Inorg. Chem. **1993**, *32*, 3851–3854 **3851**

Stereochemical Properties and X-ray Structure of a Water-Soluble Diastereomeric (Arene)ruthenium(II) Schiff-Base Complex: [Ru(η-MeC$_6$H$_4$Pr^i-p)(H$_2$O)(L*)](ClO$_4$), Containing a Weakly Bound Aqua Ligand [HL* = (S)-(α-methylbenzyl)salicylaldimine]

Sisir K. Mandal and Akhil R. Chakravarty*

Department of Inorganic & Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Received January 5, 1993

An air-stable and water-soluble diastereomeric half-sandwich ruthenium(II) complex, [Ru(η-MeC$_6$H$_4$Pr^i-p)(H$_2$O)(L*)](ClO$_4$) (**1**), has been isolated and structurally characterized [HL* = (S)-(α-methylbenzyl)salicylaldimine, 2-HOC$_6$H$_4$CH=NCHMePh]. Complex **1**, C$_{25}$H$_{30}$NO$_6$ClRu, crystallizes in the noncentric triclinic space group $P1$ with a = 9.885(1) Å, b = 10.185(1) Å, c = 14.187(2) Å, α = 110.32(1)°, β = 102.17(1)°, γ = 102.41(1)°, V = 1243(1) Å^3, and Z = 2. The X-ray structure shows the presence of two diastereomers in a 1:1 ratio having R_{Ru},S_C and S_{Ru},S_C configurations. The Ru–OH$_2$ bond distances are considerably long, and the values for R_{Ru}-**1** and S_{Ru}-**1** isomers are 2.119(5) and 2.203(5) Å, respectively. The aqua complex (**1**) exists as a single diastereomer in solution, and it forms stable adducts with P-, N-, and halide-donor ligands. The stereochemical changes associated with adduct-forming reactions follow an inversion order: PPh$_3$ ≫ P(OMe)$_3$ > pyridine bases ≫ halides (I, Br, Cl) > H$_2$O.

Introduction

Current research concerning the chirooptical properties of half-sandwich transition-metal complexes is primarily aimed toward understanding the enantioselective reactions mediated by chiral species having weakly bound ancillary ligand(s).[1-3] Such complexes are of considerable interest for their application in organic synthesis and stereochemical investigations. Among them, the water-soluble complexes are of importance as organometallic reagents in catalytic reactions.[4,5] We have prepared and structurally characterized a complex, [Ru(η-MeC$_6$H$_4$Pr^i-p)(H$_2$O)(L*)](ClO$_4$) (**1**), belonging to this category, and we find that the stereochemical properties of **1** differ considerably from those of chiral phosphine analogues[1] in showing a rare case of complete inversion during PPh$_3$ adduct formation [HL* = (S)-(α-methylbenzyl)salicylaldimine].

Experimental Section

Materials and Measurements. The preparative routes for [Ru(η-MeC$_6$H$_4$Pr^i-p)Cl(L*)] [% diastereomeric excess (de) = 70] and (S)-(α-methylbenzyl)salicylaldimine (HL*) were reported earlier.[6] AgClO$_4$ was prepared by a literature procedure.[7] The reagents were obtained from Fluka, and all reactions were performed under dinitrogen using standard Schlenk techniques.

Elemental analysis was done on a Heraeus CHN-O Rapid Instrument. ^{1}H NMR spectra were recorded on Bruker WH-270 and ACAF 200-MHz spectrometers. Polarimetric measurements were made with a Roussel Jouan Type 71 instrument. CD spectra were recorded using a Jasco J-500A spectrophotometer.

Preparation of [Ru(η-MeC$_6$H$_4$Pr^i-p)(H$_2$O)(L*)](ClO$_4$) (1). To 15 mL of acetone were added 0.2 g (0.6 mmol) of [Ru(η-MeC$_6$H$_4$Pr^i-p)-Cl(L*)] (% de = 70) and 0.05 g (0.6 mmol) of AgClO$_4$. The mixture was then stirred for 30 min at -5 °C to give a yellow solution, which was filtered through Celite. The volume of the filtrate was reduced to ~5 mL, and 10 mL of water was added to it. Slow evaporation of the mother liquor, kept at 5 °C for 3 d, gave a brown crystalline pyrophoric solid (Caution!) which was isolated and dried *in vacuo* over P$_4$O$_{10}$ (yield 90%). Anal. Calcd for C$_{25}$H$_{30}$NO$_6$ClRu: C, 51.99; H, 5.19; N, 2.42. Found: C, 52.13; H, 5.32; N, 2.40. Polarimetric data in acetone: $[\alpha]^{25}{}_{546}$ = –132, $[\alpha]^{25}{}_{589}$ = –121 (c 0.91 mg/mL). ^{1}H NMR data[8] [δ, ppm (multiplicity, nH, J (Hz))] in acetone-d_6: 1.02, 1.20 (d × 2, 6H, 7), 1.85 (s, 3H), 2.62 (sp, 1H, 7), 5.77, 5.88 (q × 2, 4H, 6) for η-MeC$_6$H$_4$Pr^i-p; 2.00 (d, 3H, 7), 6.39 (q, 1H, 7), 5.62 (t, 1H, 7), 6.91 (d, 1H, 9), 7.17–7.63 (m, 7H), 8.35 (s, 1H) for L* (s = singlet; d = doublet; t = triplet; q = quartet; sp = septet; m = multiplet). CD spectrum (1.0 mM in acetone), $[\theta]^{25}{}_{\lambda}$ (deg·cm^2·dmol^{-1}) values of maxima, minima, and nodes (λ, nm): 0 (600), +181 (475), 0 (447), –1590 (384), –590 (350), 0 (325).

Table I. Crystallographic Data for (R_{Ru},S_C;S_{Ru},S_C)-[Ru(η-MeC$_6$H$_4$Pr^i-p)(H$_2$O)(L*)](ClO$_4$) (1)

chem formula	C$_{25}$H$_{30}$NO$_6$ClRu
fw	577.04
space group	$P1$ (No. 1)
a, Å	9.885(1)
b, Å	10.185(1)
c, Å	14.187(2)
α, deg	110.32(1)
β, deg	102.17(1)
γ, deg	102.41(1)
V, Å^3	1243(1)
Z	2
ρ_{calcd}, g·cm^{-3}	1.54
T, °C	19
λ(Mo Kα), Å	0.7107
μ(Mo Kα), cm^{-1}	7.65
transm coeff	0.90–1.00
R^a	0.0414
$R_w{}^b$	0.0452

[a] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

X-ray Crystallography. A yellow rectangular crystal of dimensions 0.25 × 0.25 × 0.10 mm, obtained from slow evaporation of a water–acetone solution of complex **1** at 5 °C, was mounted on a glass fiber. A total of 4796 intensities were measured with a CAD4 diffractometer using graphite-monochromated Mo Kα radiation ($2\theta_{max}$ = 50°; $+h,\pm k,\pm l$). An absorption correction[9] based on ψ-scans was applied. There were 4630 unique reflections of which 4175 with $I > 2.5\sigma(I)$ were used for

---

(1) Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761.
(2) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 152.
(3) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 8, p 463.
(4) (a) Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H. *Organometallics* **1992**, *11*, 1990 and references therein. (b) Sommerer, S. O.; Palenik, G. J. *Organometallics* **1991**, *10*, 1223.
(5) Light, J.; Breslow, R. *Tetrahedron Lett.* **1990**, *31*, 2952.
(6) Mandal, S. K.; Chakravarty, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 1627; *J. Organomet. Chem.* **1991**, *417*, C59.
(7) Hill, A. E. *J. Am. Chem. Soc.* **1921**, *43*, 254.
(8) The ^{1}H NMR spectrum of complex **1** at 25 °C did not show any peak for the aqua ligand.
(9) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

0020-1669/93/1332-3851$04.00/0 © 1993 American Chemical Society

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters[a] ($Å^2 \times 10^3$) for $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)(H_2O)(L^*)](ClO_4)$ (**1**) with Esd's in Parentheses

atom	*x*	*y*	*z*	$U_{eq(iso)}$
Ru(1)	4679(1)	3137(1)	3967(1)	30(1)
O(1)	3570(5)	4612(5)	4325(4)	41(1)
O(2)	5138(6)	3715(5)	5675(4)	39(1)
N(1)	2879(7)	1589(7)	3864(5)	39(1)
C(1)	6931(8)	3141(9)	4107(6)	42(1)
C(2)	6669(8)	4429(8)	3933(6)	49(1)
C(3)	5531(10)	4397(11)	3153(6)	61(1)
C(4)	4617(9)	2897(10)	2329(6)	54(1)
C(5)	4782(9)	1560(9)	2477(7)	53(2)
C(6)	6046(8)	1773(10)	3338(6)	48(2)
C(7)	8078(8)	3289(11)	5073(7)	61(2)
C(8)	3427(8)	2873(8)	1481(5)	39(1)
C(9)	3986(13)	2889(15)	557(8)	127(2)
C(10)	2172(11)	1421(12)	977(7)	85(2)
C(11)	1153(8)	2873(7)	3504(2)	36(1)
C(12)	2086(7)	4241(8)	3719(6)	39(1)
C(13)	1577(8)	5182(7)	3357(5)	32(1)
C(14)	288(10)	4987(9)	2918(6)	56(2)
C(15)	–889(10)	3463(9)	2598(7)	55(1)
C(16)	–412(9)	2476(11)	2938(6)	67(2)
C(17)	1556(8)	1766(8)	3738(5)	36(1)
C(18)	3012(7)	149(7)	3929(5)	26(1)
C(19)	2076(11)	–377(9)	4540(7)	61(2)
C(20)	2881(8)	–970(8)	2874(6)	36(1)
C(21)	1366(12)	–1466(11)	2040(7)	86(2)
C(22)	1268(11)	–2599(9)	1022(8)	67(2)
C(23)	2511(12)	–3260(12)	902(9)	88(2)
C(24)	3776(11)	–2757(10)	1951(8)	73(1)
C(25)	3919(10)	–1734(9)	2853(8)	63(2)
Ru(2)	5550	7980	7123	30(1)
O(3)	6748(6)	6523(5)	6761(4)	40(1)
O(4)	4958(5)	7356(6)	5467(4)	35(1)
N(2)	7466(6)	9574(6)	7187(4)	25(1)
C(26)	3221(8)	7824(8)	7070(6)	39(1)
C(27)	4217(9)	9279(7)	7776(7)	47(1)
C(28)	5335(7)	9371(7)	8586(5)	33(1)
C(29)	5606(8)	8172(8)	8684(6)	40(1)
C(30)	4626(8)	6822(7)	8005(6)	38(1)
C(31)	3433(8)	6543(9)	7113(6)	49(2)
C(32)	1936(9)	7609(10)	6151(6)	54(1)
C(33)	6863(14)	8148(14)	9647(10)	136(2)
C(34)	8206(13)	9475(12)	10039(8)	92(2)
C(35)	6053(13)	7908(12)	10402(7)	91(2)
C(36)	9156(7)	8259(8)	7623(6)	40(1)
C(37)	8042(9)	6839(7)	7299(5)	37(1)
C(38)	8450(9)	5695(9)	7577(6)	51(2)
C(39)	10095(9)	6252(9)	8275(6)	51(1)
C(40)	10985(8)	7451(10)	8471(6)	48(2)
C(41)	10546(8)	8528(8)	8169(6)	41(1)
C(42)	8730(8)	9474(8)	7364(6)	38(2)
C(43)	7432(9)	10934(8)	7000(6)	44(1)
C(44)	6067(10)	10694(8)	6123(6)	51(2)
C(45)	7591(7)	12154(7)	8115(5)	30(1)
C(46)	8679(8)	12549(8)	8977(6)	43(1)
C(47)	8904(12)	13711(11)	9944(7)	81(1)
C(48)	7892(11)	14336(9)	10095(6)	57(1)
C(49)	6657(10)	13954(8)	9372(6)	51(1)
C(50)	6459(8)	12771(8)	8316(6)	40(1)
Cl(1)	2267(3)	2903(2)	7394(2)	65(1)
O(5)	3140(9)	3089(9)	6730(6)	102(1)
O(6)	2485(10)	4091(10)	8265(7)	119(2)
O(7)	2305(9)	1689(8)	7628(7)	95(1)
O(8)	881(10)	2944(10)	7057(8)	125(2)
Cl(2)	7958(3)	8212(3)	3888(3)	75(1)
O(9)	7259(11)	6981(9)	2657(7)	123(2)
O(10)	9031(11)	8095(11)	4667(8)	141(2)
O(11)	6606(7)	7838(7)	4105(5)	64(1)
O(12)	8289(10)	9640(9)	3912(7)	114(1)

[a] All atoms were refined anisotropically. The expression for the equivalent isotropic thermal parameter is $U_{eq(iso)} = [\sum_i \sum_j U_{ij} a_i^* \cdot a_j^* \cdot a_i \cdot a_j]/3$.

structure solution and refinement with SHELX programs.[10a] The structure was solved by direct methods in the noncentric triclinic space group $P1$ with two molecules in the crystallographic asymmetric unit using scattering factors taken from ref 10b. The absolute configurations at the metal centers were determined with reference to the S_C chiral carbon center of the Schiff-base ligand.[11] In the absence of any form of disorder in the crystal structure, the possibility of a centric space group ($P\bar{1}$) was ruled out. Pertinent crystallographic parameters are summarized in Table I. The positional parameters along with the isotropic thermal parameters are given in Table II.

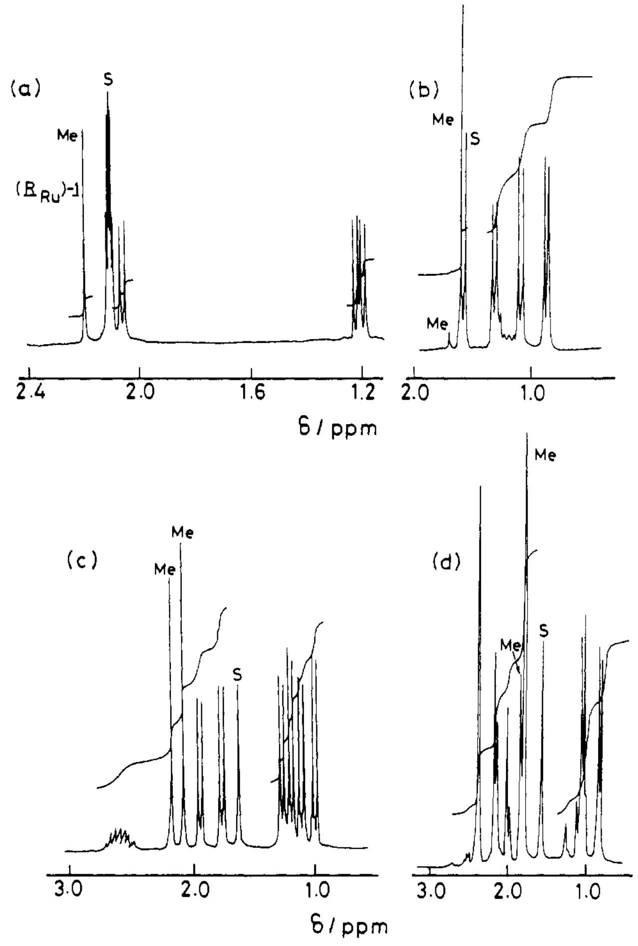


Figure 1. Selected portions of the ^1H NMR spectra of $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)(H_2O)(L^*)](ClO_4)$ (a) in acetone-d_6 and its PPh_3 (b), $P(OMe)_3$ (c), and 4-Mepy (d) adducts in $CDCl_3$ showing the diastereomeric ratios from the Me signal of the *p*-cymene ligand (S = solvent peaks).

Results and Discussion

^{1}H NMR Spectra and Crystal Structure. Complex **1** is isolated in high yield using a straightforward synthetic route[12] involving first the removal of chloride in $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)Cl(L^*)]$ by a halogen scavenger followed by addition of water to the resulting intermediate which could be a 16-electron or an acetone solvate species.[13-15] Complex **1** is a 1:1 electrolyte and exhibits moderate solubility and stability in an aqueous medium.

---

(10) (a) Sheldrick, G. M. *SHELXS 86: A program for crystal structure solution*; Universität Göttingen: Göttingen, Germany, 1986. Sheldrick, G. M. *SHELX 76: A program for crystal structure determination*; University of Cambridge: Cambridge, England, 1976. (b) *International Tables for X-ray crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(11) (a) Reisner, G. M.; Bernal, I. *J. Organomet. Chem.* **1979**, *173*, 53. (b) Bernal, I.; Ries, W.; Brunner, H.; Rastogi, D. K. *J. Organomet. Chem.* **1985**, *290*, 353. (c) The substituent at the imine carbon of –C(R)═NR*, where R* = CH(Me)Ph, is known[11b] to have critical influence on the configuration of the chiral carbon center which is stable when R = H but undergoes inversion in presence of a bulky group (R = Ph). Refinement of our data gave lower *R* factors with $(S_{Ru},S_C;R_{Ru},S_C)$-**1** than with $(R_{Ru},R_C;S_{Ru},R_C)$-**1**.

(12) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186.

(13) Kölle, U.; Kossakowski, J.; Rabbe, G. *Angew Chem., Int. Ed. Engl.* **1990**, *29*, 773.

(14) Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672.

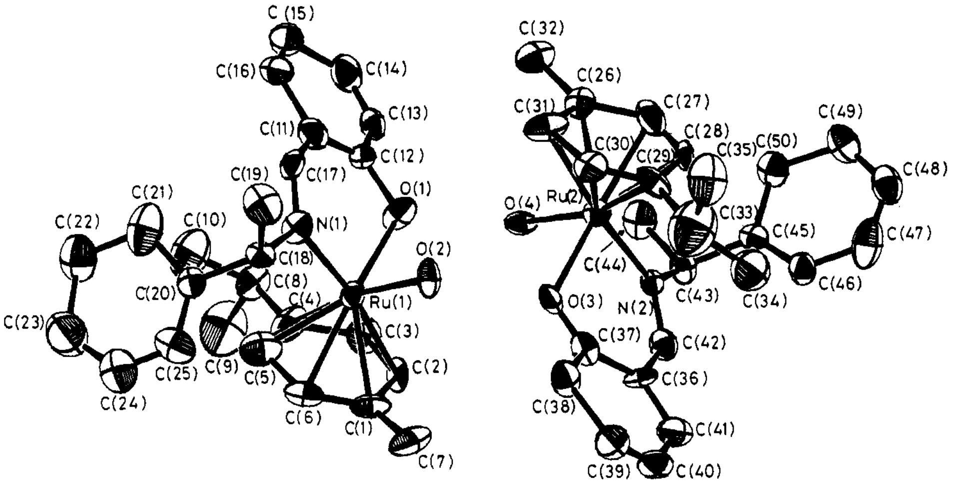


Figure 2. ORTEP diagram of two cationic diastereomers showing the thermal ellipsoids at the 50% probability level and the atom-numbering scheme.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) in $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)(H_2O)(L^*)](ClO_4)$ (1)[a]

Ru(1)–O(1)	2.032(5)	Ru(2)–O(4)	2.119(5)
Ru(1)–O(2)	2.203(5)	Ru(2)–O(3)	2.086(6)
Ru(1)–N(1)	2.049(7)	Ru(2)–N(2)	2.176(6)
Ru(1)–C_0	1.649(11)	Ru(2)–C_0'	1.706(10)
N(1)–Ru(1)–O(2)	82.8(2)	N(2)–Ru(2)–O(3)	83.7(2)
O(1)–Ru(1)–N(1)	86.9(2)	N(2)–Ru(2)–O(4)	85.0(2)
O(1)–Ru(1)–O(2)	80.3(2)	O(4)–Ru(2)–O(3)	81.8(2)

[a] C_0 and C_0' are the centroids of the *p*-cymene rings.

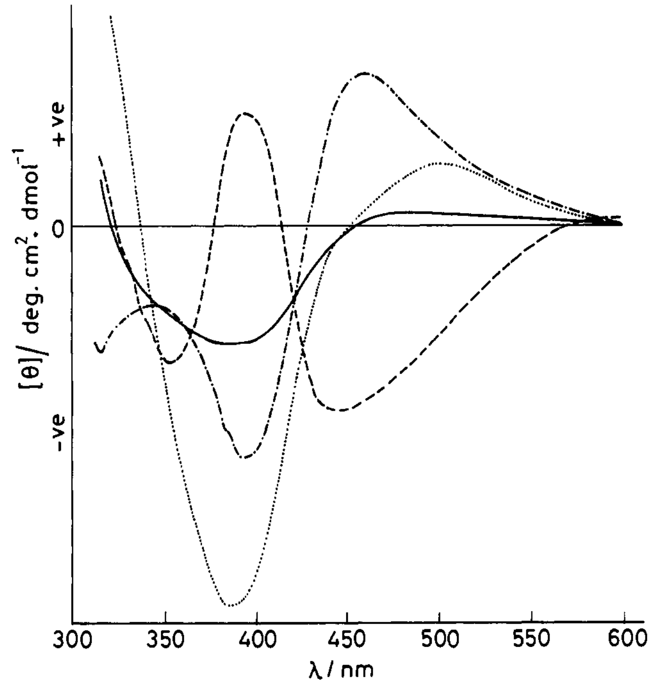


Figure 3. CD spectra of $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)(L)(L^*)](ClO_4)$ with L = H_2O (—), PPh_3 (- - -), and 4-Mepy (– • –) in acetone and of $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)Br(L^*)]$ (···) in methanol (data from ref 23).

The ^1H NMR spectra of **1** show characteristic features of an essentially pure diastereomer in solution. The isomeric ratio is determined from the peak integrations of the methyl proton signals of the *p*-cymene ligand (Figure 1). The X-ray structural study of a single crystal of **1**, however, reveals the presence of two diastereomers in a 1:1 ratio displaying opposite configurations at the metal centers. An ORTEP[16] diagram of (R_{Ru},S_C;S_{Ru},S_C)-**1** is shown in Figure 2. The loss of the centrosymmetric relationship between $S_{Ru(1)}$-**1** and $R_{Ru(2)}$-**1** is attributed to the presence of the S_C chiral carbon atom in both the diastereomers. The metal absolute configurations are determined with reference to this carbon using a priority order:[18] η-$MeC_6H_4Pr^i$-*p* > O[(*S*)-L*] > O(H_2O) > N[(*S*)-L*]. The crystalline mass was found to be uniform, and this was verified from the unit cell parameters of several crystals of **1** and the corresponding hexafluorophosphate salt.[17] The ^1H NMR spectral features of these single crystals are identical with those obtained from the powdered sample showing a single diastereomer in solution. The epimerization at the metal center during crystallization indicates[19] an equilibrium S_{Ru}-**1** $\rightleftharpoons$ R_{Ru}-**1** to be operative in the solution phase.

In the molecules, the considerably long Ru–OH_2 bond distances, compared to those reported[20] for $[Ru(\eta\text{-}C_6H_6)(H_2O)_3](SO_4)$, suggest a weak coordination of the aqua ligand. An intriguing structural feature is the difference of 0.09 Å between (*S*)-Ru(1)–O(2) and (*R*)-Ru(2)–O(4) distances (Table III). In the S_{Ru}-**1** isomer, the Ru–OH_2 bond length is considerably longer than the Ru(1)–O(1) and Ru(1)–N(1) distances. In comparison, the Ru–OH_2 bond in the R_{Ru}-**1** isomer is marginally longer than Ru(1)–O(3) bond but significantly shorter than the Ru(1)–N(2) bond (Table III). The diastereomer with a shorter Ru–OH_2 distance, viz. R_{Ru}-**1**, is expected to be prevalent in the solution phase.[17] The ^1H NMR and CD spectral studies of **1** and its adducts also suggest a R_{Ru} metal configuration of **1** in solution (vide infra).

Reactivity and Stereochemistry.[21] Complex **1** forms stable 1:1 adducts with P-, N-, and halide-donor ligands.[22] The preparative routes are given in Scheme I. The diastereomeric ratio in the adduct species is obtained from the ^1H NMR peak integrations of the methyl protons of η-$MeC_6H_4Pr^i$-*p* (Figure 1). The stereochemical changes associated with the ligand substitution reactions are studied by using the CD spectral data[23] (Figure 3).

While the reactions of **1** with halides are found to be highly stereoselective, showing a retention of metal configuration, an epimerization is observed during $P(OMe)_3$ adduct formation. The PPh_3 ligation results in a net inversion of the metal

---

(15) (a) Wilczewski, T. *J. Organomet. Chem.* **1982**, *224*, C1. (b) Haines, R. J.; Du Preez, A. L. *J. Organomet. Chem.* **1975**, *84*, 357.

(16) Johnson, C. K. *ORTEP II: A program for thermal ellipsoid plotting*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

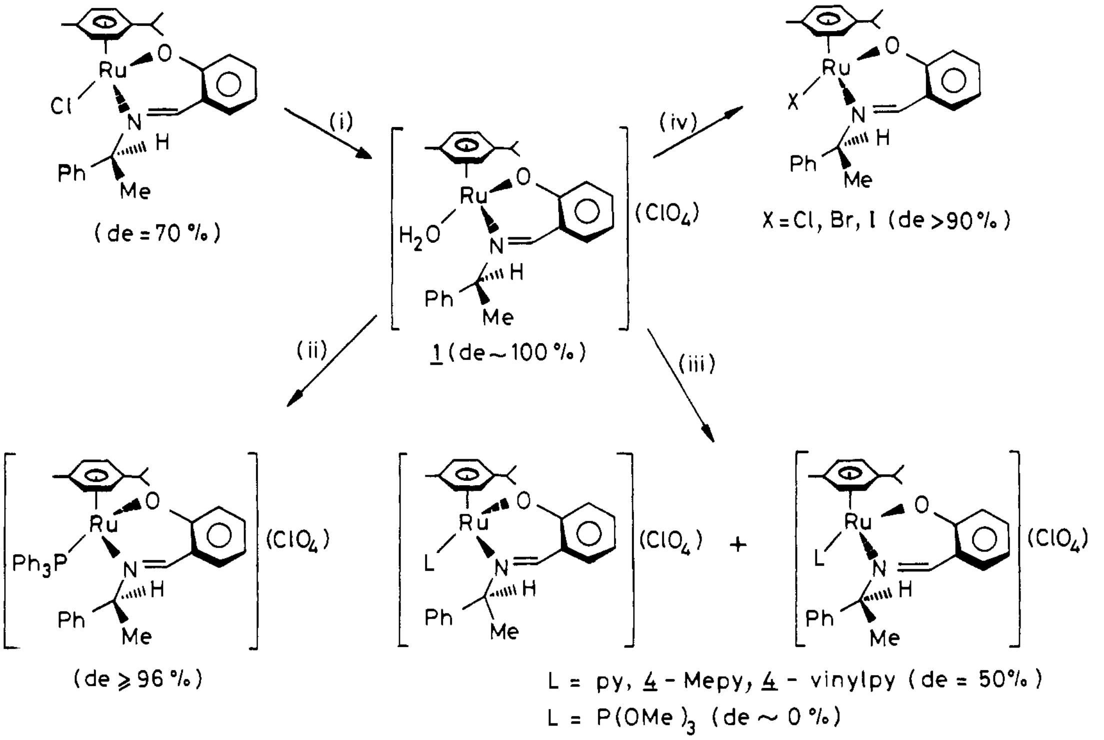
(17) The PF_6 salt of the complex, showing a single diastereomeric form in the solution phase, crystallizes in the space group *P*1 (No. 1) with the following cell parameters: $a = 10.313(2)$ Å, $b = 10.420(1)$ Å, $c = 13.983(1)$ Å, $\alpha = 68.59(1)°$, $\beta = 110.14(1)°$, $\gamma = 102.91(1)°$, $V = 1305(1)$ Å^3, $Z = 2$. The X-ray structural features of $[Ru(\eta\text{-}C_6H_4Pr^i\text{-}p)(H_2O)(L^*)](PF_6)$ are similar to those observed for the ClO_4 salt, **1**. The Ru–OH_2 bond distances for the R_{Ru} and S_{Ru} isomers are 2.123(7) and 2.184(4) Å, respectively, in the structure refined to R (R_w) = 0.0565 (0.0611): Mandal, S. K.; Chakravarty, A. R. Unpublished results.

(18) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598.

(19) Faller, J. W.; Ma, Y. *Organometallics* **1992**, *11*, 2726.

(20) Stebler-Rŏthlisberger, M.; Hummel, W.; Pittet, P. A.; Bürgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358.

Scheme I. Reactions Involving the aqua complex (1) with P-, N-, and Halide-Donor Ligands Using 1:1.3 Molar Proportions[a]



[a] Key: (i) Me_2CO–$AgClO_4$, –5 °C, H_2O; (ii) Me_2CO, PPh_3, 0 °C; (iii) Me_2CO, L, –5 °C (the diastereomeric ratios of the $P(OMe)_3$ and py base adducts are 1:1 and 3:1, respectively); (iv) H_2O, NaX, ~0 °C.

configuration. The absolute configuration of metal in the PPh_3 adduct has earlier been determined[6] as R_{Ru} from its crystal structure. The formation of the pyridine adducts is less stereoselective, showing a % de of 50 (de, diastereomeric excess). The CD spectral bands appearing at 396 and near 450 nm for the PPh_3 and 4-Mepy adducts are almost mirror images of each other (Figure 3). This suggests a stereochemical retention during 4-Mepy adduct formation. The sign and shape of the spectral bands compare well with those of the aqua complex.

The selectivity in the substitution reactions with py bases has been found to be virtually unaffected by the electronic effects of the para substituents of the 4-Mepy and 4-(vinyl)py ligands (py = pyridine). The stereochemical changes associated with the metal in the adduct-forming reactions follow an inversion order: $PPh_3 \gg P(OMe)_3 >$ pyridine bases (py, *4*-Mepy, *4*-(vinyl)py) $\gg$ halides (I, Br, Cl) > H_2O.

Conclusions

A new water-soluble and air-stable diastereomeric organometallic complex containing a weakly bound aqua ligand was prepared and structurally characterized. In the aqua complex, the metal–ligand ancillary bond distances are found to vary drastically, and the results indicate the prevalence of the R_{Ru}-**1** isomer in the solution phase. The results exemplifying a rare case of net inversion of metal configuration during PPh_3 adduct formation are of significance since similar reactions with analogous chiral diphosphine complexes are known[1,24] to be stereospecific in nature.

Supplementary Material Available: Textural details of the crystal structure determination, a unit-cell stereo packing diagram, and tables listing additional crystallographic data, bond distances, bond angles, and anisotropic thermal parameters for $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)(H_2O)(L^*)](ClO_4)$ and tables of elemental analytical and ^1H NMR data for the adduct species (18 pages). Ordering information is given on any current masthead page.

---

(21) The formal absolute configuration at the metal center is determined[18] using a general priority order: I > Br > *p*-cymene > Cl > $P(OMe)_3$ > PPh_3 > O(L*) > H_2O > N(L*) > pyridine bases. While the halide adduct formation from R_{Ru}-**1** takes place with a retention of configuration, the formal absolute configurations of the metal center in the iodo, bromo, and chloro adducts are determined as R_{Ru}, R_{Ru}, and S_{Ru}, respectively, on the basis of the above priority order. Similarly, the spatial arrangements of ligands in the aqua and PPh_3 complexes are different although they have the same R_{Ru} configuration. The stereoselectivity of the substitution reactions is obtained from the CD spectral studies. Complexes showing similar CD spectral features are tentatively assigned so that they have the same spatial arrangement of ligands around the metal atom.

(22) All the complexes gave satisfactory elemental analysis and ^1H NMR spectral results fitting with their formulations. Selected ^1H NMR data for $[Ru(\eta\text{-}C_6H_4Pr^i\text{-}p)(L)(L^*)](ClO_4)$ and $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)X(L^*)]$ in $CDCl_3$ [δ(Me) of *p*-cymene (isomeric ratio)]: L = PPh_3, 1.70, 1.59 (1:49); L = 4-Mepy, 1.83, 1.79 (1:3); L = py, 1.96, 1.78 (1:3); L = 4-(vinyl)py, 2.00, 1.81 (1:3); L = $P(OMe)_3$, 2.06, 2.15 (1:1); X = Cl, 2.11, 2.16 (19:1); X = Br, 2.14, 2.18 (19:1); X = I, 2.28, 2.36 (49:1).

(23) CD spectral data for $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)(L)(L^*)](ClO_4)$ in acetone and $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)X(L^*)]$ in methanol [$[\theta]^{25}{}_{\lambda}$ ($deg\cdot cm^2\cdot dmol^{-1}$) values of maxima, minima, and nodes (λ, nm)]: L = PPh_3, +113 (600), –2454 (443), 0 (418), +1545 (396), –1818 (353), 0 (328); L = 4-Mepy, 0 (600), +2090 (459), 0 (428), –3090 (396), –1068 (348); X = Cl, 0 (600), +4200 (500), 0 (454), –28 600 (374), 0 (341); X = Br, 0 (600), +3200 (498), 0 (448), –20 600 (382), 0 (330); X = I, 0 (600), +1400 (530), 0 (496), –1600 (470), –22 400 (364).

(24) Hoffman, P. *Angew. Chem.* **1977**, *89*, 551.