2)(H_2NPh)] **2**, and [$RhCl_2$(L–NH_2)(MeOH)], **3**. The sequential transformation of **1** to **2** followed by **3** has been established where the –N=N– cleavage occurs during the conversion of **1** to **2**. Further, treatment of **3** with HL–NH_2 in dichloromethane furnished **1** to complete a reaction cycle.

Keywords: 2-(phenylazo) aniline, azo cleavage, Rh(III)/Rh(I), transformation series, reaction cycle

The reductive cleavage of an azo (–N=N–) function leading to the formation of corresponding primary amines was reported to occur using a mixture of nickel (II) chloride dihydrate, excess lithium powder and catalytic amounts of arenes.[1,2] Also there are a few reports on transition metal mediated cleavage of the –N=N– bond.[3-7] Recently we have also reported the azo (–N=N–) scission in 2-(phenylazo) aniline, HL-NH_2, using $RhCl_3$ in refluxing methanol (Eqn (1)).[7] It was believed that a Rh(I) species, formed *in situ* by $RhCl_3$ in methanol, was the reducing agent for this reductive cleavage of –N=N– function *via* coordination of HL–NH_2 to Rh(III) in a monodentate fashion as in [$RhCl_2$(L–NH_2)(HL–NH_2)]. Isolation and characterisation of [$RhCl_2$(L–NH_2)(H_2NPh)] enabled us to recognise the azo (–N=N–) cleavage unambiguously.[7]



(1)

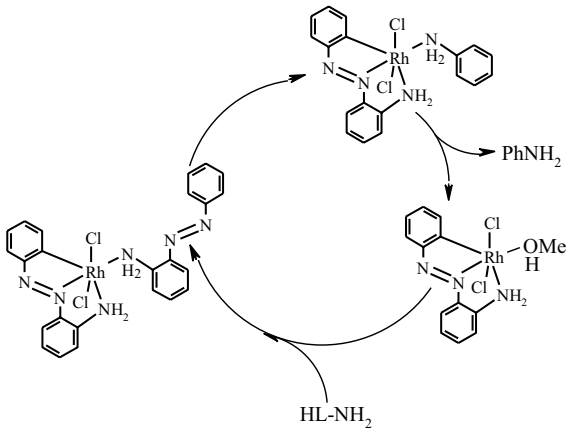
(L-NH_2)$RhCl_2$(HL-NH_2) (L-NH_2) $RhCl_2$(H_2NPh)

1 **2**

Here we report the reaction of HL–NH_2 with $RhCl_3$ under appropriate conditions to obtain the new methanol-coordinated complex, [$RhCl_2$(L–NH_2)(MeOH)], **3**, through the *in situ* formations of [$RhCl_2$(L–NH_2)(HL–NH_2)], **1**, and [$RhCl_2$(L–NH_2)(H_2NPh)], **2**. The conversion of **3** to **1** was further studied, indicating a non-repetitive cyclic sequence of reactions, as shown in Scheme 1.

Results and discussion

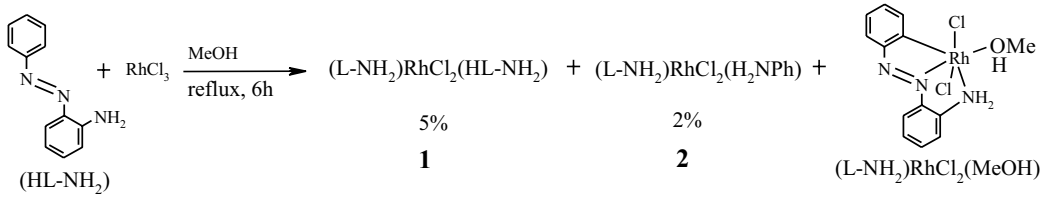
Reaction of 2-(phenylazo) aniline, HL–NH_2, with $RhCl_3.3H_2O$, in 2:1 stoichiometric ratio, in refluxing methanol for 6 h afforded three complexes [$RhCl_2$(L–NH_2)(HL–NH_2)],



Scheme 1

1; [$RhCl_2$(L–NH_2)(NH_2Ph)], **2;** and [$RhCl_2$(L–NH_2)(MeOH)], **3**; in 5%, 2% and 40% yields respectively (Eqn (2)). All the complexes were isolated by silica gel thin layer chromatography where the mobility order was **1** (R_f = 0.8) > **2** (R_f = 0.7) > **3** (R_f = 0.3) in toluene–acetonitrile (9: 1 V/V) mixed solvent. In contrast, the complexes [$RhCl_2$(L–NH_2)(HL–NH_2)] and [$RhCl_2$(L–NH_2)(NH_2Ph)] were isolated in 40% and 15% yields after refluxing HL–NH_2 with $RhCl_3$ for 4 h as reported earlier,[7] along with a minimum amount of **3** (~1%).

Therefore the duration of reaction was important in controlling the relative yields of the products **1**, **2** and **3**. The new complex [$RhCl_2$(L–NH_2)(MeOH)] was characterised by recording the ^{1}H NMR spectrum. The ^{1}H NMR spectrum of [$RhCl_2$(L–NH_2)(MeOH)] displayed the signal due to methyl proton of the coordinated methanol at 2.51 ppm while the integration of other resonances in the aromatic region (8.23–7.29 ppm) were in agreement with the total number of protons for one equivalent of the $(L–NH_2)^-$ ligand. A relatively broad resonance at 5.35 ppm was observed for the –NH_2 protons of $(L–NH_2)^-$ in the spectrum of [$RhCl_2$



(2)

* Correspondent. E-mail: scha8@rediffmail.com

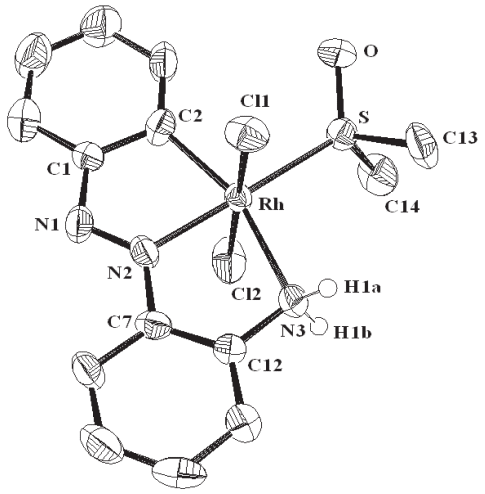


Fig.1 Perspective view of molecular structure of [$RhCl_2$(L–NH)(Me_2SO)] with atom numbering scheme. Hydrogen atoms, except that on N3, are omitted for clarity.

(L–NH_2)(MeOH)] in contrast to two such resonances for [$RhCl_2$(L–NH_2)(HL–NH_2)][7] and [$RhCl_2$(L–NH_2)(NH_2Ph)][7] which indicated the presence of only one tridentate (L–NH_2)$^-$ ligand in [$RhCl_2$(L–NH_2)(MeOH)]. The characterisation data (UV-Vis; IR; CHN and ^{1}H NMR) are collected in the Experimental section for this new MeOH coordinated complex.

The new complex [$RhCl_2$(L–NH_2)(MeOH)] was crystallised from its dimethylsulfoxide (Me_2SO) solution and an X-ray structure of the product was determined. This revealed that, instead of containing MeOH, the molecule is a Me_2SO coordinated species, [$RhCl_2$(L–NH_2)(Me_2SO)], which formed due to substitution of MeOH by Me_2SO during crystallisation. A perspective view of the molecular structure is shown in Fig. 1. Selective bond distances and angles are collected in Table 1. The HL–NH_2 ligand binds the Rh(III) in a tridentate fashion (C,N,N) in its anionic form [L–NH_2]$^-$ due to orthometallation. Two chlorides and an S-coordinated Me_2SO satisfy the hexacoordination about Rh(III).

The ^{1}H NMR spectrum of [$RhCl_2$(L–NH_2)(Me_2SO)] was compared with that of [$RhCl_2$(L–NH_2)(MeOH)] and it was noticed that the pattern of proton resonances in the aromatic region and of the amino group for both the complexes were similar, with little difference in chemical shifts, signifying equivalent binding of (L–NH_2)$^-$. A singlet resonance at 3.47 ppm for six equivalent protons was observed in the ^{1}H NMR spectrum of [$RhCl_2$(L–NH_2)(S(O)($Me)_2$)] for coordinated Me_2SO while in the case of [$RhCl_2$(L–NH_2)(MeOH)] there was a resonance at 2.51 ppm for three equivalent protons due to the coordinated MeOH. Thus the MeOH coordination and the structure of [$RhCl_2$(L–NH_2)(MeOH)] could be inferred by confirming the structure of this subsidiary complex [$RhCl_2$(L–NH_2)(S(O)($Me)_2$)].

Reaction of [$RhCl_2$(L–NH_2)(HL–NH_2)] with $RhCl_3$ in refluxing methanol afforded only [$RhCl_2$(L–NH_2)(H_2NPh)] after 30 min as reported earlier,[7] while on prolonged reflux (for 4 h) the same reaction mixture yielded [$RhCl_2$(L–NH_2)(MeOH)], almost exclusively, and the isolated yield was 70% (Eqn (3)).

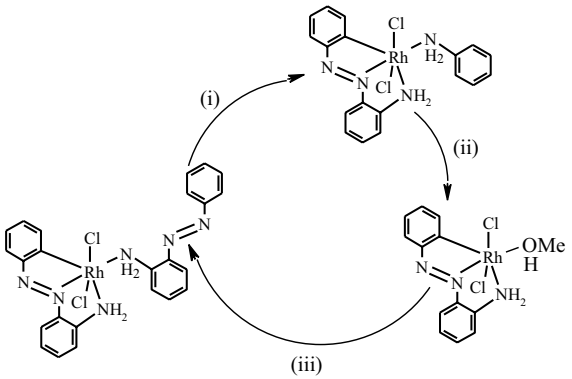
Table 1 Selected bond distances (Å) and angles (°) for [$RhCl_2$(L–NH_2)(Me_2SO)]

Rh–Cl(1)	2.333(19)	N(3)–C(12)	1.440(8)
Rh–Cl(2)	2.319(2)	S–C(13)	1.775(8)
Rh–N(3)	2.211(6)	Rh–S	2.301(2)
Rh–N(2)	1.971(5)	N(1)–C(1)	1.377(10)
Rh–C(2)	1.980(7)	N(2)–C(7)	1.419(9)
S–O	1.483(5)	N(1)–N(2)	1.270(8)
Cl(1)–Rh–Cl(2)	176.29(8)	S–Rh–C(2)	99.4(2)
Cl(1)–Rh–N(3)	87.41(15)	N(2)–Rh–C(2)	79.2(3)
Cl(1)–Rh–N(2)	90.04(17)	N(2)–Rh–S	178.66(18)
Cl(1)–Rh–S	90.16(7)	N(3)–Rh–C(2)	160.2(3)
Cl(1)–Rh–C(2)	91.8(2)	N(3)–Rh–S	100.35(15)
Cl(2)–Rh–N(2)	87.32(17)	N(2)–Rh–N(3)	81.0(2)
Cl(2)–Rh–S	92.54(7)	Cl(2)–Rh–C(2)	90.2(2)

Therefore, we assume that upon prolonged reflux, [$RhCl_2$(L–NH_2)(HL–NH_2)] in methanol and in presence of $RhCl_3$ underwent azo cleavage forming [$RhCl_2$(L–NH_2)(NH_2–Ph)] followed by [$RhCl_2$(L–NH_2)(MeOH)] due to *in situ* substitution of $PhNH_2$ by MeOH. This sequence of transformations was further corroborated by isolating [$RhCl_2$(L–NH_2)(MeOH)] in 70% yield upon refluxing pure [$RhCl_2$(L–NH_2)(H_2NPh)] in methanol for 3 h separately (Eqn (3)).

It was further attempted to transform [$RhCl_2$(L–NH_2)(MeOH)] into [$RhCl_2$(L–NH_2)(HL–NH_2)], *in situ*, by treating with excess HL–NH_2 to complete the reaction cycle but that was unsuccessful.

Substitution of coordinated methanol of isolated [$RhCl_2$(L–NH_2)(MeOH)] with Me_2SO during crystallisation (vide supra) indicated the possibility to obtain [$RhCl_2$(HL–NH_2)(HL–NH_2)] from [$RhCl_2$(L–NH_2)(MeOH)]. Reaction of isolated [$RhCl_2$(L–NH_2)(MeOH)] with HL–NH_2 in refluxing dichloromethane afforded the initial complex [$RhCl_2$(L–NH_2)(HL–NH_2)] in good yield (75%) completing a reaction cycle (not repetitive) as shown in Scheme 2. Therefore, although *in situ* substitution of MeOH by HL–NH_2 was not possible in excess methanol (solvent), a choice of appropriate solvent might yield a better system. Moreover, the challenge of repeating the reaction cycle (Scheme 2) to obtain a catalytic –N = N– cleavage process has emerged from this work.



(i) $RhCl_3$, MeOH, reflux
(ii) MeOH, reflux
(iii) HL-NH_2, CH_2Cl_2, reflux

Scheme 2

$$(L\text{-}NH_2)RhCl_2(HL\text{-}NH_2) \xrightarrow[\text{MeOH, reflux, 4h}]{RhCl_3} (L\text{-}NH_2)RhCl_2(MeOH) \xleftarrow[\text{reflux, 3h}]{MeOH} (L\text{-}NH_2)RhCl_2(H_2NPh) \quad \cdots (3)$$

Experimental

Materials and physical measurements

All starting materials were used as received from commercial sources; the solvents were purchased from E. Merck, Kolkata, India, and purified and dried by reported procedure.[7,8] *o*-Phenylenediamine and nitrobenzene were purchased from Loba, Kolkata, India. Rhodium trichloride was purchased from Arora Matthey, India. The ligand 2-(phenylazo) aniline was prepared following the reported procedure.[8] Microanalysis (C, H, N) was performed using a Perkin-Elmer 240C elemental analyser. Infrared spectra were recorded on a Perkin-Elmer L120-00A FT–IR spectrometer with the samples prepared with KBr pellets. UV-Vis spectra were recorded on a Shimadzu UV- 2401 PC spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker RPX 500 NMR spectrometer in $CDCl_3$ using TMS as the internal standard.

Syntheses

[$RhCl_2$(L–NH_2)(CH_3OH)]: 2-(Phenylazo) aniline, (0.15 g, 0.76 mmol) was dissolved in methanol (40 ml), and to it $RhCl_3$ (0.1 g, 0.38 mmol) was added. The mixture was then heated to reflux for 6 h to afford a dark brown solution. Evaporation of the solvent gave a brown residue, which was purified by thin layer chromatography on silica gel. Three deep brown bands were separated in toluene-acetonitrile (9 : 1, V/V) mixed solvent. The brown band of lowest R_f (0.3) value afforded the complex [$RhCl_2$(L–NH_2)(CH_3OH)] as the major product. Yield: 40%. The first two bands of preparative TLC afforded [$RhCl_2$(L–NH_2)(HL–NH_2)] and [$RhCl_2$(L–NH_2)(H_2NPh)] in low yields (5% and 2% respectively). The characterisation and structure of [$RhCl_2$(L–NH_2)(HL–NH_2)] and [$RhCl_2$(L–NH_2)(H_2NPh)] have been reported in the earlier communication.[7] Complex [$RhCl_2$(L–NH_2)(CH_3OH)]. *Anal.* Calc. for $C_{13}H_{14}N_3Cl_2ORh$: C, 38.8; H, 3.5; N, 14.45. Found: C, 38.75; H, 3.5; N, 14.0%. IR (KBr disc, cm^{-1}): ν_{NH2} 3244, 3193; $\nu_{N=N}$ 1483; ν_{Rh-Cl} 350, 322. ^{1}H NMR ($CDCl_3$): δ = 2.51 (s, CH_3, 3H), 5.35(s, NH_2, 2H), 7.29(t, 1H), 7.35 (t, 1H), 7.46(t, 1H), 7.51–7.56 (m, 2H), 7.91 (d, 1H), 8.18–8.23 (m, 2H). UV-Vis (CH_2Cl_2): (λ_{max}, nm, (ε, M^{-1}, cm^{-1})): 520 (4800), 360 (32600), 250 (28950), 230 (32800).

[$RhCl_2$(L–NH_2)(CH_3OH)] from [$RhCl_2$(L–NH_2)(HL–NH_2)]: $RhCl_3.3H_2O$ (0.023 g, 0.088 mmol) was added to a methanolic (20 ml) solution of (0.05 g, 0.088 mmol) of [$RhCl_2$(L–NH_2)(HL–NH_2)] and refluxed for 4 h. The solid mass, obtained upon evaporation of methanol, was introduced on a thin layer chromatographic plate prepared with silica gel. [$RhCl_2$(L–NH_2)(CH_3OH)] was separated almost exclusively using toluene–acetonitrile (9 : 1 V/V) mixed solvent. The pure [$RhCl_2$(L–NH_2)(CH_3OH)] was isolated from the TLC plate. Yield: 70%.

[$RhCl_2$(L–NH_2)(CH_3OH)] from [$RhCl_2$(L–NH_2)(H_2NPh)]: [$RhCl_2$(L–NH_2)(H_2NPh)] (0.04 g, 0.088 mmol) was refluxed in methanol for 4 h. The solid mass, obtained upon evaporation of methanol, was introduced on a thin layer chromatographic plate prepared with silica gel. [$RhCl_2$(L–NH_2)(CH_3OH)] was separated almost exclusively using toluene–acetonitrile (9 : 1 V/V) mixed solvent. The pure [$RhCl_2$(L–NH_2)(CH_3OH)] was isolated from the TLC plate. Yield: 70%.

[$RhCl_2$(L–NH_2 (Me_2SO)]: Complex [$RhCl_2$(L–NH_2)(Me_2SO)] was prepared by slow evaporation of dichloromethane (5 ml) solution of [$RhCl_2$(L–NH_2)(CH_3OH)] (0.03 g, 0.075 mmol) adding dimethyl sulfoxide (0.001 ml, 0.075 mmol). Pure crystals of [$RhCl_2$(L–NH_2)(dmso)] was isolated by filtration. Yield: 95%. *Anal.* Calc. for $C_{14}H_{16}Cl_2N_3ORhS$: C, 37.5; H, 3.6; N, 9.4. Found: C, 37.5; H, 3.6; N, 9.4%. IR (KBr disc, cm^{-1}): ν_{NH2} 3188, 3111; $\nu_{N=N}$1485; ν_{Rh-Cl} 342, 331. ^{1}H NMR ($CDCl_3$): δ = 3.46 (s, CH_3, 6H), 5.33 (s, NH_2, 2H), 7.29 (t, 1H), 7.37 (t, 1H), 7.41(t, 1H), 7.52–7.55 (m, 2H), 7.92 (d, 1H), 8.19–8.26 (m, 2H). UV-Vis (CH_2Cl_2): [λ_{max}, nm, (ε, M^{-1}, cm^{-1})]: 500 (4700), 360 (26400), 255 (25150), 230 (32550).

[$RhCl_2$(L–NH_2)(HL–NH_2)] from [$RhCl_2$(L–NH_2)(CH_3OH)]: 2-(phenylazo) aniline, (0.03 g, 0.152 mmol) was dissolved in dichloromethane (40 ml), and to it complex [$RhCl_2$(L–NH_2)(CH_3OH)] (0.061 g, 0.152 mmol) was added. The mixture was then heated to reflux for 5 h to afford a dark brown solution. Evaporation of the solvent gave a brown residue, which was introduced for purification by thin layer chromatography prepared with silica gel. [$RhCl_2$(L–NH_2)(HL–NH_2)] was separated almost exclusively using toluene–acetonitrile (95:5 V/V) mixed solvent. The pure [$RhCl_2$(L–NH_2)(HL–NH_2)] was isolated from the TLC plate. Yield: 90%.

Table 2 Crystallographic data for [$RhCl_2$(L–NH_2)(Me_2SO)]

Chemical formula	$C_{14}H_{16}Cl_2N_3ORhS$
Formula weight	448.18
Crystal system	Orthorhombic
Space group	Orthorhombic, Pcab (No 61)
a(Å)	11.283(3)
b(Å)	11.401(13)
c(Å)	26.543(3)
λ(Å)	0.71073
V(Å^3)	3414.6(11)
Z	8
F [000]	1792
Temperature (K)	293
ρ_{cald} (Mg/m^3)	1.744
μ (mm^{-1})	1.439
θ range for data collection (^{0})	2.3–25.0
Reflection collected	2998
Observed reflections	1954
R[a](all data)	0.0431
wR_2[b] [$I>2\sigma(I)$]	0.1133
GOFc	1.08

[a]$R = \Sigma||F_o| - |F_o||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$ where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$. [c]GOF = $[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$.

Crystallography

Crystal data were collected by the ω-scan technique on a Enraf-Nonius CAMX-3 diffractometer using Mo-Kα monochromator (λ = 0.71043). The structure solution was done by direct method with the SHELXS-97 program.[9] Full matrix least square refinements were performed using the SHELX-97 program (PC version). All non hydrogen atoms were refined anisotropically using reflections $I>2\sigma(I)$. Hydrogen atoms were included at the calculated positions. The crystal data and data collection parameters are listed in Table 2.

Supplementary data

Figures S1-S6 are supplied as supplementary data of UV-Vis, IR and ^{1}H NMR spectra for [$RhCl_2$(L–NH_2)(MeOH)] and [$RhCl_2$(L–NH_2)(Me_2SO)]. Crystallographic data of [$RhCl_2$(L–NH_2)(Me_2SO)] for the structural analysis have been deposited with The Cambridge Crystallographic Data Centre CCDC Reference Number 299571 (in CIF format). Copies of this information may be obtained free from the Director, CCDC, 12 Union Road, Cambridge CB2 1EW, UK (fax: + 44 1223 336 033; e-mail: deposite@ccdc.cam.ac.uk or http: //www.ccdc.cam.ac.uk).

We thank the DST (New Delhi) for funding and fellowship to JP under DST-SERC project (No. SR/S1/IC-09/2003). The necessary laboratory and infrastructural facility were provided by the Department of Chemistry, University of Kalyani. The support of DST under FIST program to the Department of Chemistry, University of Kalyani is acknowledged.

Received 28 March 2006; accepted 11 May 2006
Paper 06/3864

References

1 F. Alonso and M. Yus, *Chem. Soc. Rev*., 2004, **33**, 284.
2 B.T. Newbold, In *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*, Patai, S. Ed, J. Wiley and Sons, New York, 1975. p. 382.
3 K. Majumder, S.–M. Peng and S. Bhattacharya, *J. Chem. Soc., Dalton Trans*., 2001, 284.
4 A.K. Ghosh, P. Majumdar, L.R. Falvello, G. Mostafa and S. Goswami, *Organometallics*., 1999, **18**, 5086 and references therein.
5 F.Y. Petillon, P. Schollhammer, J. Talarmin and K.W. Muir, *Inorg. Chem*., 1999, **38**, 1954.
6 M.A. Aubart and R.G. Bergman, *Organometallics*., 1999, **18**, 811.
7 J. Pratihar, N. Maiti and S. Chattopadhyay, *Inorg. Chem*., 2005, **44**, 6111, and references therein.
8 N. Maiti, S. Pal and S. Chattopadhyay, *Inorg. Chem*., 2001, **40**, 2204, and references therein.
9 G.M. Sheldrick, *SHELXS-97 AND SHELX-97*, Fortran Programs for Crystal Structure Solution and refinement, University of Gottingen, Gottingen, Germany, 1997.