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(2,7-Dimethyloctadienediyl)ruthenium(IV) Complexes: Isomerism and Solution Equilibria for Dichlorobis(μ-chloro)bis[(1-3-η:6-8-η)-2,7-dimethyloctadienediyl]diruthenium(IV) and Related Monomeric Solvates

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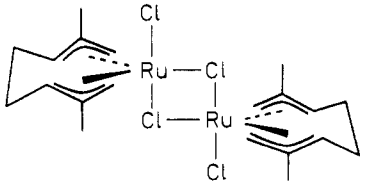
The ^{1}H NMR spectra of $[RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})]_2$ (**1**) in noncoordinating solvents indicate that an equilibrium between two diastereoisomeric forms is rapidly established in solution ($k_{298} = (3 \pm 2) \times 10^{-1}$ s^{-1}; $\Delta G^{\ddagger}_{298} = 76 \pm 2$ kJ mol^{-1}) and provide evidence that the local C_2 symmetry of the $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})]$ fragments is retained. Monomeric solvates of formula $[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})S]$ form on dissolution of **1** in coordinating solvents and have been isolated for S = pyridine (**2**), DMSO (S-bound) (**3**), MeCN (**4**), and DMF (O-bound) (**5**). A trigonal-bipyramidal ruthenium coordination, with the octadienediyl ligand locked in a local C_2 symmetry configuration and occupying two of the equatorial sites, is proposed for all the solvates. In solution, **2** and **3** feature solvent coordination uniquely in the third equatorial site, and the chiral octadienediyl configuration results in diastereotopic methyl groups coordinated to sulfur in **3**. Variable-temperature ^{1}H NMR measurements in acetone-d_6 show that these diastereotopic methyl groups are rendered equivalent as a result of intermolecular DMSO exchange between the enantiomers ($\Delta G^{\ddagger}_{308} = 66.5 \pm 0.5$ kJ mol^{-1}). The formation of **4** and **5** from **1** proceeds via initial formation of equatorial solvates, which rapidly isomerize to an equilibrium mixture containing both axially and equatorially solvated isomers. Equilibrium constants and reaction enthalpies for the isomerizations have been determined. The kinetic activation parameters for the interconversion of the isomers of **4** have also been evaluated. A mechanism involving solvent exchange is proposed. Equilibria of the type $[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})S] \rightleftarrows [RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})S']$ or $[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})S] \rightleftarrows$ **1** are set up on dissolution of **2-5** in certain coordinating or noncoordinating solvents, respectively. Evaluation of the equilibrium constants suggests that the affinities for coordination to the monomers of **1** fall in the sequence pyridine > DMSO > MeCN > DMF.

Introduction

The chloro-bridged dimer $[RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})]_2$ (**1**) has recently been shown to be a useful reagent in organoruthenium chemistry, since it can effectively be used to provide in situ sources of Ru^{2+} and $[RuL]^{2+}$ ions (L = a two-electron ligand).[2] In comparison with related chloro-bridged dimers, such as $[RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})]_2$ or $[RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_2$,[3] however, knowledge of the chemistry of **1** remains very scant. Hence, although brief details of a synthesis of **1** and a molecular structure were published by Allegra and co-workers in 1965,[4] the only derivatives subsequently reported were the neutral monomeric adducts $[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})L]$, where L = CO, PPh_3, PF_3, PF_2NMe_2, PCl_2CF_3, or $P(OCH_2)_3CPh$, which were isolated by Nixon and co-workers in 1974. A common structural type for all these adducts was proposed on the basis of NMR data.[5]

The reported structure for **1**, determined by Colombo and Allegra,[6] is shown schematically in the illustration. It has overall C_i molecular symmetry, with the 2,7-dimethyloctadienediyl ligands locked in a local C_2 symmetry configuration and with syn-substituted allyl groups. The coordination about each ruthenium atom was described as trigonal bipyramidal, with the organic ligand occupying two of the equatorial sites.



C_i

The structural type for the known neutral monomeric adducts was later established by Hitchcock, Nixon, and Sinclair, who reported crystallographic data for $[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})PF_3]$.[7] The octadienediyl ligand configuration and the ruthenium coordination geometry observed in **1** were found to be conserved, with both chlorides being axial and the two-electron ligand equatorial.

In view of the potential synthetic importance of **1**, and because of our previous interests in octadienediyl complexes of ruthenium,[8] we have started a systematic study of its chemistry. In this paper we report a modified synthesis of **1**, identify the nature of the species present on dissolution of **1** in a range of organic solvents, and show the existence of a series of solution equilibria between these species. The chirality of the octadienediyl configuration in these complexes is recognized for the first time, and some of its consequences are discussed. In a future article, the synthesis and properties of the first cationic derivatives of the $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})]$ fragment will be described.

Experimental Section

General Considerations. Microanalyses were carried out by Ilse Beetz Microanalytisches Laboratorium, Kronach, West Germany. Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer (4000-400 cm^{-1}) as KBr disks and calibrated with polystyrene film. A Bruker IFS 113v interferometer was used to record spectra in the region 650-150 cm^{-1} from polyethylene disks. NMR spectra were recorded on Bruker WH-360 and AC-200 FT spectrometers with Me_4Si as internal reference. Conductivity measurements were made on ca. 10^{-3} M solutions at 20 °C by using a Metrohm 660 conductometer. $RuCl_3 \cdot nH_2O$ was supplied by Johnson Matthey Ltd. Isoprene (Fluka) and all solvents (reagent grade) were deoxygenated prior to use, and all manipulations were routinely carried out under nitrogen by using standard Schlenk techniques.

Dichlorobis(μ-chloro)bis[(1-3-η:6-8-η)-2,7-dimethyloctadienediyl]diruthenium(IV) (1). Isoprene (190 mL) was added to a solution of $RuCl_3 \cdot nH_2O$ (5.3 g) in absolute ethanol (80 mL), and the mixture was refluxed under nitrogen. The formation of **1** as a purple precipitate was first apparent after 4 days, and after 14 days of reflux it was collected on a Büchner funnel, washed with ethanol and diethyl ether, and dried under vacuum. Yield: 4.7 g (ca. 75%). Anal. Calcd for $C_{10}H_{16}Cl_2Ru$: C, 38.97; H, 5.23. Found: C, 39.12; H, 5.40. Mp: 195-205 °C dec.

(1) New address: Department of Chemistry, University of Lancaster, Lancaster LA1 4YA, U.K.
(2) Cox, D. N.; Roulet, R. *J. Chem. Soc., Chem. Commun.* **1988**, 951.
(3) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon, Oxford, U.K., 1982; Vol. 4, p 796. Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301.
(4) Porri, L.; Gallazzi, M. C.; Colombo, A.; Allegra, G. *Tetrahedron Lett.* **1965**, 4187.
(5) Head, R. A.; Nixon, J. F.; Swain, J. R.; Woodard, C. M. *J. Organomet. Chem.* **1974**, *76*, 393.
(6) Colombo, A.; Allegra, G. *Acta Crystallogr.* **1971**, *B27*, 1653.
(7) Hitchcock, P. B.; Nixon, J. F.; Sinclair, J. *J. Organomet. Chem.* **1975**, *86*, C34.
(8) Cox, D. N.; Roulet, R.; Chapuis, G. *Organometallics* **1985**, *4*, 2001. Cox, D. N.; Roulet, R. *J. Organomet. Chem.* **1988**, *342*, 87.

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IR: 3088 w, 3009 m, 2958 m, 2903 m, 2848 m, 1451 s, 1385 s, 1355 m, 1321 m, 1289 w, 1169 m, 1125 w, 1076 w, 1042 m, 1019 s, 997 m, 947 m, 929 s, 912 m, 896 w, 848 s, 776 m, 708 m, 563 w, 550 w, 450 m, 416 w, 357 m, 331 m, 249 s, 238 m cm^{-1}.

Dichloro(pyridine)[(1-3-η:6-8-η)-2,7-dimethyloctadienediyl]ruthenium(IV) (2). Pyridine (150 μL, 1.86 mmol) was added to a solution of **1** (440 mg, 0.71 mmol) in chloroform (20 mL), and the mixture was stirred at room temperature for 1 h. The solution was partially evaporated, and addition of hexane and cooling gave **2** as orange-red microcrystals, which were collected by filtration and dried under vacuum. Yield: 450 mg (82%). Anal. Calcd for $C_{15}H_{21}Cl_2NRu$: C, 46.51; H, 5.46; N 3.61. Found: C, 46.58; H, 5.59; N, 3.67. Mp: 145–147 °C dec. Conductivity (pyridine solution): Λ_M = 0.4 S cm^2 mol^{-1}. ^1H NMR (acetone-d_6, 298 K): δ 9.26 (m, 2 H, py), 7.95 (m, 1 H, py), 7.47 (m, 2 H, py), 5.22 (m, 2 H, methynes), 4.53 and 4.40 (2 s, 4 H, terminal methylenes), 3.00 and 2.42 (2 m, 4 H, chain methylenes), 2.37 (s, 6 H, methyls). IR: 3107 w, 3077 w, 3045 w, 2999 m, 2960 m, 2909 m, 2848 w, 1603 m, 1487 m, 1444 s, 1383 s, 1360 w, 1347 w, 1314 w, 1281 m, 1223 s, 1153 m, 1071 s, 1041 m, 1024 s, 984 w, 964 m, 958 m, 949 m, 920 w, 862 m, 823 m, 784 m, 762 s, 697 s, 633 w, 498 m, 453 m, 313 s, 288 m, 247 m, 223 s, 208 w, 190 w cm^{-1}.

Dichloro(dimethyl sulfoxide)[(1-3-η:6-8-η)-2,7-dimethyloctadienediyl]ruthenium(IV) (3). Dimethyl sulfoxide (200 μL, 2.82 mmol) was added to a solution of **1** (440 mg, 0.71 mmol) in chloroform (20 mL), and the mixture was stirred at room temperature for 1 h. The solution was partially evaporated, and addition of hexane and cooling gave **3** as orange microcrystals, which were collected by filtration and dried under vacuum. Yield: 410 mg (75%). Anal. Calcd for $C_{12}H_{22}Cl_2ORuS$: C, 37.31; H, 5.74. Found: C, 37.28; H, 5.72. Mp: 152 °C. Conductivity (DMSO solution): Λ_M = 0.3 S cm^2 mol^{-1}. ^1H NMR (acetone-d_6, 200 K): δ 5.06 (m, 2 H, methynes), 4.76 and 3.89 (2 s, 4 H, terminal methylenes), 3.30 and 3.23 (2 s, 6 H, Me_2SO), 3.20 and 2.48 (2 m, 4 H, chain methylenes), 2.19 (s, 6 H, methyls). ^{13}C NMR (acetone-d_6, 200 K): δ 130.5 (s), 102.3 (d, J_{CH} = 162 Hz), 75.8 (t, J_{CH} = 160 Hz), 44.0 (q, J_{CH} = 140 Hz, Me_2SO), 43.2 (q, J_{CH} = 140 Hz, Me_2SO), 36.1 (t, J_{CH} = 130 Hz), 21.2 (q, J_{CH} = 129 Hz). IR: 3018 m, 2999 w, 2965 w, 2911 m, 2854 w, 1494 w, 1460 m, 1422 s, 1381 s, 1346 w, 1315 m, 1298 w, 1280 m, 1194 w, 1100 vs, 1031 vs, 983 w, 973 w, 963 m, 945 w, 920 m, 856 m, 821 w, 792 w, 783 w, 718 m, 676 m, 425 s, 373 m, 348 w, 339 w, 316 s, 256 m, 241 m, 232 m, 195 w cm^{-1}.

Dichloro(acetonitrile)[(1-3-η:6-8-η)-2,7-dimethyloctadienediyl]ruthenium(IV) (4). Complex **1** (300 mg, 0.49 mmol) was dissolved in acetonitrile (20 mL), and the orange solution obtained was partially evaporated. Addition of diethyl ether and cooling gave orange-yellow microcrystals of **4**, which were collected by filtration and dried under vacuum. Yield: 260 mg (76%). Anal. Calcd for $C_{12}H_{19}Cl_2NRu$: C, 41.27; H, 5.48; N, 4.01. Found: C, 41.34; H, 5.44; N, 4.07. Mp: ca. 160 °C (re-forms **1**). Conductivity (MeCN solution): Λ_M = 0.7 S cm^2 mol^{-1}. IR: 3086 w, 3008 w, 2964 m, 2911 m, 2858 m, 1456 s, 1413 m, 1387 s, 1379 s, 1361 m, 1342 w, 1314 m, 1276 m, 1063 w, 1044 m, 1029 s, 1016 s, 978 w, 965 m, 949 m, 941 m, 918 m, 898 w, 865 s, 821 m, 790 s, 569 w, 543 w, 518 w, 499 m, 458 w, 441 w, 315 m, 294 m, 274 m, 222 m, 192 w cm^{-1}.

Dichloro(*N*,*N*-dimethylformamide)[(1-3-η:6-8-η)-2,7-dimethyloctadienediyl]ruthenium(IV) (5). Complex **1** (300 mg, 0.49 mmol) was dissolved in warm *N*,*N*-dimethylformamide (3 mL). Addition of diethyl ether and cooling gave brown microcrystals of **5**, which were collected by filtration and dried under vacuum. Yield: 255 mg (69%). Anal. Calcd for $C_{13}H_{23}Cl_2NORu$: C, 40.95; H, 6.08; N, 3.67. Found: C, 41.07; H, 6.02; N, 3.78. Mp: ca. 105 °C (re-forms **1**). Conductivity (DMF solution): Λ_M = 1.2 S cm^2 mol^{-1}. IR: 3069 w, 2999 m, 2955 m, 2910 m, 2850 w, 1631 br, s, 1491 w, 1450 m, 1426 s, 1383 m, 1361 s, 1316 w, 1284 w, 1251 m, 1118 s, 1023 m, 992 w, 962 m, 955 w, 942 w, 928 m, 868 m, 843 m, 820 w, 805 w, 786 m, 699 s, 562 w, 502 w, 456 w, 447 w, 405 m, 351 m, 313 m, 301 m, 230 s cm^{-1}.

Kinetic Measurements. The kinetic data reported for **1** and **4** are derived from integration of appropriate regions of the 200-MHz ^1H NMR spectra recorded on a Bruker AC 200 spectrometer equipped with a B-VT-1000 temperature control unit. Temperatures (constant to ±0.3 °C) were measured before and after each run, using a 100-Ω platinum resistance attached to a Hewlett Packard 2802A digital thermometer, by the substitution technique.[9] Samples were kept in the thermostated probe for the entire duration of each experiment. In general, each kinetic run consisted of 8–15 spectra collected over 2–3 half-lives, with a further spectrum of the system at equilibrium. For the fastest reactions, each spectrum was acquired over a 16-s period with 2 min between successive samplings.

(9) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.

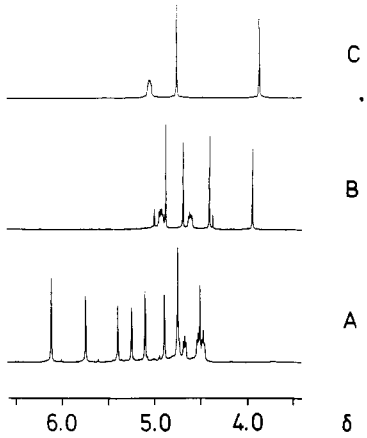


Figure 1. Allyl proton region of the room-temperature ^1H NMR spectra (360 MHz) of solutions prepared by dissolution of **1** in (A) $CDCl_3$, (B) CD_3CN, and (C) DMSO-d_6.

Results and Discussion

Modified Preparation of $[RuCl(\mu\text{-}Cl)(\eta^3:\eta^3\text{-}C_{10}H_{16})]_2$ and Isolation of Solvent-Coordinated Monomers. The original preparation of **1**, from 2-methylbutadiene (isoprene) and ruthenium trichloride, involved temperatures that can only be sustained in a sealed vessel, and no yield was reported. We have found, however, that **1** is more conveniently prepared in high yield (ca. 75%), and at lower temperature, by prolonged reflux of commercial "$RuCl_3 \cdot nH_2O$" in a 7:3 by volume mixture of isoprene and ethanol. This method gives **1** as a purple powder, rather than the red-brown crystallites originally obtained by Allegra and co-workers.[4]

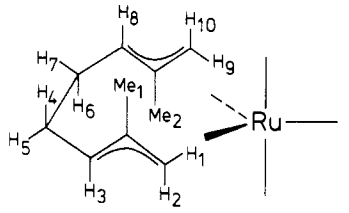
Although **1** is soluble in several organic solvents, purple solutions are obtained only in noncoordinating solvents such as chloroform or dichloromethane. In pyridine, dimethyl sulfoxide (DMSO), acetonitrile, or *N*,*N*-dimethylformamide (DMF), **1** dissolves to give orange nonconducting solutions. Air-stable microcrystalline solvates of composition $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})S]$, with S = pyridine or pyridine-d_5 (**2** or **2d**), DMSO or DMSO-d_6 (**3** or **3d**), CH_3CN or CD_3CN (**4** or **4d**), and DMF or DMF-d_7 (**5** or **5d**), were subsequently isolated from these orange solutions.

The infrared spectra of **3** and **5** provide evidence for the mode of coordination of the DMSO and DMF ligands in these complexes. Two intense absorptions in the infrared spectrum of **3**, associated with the DMSO ligand, occurred at 1100 and 1031 cm^{-1}, and are assigned to SO stretching and methyl rocking, respectively. This assignment is confirmed by the infrared spectrum of **3d**, where these bands occurred at 1097 and 830 cm^{-1}, respectively. Hence, since ν(SO) in **3** occurs to significantly higher wavenumber than 1040 cm^{-1}, the DMSO ligand is S-bound.[10] In the infrared spectrum of **5**, the intense absorption centred at 1631 cm^{-1} is assigned to the CO stretch of the DMF ligand, and is at significantly lower wavenumber than the corresponding absorption in neat DMF (1679 cm^{-1}). According to Gioria and Susz,[11] a reduction in frequency of ν(CO) on coordination is characteristic of O-bound DMF, and hence the DMF ligand in **5** is O-bound. The infrared spectrum of **4** is notable for the absence of a band assignable to the CN stretch. The weak or unobservable nature of ν(CN) in certain acetonitrile complexes is, however, documented.[12] For all of the complexes **1–5**, the regions 600–150 cm^{-1} are too complicated for the number and location of the Ru–Cl stretches to be unambiguously defined.

Solvent-Variable ^1H NMR Spectra of 1. ^1H NMR spectra for **1** have not previously been reported, although their pronounced temperature dependence, in an unspecified solvent, has been claimed.[5] The ^1H NMR spectra of **1**, however, are highly solvent

(10) Cotton, F. A.; Francis, R.; Horrocks, W. *J. Phys. Chem.* **1960**, *64*, 1534. Reynolds, W. L. *Prog. Inorg. Chem.* **1970**, *12*, 10.
(11) Gioria, J. M.; Susz, B. P. *Helv. Chim. Acta* **1971**, *54*, 2251.
(12) Endres, H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 2, p 261. Miedaner, A.; DuBois, D. L. *Inorg. Chem.* **1988**, *27*, 2479.

Table I. Solvent-Dependent ^{1}H NMR Spectra (360 MHz) Obtained on Dissolution of $[RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$[a]

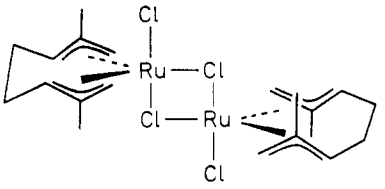


solvent	proton assignment: terminal allyl[b] (H_1, H_9; H_2, H_{10})	internal allyl[c] (H_3, H_8)	methylene chain[c] (H_4, H_6; H_5, H_7)	methyl[d] (Me_1, Me_2)
$CDCl_3$	6.11, 5.73,[e] 5.38,[e] 5.23,[e] 5.09, 4.88, 4.74, 4.49[e]	4.72, 4.66,[e] 4.51,[e] 4.46	ca. 2.7–2.4	2.49, 2.39,[e] 2.30,[e] 2.25
CD_2Cl_2[f]	5.73, 5.34, 5.19, 4.30	4.57, 4.49	2.6–2.5	2.38, 2.26
DMSO-d_6	4.75, 3.86	5.04	3.11, 2.50	2.22
C_5D_5N	4.67,[g] 4.67[g]	5.44	2.94, 2.26	2.48
CD_3CN	5.00,[h] 4.88, 4.70, 4.42, 4.38,[h] 3.96	4.93, 4.90,[h] 4.61	3.0,[i] 2.4[i]	2.31, 2.29,[h] 2.28
DMF-d_7	5.19, 5.11, 4.89,[h] 4.64,[h] 4.44, 3.46	4.96, 4.81,[h] 4.41	3.1,[i] 2.5[i]	2.34,[h] 2.29, 1.94

[a] At 298 K, unless otherwise stated. Chemical shifts in δ with Me_4Si as reference. Relative integrations are all consistent with assignment. [b] Singlets, ^2J(syn/anti) < 1.5 Hz. [c] Multiplets. [d] Singlets. [e] Signals of C_i isomer. [f] Spectrum recorded at 200 K immediately following dissolution at 220 K. [g] Accidental degeneracy of two signals is raised on addition of $CDCl_3$. [h] Signals of equatorially solvated isomer. [i] Complexity of multiplets consistent with four inequivalent protons. Signals of equatorially solvated isomer obscured.

dependent, and in ways which are extremely informative. A comparison of the regions δ 6.5–3.5 in the ^{1}H NMR spectra of solutions prepared by room-temperature dissolution of **1** in $CDCl_3$, CD_3CN, and DMSO-d_6 is shown in Figure 1. Only the allyl protons of the 2,7-dimethyloctadienediyl chains resonate in this region. The singlets are due to the terminal methylene protons on C(1) and C(8) (^2J(syn–anti) unobserved), and the multiplets to the methyne protons on C(3) and C(6). Complete ^{1}H NMR spectral data for solutions prepared by dissolution of **1** in the range of solvents studied is given in Table I. The information contained in the above spectra, and in additional spectra including low-temperature dissolution experiments and variable-temperature studies, is discussed below.

Existence of Diastereoisomeric Forms of 1. The ^{1}H NMR spectra of **1** following room-temperature dissolution in $CDCl_3$, CD_2Cl_2, and 1,1,2,2-tetrachloroethane-d_2 are essentially identical in appearance. The spectra indicate eight distinct environments for the terminal methylene protons on C(1) and C(8) and four distinct environments for the methyl groups on C(2) and C(7). In terms of the previously reported molecular structure of C_i symmetry for **1**, exactly twice the number of expected proton environments are present. This suggests that an approximately equimolar mixture of two isomers is present in solutions at room temperature, and we propose that the new isomer has the following structure of C_2 symmetry:



C_2

The previously unrecognized existence of two forms of **1** is a stereochemical consequence of the configuration adopted by the 2,7-dimethyloctadienediyl ligands. The local C_2 symmetry of this configuration renders the $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]$ fragments chiral, and hence the crystallographically characterized structure of C_i symmetry and the newly proposed diastereoisomer of C_2 symmetry are the meso and rac forms of **1**, respectively. A related example of diastereoisomerism has been recently reported in $[RuCl_2(\eta^6\text{-arene})]_2$ chemistry, for an arene ligand with different ortho-related substituents.[13] The apparent variations in color and form of **1** in the solid state, from red-brown crystals to purple powder, were therefore further investigated.

The original literature preparation of **1** was repeated and, in our hands, gave lustrous black crystals that appeared red-brown to transmitted light (ca. 65% yield). On grinding of the crystals, however, a purple powder was produced. Furthermore, recrystallization of a sample of **1** prepared by our synthesis gave crystals similar in appearance to those described above. The infrared spectra of all the samples were identical. Low-temperature dissolution of the samples in CD_2Cl_2 (ca. 220 K), and immediate ^{1}H NMR spectral observation at 200 K, provided further information. From these experiments it was evident that **1**, as precipitated from our synthesis, contains essentially only a single diastereoisomer (>95%), and the ^{1}H NMR spectrum is detailed in Table I. The crystalline samples of **1** were all observed to be meso and rac mixtures containing between ca. 50% (rapid crystallization) and 90% (slow crystallization) of this same diastereoisomer. Since only slow crystallization gave single crystals of diffraction quality,[14] it can be concluded with reasonable confidence that it is the C_i isomer of **1** that is obtained from our synthesis. Very slow precipitation, throughout the 2 weeks' duration of our reaction, must account for the selective isolation of the meso form.

Kinetics of the Interconversion of the Diastereoisomers of 1 in Solution. Within 2 min of dissolution in chlorinated hydrocarbon solvents at room temperature, the C_i and C_2 isomers of **1** are at equilibrium. An equilibrium constant, $K = [C_2]/[C_i] = 1.25 \pm 0.05$, for the $C_i \rightleftarrows C_2$ equilibrium at 298 K, in both $CDCl_3$ and CD_2Cl_2, was evaluated by spectral integration. Precise measurements were possible since the ^{1}H NMR resonances due to each isomer were deduced from the low-temperature dissolution studies.

The rate at which the $C_i \rightleftarrows C_2$ equilibrium is established was measured at five temperatures over the range 230–250 K. This was done by low-temperature dissolution of the C_i isomer in CD_2Cl_2, transfer to a thermostated ^{1}H NMR probe, and spectral sampling at fixed time intervals. The percentage abundance of the C_i isomer at each sampling was evaluated from the relative integrals of the higher field methyl resonances of each isomer. Plots of ln [(% C_i) − (% C_i at equilibrium)] vs time were linear and gave the sum of the rate constants for the forward and reverse reactions from their negative gradients. The observed rate constants for the forward reaction $C_i \rightarrow C_2$ at each temperature were 6.4×10^{-5} s^{-1} (230.3 K), 2.1×10^{-4} s^{-1} (235.3 K), 4.2×10^{-4} s^{-1} (240.5 K), 6.4×10^{-4} s^{-1} (245.4 K), and 1.3×10^{-3} s^{-1} (250.1 K). An Eyring plot of these results yields the following activation

(13) Pertici, P.; Salvadori, P.; Biasci, A.; Vitulli, G.; Bennett, M. A.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1988**, 315.

(14) The presence of two crystalline modifications could not be discerned with certainty under an optical microscope.

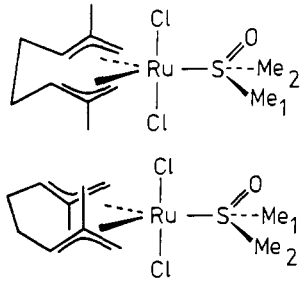


Figure 2. Proposed enantiomeric structures for the DMSO solvate **3**.

parameters: $k_{298} = (2.9 \pm 2.2) \times 10^{-1}$ s^{-1}; $\Delta G^{\ddagger}_{298} = 76 \pm 2$ kJ mol^{-1}; $\Delta H^{\ddagger} = 67 \pm 8$ kJ mol^{-1}; $\Delta S^{\ddagger} = -30 \pm 32$ J K^{-1} mol^{-1}.

Solutions of **1** in $CDCl_3$ or CD_2Cl_2 at room temperature do not subsequently exhibit temperature-dependent ^{1}H NMR spectra. In 1,1,2,2-tetrachloroethane-d_2 solution above 323 K, however, the ^{1}H NMR resonances of **1** begin to broaden and coalesce. The spectrum at 373 K shows only five broad resonances at δ 5.6 (2 H), 4.9 (2 H), 4.6 (2 H), 2.5 (4 H), and 2.3 (12 H). The three low-field signals are assigned to the allyl protons of the octadienediyl ligands and indicate that the syn and anti methylene protons on C(1) and C(8) are still distinct. The octadienediyl ligands are therefore not fluxional. Hence, the observed spectral changes, which must be due to the $C_i \rightleftarrows C_2$ interconversions entering the fast-exchange domain on the NMR time scale, are evidence that the interconversions do not occur intramolecularly, but involve chloride bridge rupture and monomer formation.

The order of magnitude for k_{298} of 10^{-1} s^{-1} for the $C_i \rightleftarrows C_2$ interconversion is a particularly interesting result, in view of the wide range of known organoplatinum–metal dimers containing bis(μ-chloro) bridges.[3] Hitherto, there had been no indication of a likely rate at which the component monomer units may be exchanging partners in solution.

It is a beautiful feature of the system that no osmometric determinations of molecular weight are necessary to confirm the dimeric nature of **1** in these solutions. The retention of both the C_2 symmetry conformation of the octadienediyl ligands and the dimeric structure is readily ascertained by an informed glance at the room-temperature ^{1}H NMR spectrum. Similarly, inspection of the ^{1}H NMR spectra from solutions obtained by room-temperature dissolution of **1** in pyridine-d_5, DMSO-d_6, CD_3CN, and DMF-d_7 all show that the pair of diastereoisomeric dimers do not remain intact in these solvents. The nature of the solvent-coordinated monomers **2d**, **3d**, **4d**, and **5d**, respectively, present in these solutions is discussed below.

Proposed Structures for 2 and 3 and Solution Dynamics for 3. The ^{1}H and ^{13}C NMR spectra of **3** in acetone-d_6 at 200 K show that the halves of the 2,7-dimethyloctadienediyl ligand are chemically equivalent. The DMSO methyl groups, however, are inequivalent, and their protons resonate at δ 3.23 and 3.30. These resonances coalesce at 308 ± 2 K on the 200-MHz ^{1}H NMR time scale, although the resonances arising from the octadienediyl ligand remain unaffected. Proposed enantiomeric structures for the racemate **3**, closely related to the structures of **1**, and consistent with the observed spectral data, are shown in Figure 2. The DMSO methyl groups in the proposed structures are diastereotopic, and hence their observed inequivalence is convincing evidence in support of these structures. Further, the chemical shifts of the DMSO methyl groups are in the range characteristic of S-bound DMSO,[15] and so support the infrared evidence for this coordination mode.

The mechanism by which the diastereotopic methyl groups of the DMSO ligand become equivalent does not involve an intramolecular racemization, which could have been postulated to occur via η^1:η^3-coordinated octadienediyl intermediates, since the NMR spectra show that syn/anti proton exchange at the octadienediyl ligand termini does not occur. Dissociation of DMSO and/or

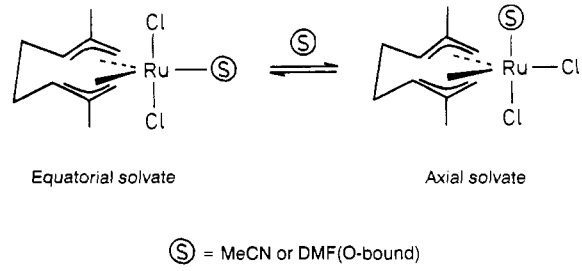


Figure 3. Proposed equilibrium between two structural isomers for the acetonitrile and DMF solvates, **4** and **5**, in solution. *Only one enantiomer of each structural isomer is illustrated.*

exchange of DMSO between the enantiomers is therefore the simplest mechanism consistent with the observations. From the coalescence temperature it is estimated[16] that $\Delta G^{\ddagger}_{308} = 66.5 \pm 0.5$ kJ mol^{-1} for this process in acetone-d_6.

The proposed structures of **3** are closely related to those mentioned above for the series of $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})L]$ complexes isolated by Nixon and co-workers. These authors noted that the fluorine atoms of the complex with L = PF_2NMe_2 were inequivalent, although a restricted rotation about the Ru–P bond was considered to be responsible.[5] Recognizing the chirality of the C_2 symmetry configuration of the octadienediyl ligand, however, we must reinterpret the inequivalence of the fluorine atoms in this complex only as evidence for a retention of the octadienediyl configuration in solution.

The NMR spectra of the pyridine adduct **2**, in acetone-d_6, show that the halves of the 2,7-dimethyloctadienediyl ligand are equivalent. Hence, enantiomeric structures similar to those of **3**, but with a pyridine ligand N-bound in the third equatorial site, are proposed.

Solution Isomerism in 4 and 5. The MeCN and O-bound DMF adducts **4** and **5** decompose in acetone with precipitation of **1**. This is an indication that **4** and **5** are less stable than the pyridine and S-bound DMSO adducts, **2** and **3**. The ^{1}H NMR spectra of **4** and **5** were therefore first obtained following room-temperature dissolution in CD_3CN and DMF-d_7 solution, respectively. Under these conditions, the ruthenium-containing species present in solution are **4d** and **5d**, respectively, since the presence of a resonance corresponding to ca. 1 mol equiv of free undeuterated solvent shows that exchange between free and coordinated solvent occurs. The rates of solvent exchange are too rapid to observe by a sampling technique at room temperature. Inspection of the spectra (Table I) show that for both **4d** and **5d** two distinct structural isomers are present in these solutions, and proposed structures are shown in Figure 3.

The unsymmetrical isomer with the solvent molecule coordinated in an axial site is the predominant form of **4d** in CD_3CN and of **5d** in DMF-d_7, and the relative abundance of the two isomers is independant of the total concentration. Furthermore, the two isomers of **4d**, and of **5d**, were shown to be in equilibrium in these solutions, since progressive addition of $CDCl_3$ resulted in reduced relative abundances of the axial solvates. These changes were reversed on readdition of CD_3CN or DMF-d_7, respectively. The equilibrium constants, $K_{ax/eq}$, as defined in Figure 3, were evaluated from spectral integration. Their values at 298 K are as follows: $K_{ax/eq} = 11$ for **4** in acetonitrile solution; $K_{ax/eq} = 1.7$ for **4** in a 9:1 mixture by volume of chloroform/acetonitrile; $K_{ax/eq} = 3.3$ for **5** in DMF; $K_{ax/eq} = 1.7$ for **5** in a 9:1 mixture by volume of chloroform/DMF. On room-temperature dissolution of **4** in $CDCl_3$, although significant quantities of the diastereoisomers of **1** are re-formed, the symmetrical isomer with the acetonitrile ligand in the third equatorial site is the predominant form of **4** in solution and $K_{ax/eq} = 0.5$. On room-temperature dissolution

(15) Evans, P. I.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

(16) Kessler, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

of **5** in $CDCl_3$, the diastereoisomers of **1** are quantitatively reformed in solution (vide infra).

Temperature-dependent behavior of $K_{ax/eq}$ was also observed. Measurements[17] on **4** in a CD_3CN solution yielded the following values for $K_{ax/eq}$: 5.3 (330 K); 6.7 (320 K); 8.5 (310 K); 11 (298 K). For **4** in a solution of 10% by volume CD_3CN in CD_2Cl_2 values for $K_{ax/eq}$ were as follows: 2.5 (298 K); 3.6 (290 K); 4.5 (280 K); 6.1 (270 K). For **5** in DMF-d_7 solution values for $K_{ax/eq}$ were as follows: 3.3 (298 K); 3.7 (290 K); 4.1 (280 K); 4.8 (270 K); 6.0 (260 K); 7.8 (250 K). For solutions of both **4** and **5**, the percentage abundance of the axial solvate increases as the temperature is lowered. This behavior characterizes the equatorial → axial solvate conversions as exothermic. Application of the van't Hoff isochore to these results leads to the following reaction enthalpies: $\Delta H° = -19 \pm 1$ kJ mol^{-1} for **4** in CD_3CN; $\Delta H° = -21 \pm 2$ kJ mol^{-1} for **4** in 10% CD_3CN in CD_2Cl_2; $\Delta H° = -11 \pm 1$ kJ mol^{-1} for **5** in DMF. The lower value for **5** may arguably be taken as an indication that the Ru–DMF interactions are generally weaker than the Ru–NCMe interactions.

Kinetic Control in the Formation of 4 and 5 from 1. The progress of the reactions of acetonitrile and DMF with **1** can be observed at low temperature by ^{1}H NMR spectroscopy. A solution of **1** (ca. 0.05 M) in CD_2Cl_2 at room temperature was cooled to 240 K, and a measured quantity of cold acetonitrile-d_3 was then added, so as to produce a 10% by volume CD_3CN solution. Subsequent monitoring of the ^{1}H NMR spectrum at 240 K clearly indicated that both diastereoisomers of **1** react at similar rates and are essentially completely consumed within 40 min of the CD_3CN addition. The more interesting observation, however, was that the product initially formed is exclusively the equatorially solvated form of **4d**. A related experiment at 235 K, using a similarly prepared solution of **1** in a mixture of volume composition CD_2Cl_2 (70%)/DMF-d_7 (30%), also showed that the equatorially solvated form of **5d** is the unique initial product.

The reported molecular structure of the C_i isomer of **1** may provide a partial explanation for the exclusive initial formation of the equatorial solvates. The Ru–Cl bridge bonds of **1** were reported to be significantly asymmetric: Ru–μ-Cl_{eq} = 256 pm; Ru–μ-Cl_{ax} = 247 pm.[6] Preferential cleavage of the dimer by rupture of the longer Ru–Cl_{eq} bonds would therefore appear logical.

Kinetics of the Interconversion of the Equatorially and Axially Solvated Isomers of 4. The dissolution of **1** in cold acetonitrile is a very slow process. This effectively precludes the use of a sampling technique, in acetonitrile solvent, to measure the rates of the forward reaction for the equilibrium shown in Figure 3 (S = MeCN). These rates were therefore determined in solutions that were 10% by volume CD_3CN in CD_2Cl_2.

The low-temperature preparation of the samples was identical with that described in the previous section, and the complete consumption of **1** was verified before the first measurement included in the kinetic analyses was taken. Rate constants for the equatorial → axial isomerization were then determined at four temperatures in the range 260–275 K. This was done by ^{1}H NMR spectral sampling of the thermostated solution at fixed time intervals. The percentage abundance of the equatorial solvate at each sampling was evaluated from the relative integrals of the highest field allyl singlets of the two isomers. Plots of ln [(% equatorial solvate) − (% equatorial solvate at equilibrium)] vs time were linear and gave the sum of the rate constants for the forward and reverse isomerization reactions from their negative gradients. The observed rate constants for the equatorial → axial solvate isomerization of **4d** were 1.2×10^{-4} s^{-1} (259.8 K), 3.1×10^{-4} s^{-1} (265.1 K), 6.9×10^{-4} s^{-1} (270.4 K), and 1.6×10^{-3} s^{-1} (275.0 K). An Eyring plot of these results yields the following activation parameters: $k_{298} = (4.6 \pm 0.9) \times 10^{-2}$ s^{-1}; $\Delta G^{\ddagger}_{298} = 80.6 \pm 0.5$ kJ mol^{-1}; $\Delta H^{\ddagger} = 98 \pm 4$ kJ mol^{-1}; $\Delta S^{\ddagger} = 57 \pm 15$ J K^{-1} mol^{-1}.

Some further information came from a study of crystals of **4**, prepared as described in the Experimental Section. A sample was dissolved in acetonitrile-d_3 at 240 K and the ^{1}H NMR spectrum at this temperature immediately recorded. The spectrum indicated the unique presence of the axial solvate. No free CH_3CN was initially present, and the resonance due to the axially coordinated CH_3CN occurred at δ 2.29, superimposed on the octadienediyl methyl group resonances. In a subsequent experiment, following low-temperature dissolution of crystalline **4** in acetonitrile-d_3, the rate of liberation of coordinated CH_3CN from **4** was determined at 275 K by spectral sampling. A rate constant of $k_{275} = 3.0 \times 10^{-4}$ s^{-1} was evaluated. The rate constant for the reverse reaction of the equatorial ⇄ axial equilibrium could not be directly determined from the spectra, in view of the unfavorable equilibrium constant. In a solution of 10% CD_3CN in CD_2Cl_2 at this temperature, a rate constant for axial → equatorial isomerization of $k_{275} = 2.8 \times 10^{-4}$ s^{-1} ($1.6 \times 10^{-3}/K_{ax/eq}$) has been determined. The similarity of these rate constants provides evidence that the liberation of coordinated acetonitrile and the isomerization reaction are intimately related processes. Hence, an intramolecular mechanism for the equatorial ⇄ axial interconversions must be considered unlikely.

Low-Temperature Dissolution of 5. A crystalline sample of **5**, prepared as described in the Experimental Section, was dissolved in DMF-d_7 at 220 K. Immediate observation of the ^{1}H NMR spectrum at 220 K suggested that the crystals were uniquely the axial isomer. A resonance assigned to the formamide proton of the coordinated $(CH_3)_2NCHO$ ligand was observed at δ 7.81. From further spectral observations at 250 K, it was estimated that both release of $(CH_3)_2NCHO$ and partial formation of the equatorial solvate were occurring at rates approximating to $k_{250} \approx (5 \pm 3) \times 10^{-4}$ s^{-1}. These rates are over an order of magnitude greater than those expected for the corresponding processes for **4** at this temperature. Further studies of the kinetics of this system were not pursued.

On warming of a DMF-d_7 solution of **5** above room temperature, the ^{1}H NMR resonances of **5d** begin to broaden considerably. At 363 K, although the rate of decomposition is appreciable, it is clear that the allyl proton resonances due to the two isomers have coalesced to three broad signals at δ 5.0, 4.8, and 4.4. Hence, the syn and anti methylene protons on C(1) and C(8) are still distinct, and therefore the observed spectral changes are not due to any fluxionality of the octadienediyl ligands. It can thus be concluded that the observed coalescences result from the entry into the fast-exchange domain of a DMF solvent exchange mechanism that interconverts the axially and equatorially solvated isomers of **5**.

When a CD_3CN solution of **4** is warmed, only slight changes in the overall appearance of the ^{1}H NMR spectra occur (i.e., $K_{ax/eq}$ decreases, as reported above). On detailed examination of the spectrum recorded at 343 K, differential broadening of the allyl singlets due to the equatorial and axial solvates was evident ($\omega_{1/2}$ = ca. 12 and 3.5 Hz, respectively, vs <2 Hz at 298 K). The increasing rapidity of the equatorial ⇄ axial solvate isomerizations is believed responsible for the broadening, and it is differential due to the smaller equilibrium concentration of the equatorial solvate. Although consistent with a solvent-exchange mechanism for the isomerizations, this phenomenon does not provide further evidence against the intramolecular alternative. The spectral changes observed on warming the solution are clearly much less pronounced than for **5** in DMF solution, and this is consistent with the independent estimation (vide supra) that the rates of isomerization in **5** are at least an order of magnitude greater than those in **4**.

The ^{1}H NMR spectra of **2** or **3** in pyridine-d_5 or DMSO-d_6, respectively, show that complete exchange of free and originally coordinated solvent occurs within 2 min of dissolution at room temperature. The spectra also confirm the exclusive presence of symmetrical isomers, with the solvent coordinated in the equatorial site, as originally observed in acetone-d_6. There is no evidence for the presence of alternative isomers with the solvent axial. Hence, if an equilibrium of the form shown in Figure 3 exists for **2** or **3**, then $K_{ax/eq} < 10^{-2}$.[18] These solutions of **2** and **3** do not

(17) By spectral integration. For the CD_3CN solution, especially above room temperature, cutting and weighing of estimated Lorenzian forms was necessary due to partial overlap of the resonances ca. δ 4.4.

Table II. Equilibrium Constants at 298 K for the Equilibria Defined in Scheme I[a]

S	$K_{1/RuS}$	$K_{RuS/2}$	$K_{5/RuS}$
pyridine	$<5 \times 10^{-8}$		1.8×10^{-4}
DMSO	2.1×10^{-4}	5.7×10^{-2}	5.9×10^{-2}
MeCN	2.6×10^{-4}	1.1×10^{-2}	3.7×10^{-1}
DMF	2.0	1.8×10^{-4}	

[a] Estimated errors ±20%.

exhibit any reversible temperature-dependent changes in the ^1H NMR spectrum.

Solution Equilibria between Complexes 1–5. The ^1H NMR spectra of solutions prepared by dissolution of **2**, **3**, **4**, or **5** in the solvents $CDCl_3$, pyridine-d_5, DMSO-d_6, CD_3CN, and DMF-d_7 show that two types of chemical equilibria, involving displacement of the two-electron ligand, can be established in solution.

In chloroform, equilibria of the type shown in eq 1 are established. Hence, in solutions prepared by dissolution of **3** or **4** in

$$2[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})S] \rightleftarrows \mathbf{1} + 2S \quad (1)$$

$CDCl_3$ significant quantities of the diastereoisomers of **1** re-form. On dissolution of **2** in $CDCl_3$, however, the equilibrium constant is too small for the resonances of **1** to be observed. On dissolution of **5** in $CDCl_3$, on the other hand, **1** is quantitatively formed.

In coordinating solvents, equilibria of the type shown in eq 2 are established, and hence, for example, dissolution of **2** in DMSO-d_6, CD_3CN, or DMF-d_7 results in partial formation of **3d** or the isomers of **4d** or **5d**, respectively.

$$S' + [RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})S] \rightleftarrows [RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})S'] + S \quad (2)$$

Selected equilibria, and their associated equilibrium constants, are defined more completely in Scheme I. Quantitative values at 298 K are listed in Table II, and were obtained by integration of the characteristic allyl proton resonances in the ^1H NMR spectra of solutions of known analytical composition. Some additional observations: (i) dissolution of **3**, **4**, or **5** in pyridine-d_5 results in complete formation of **2d**; (ii) dissolution of **4** or **5** in DMSO-d_6 results in complete formation of **3d**; (iii) dissolution of **3** or **5** in CD_3CN results in complete formation of **4d**; (iv) dissolution of **1** in an equimolar mixture of DMSO-d_6 and CD_3CN gives a solution containing **3d** and **4d** in the ratio 3:1. Inspection of these results clearly suggests that the affinities for coordination to the $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2]$ monomer fall in the sequence pyridine > DMSO > MeCN > DMF. In particular, the values of $K_{1/RuS}$ and $K_{5/RuS}$ increase in this order, and the values of $K_{RuS/2}$ decrease.

(18) An alternative interpretation of the spectra of **2d** and **3d** in their parent solvents that is difficult to totally exclude is that the forward and backward reactions of an equilibrium of the form shown in Figure 3 are occurring very rapidly on the NMR time scale and that $K_{ax/eq}$ is therefore undetermined. No evidence to support this hypothesis was obtained on dilution of the solutions with CD_2Cl_2 and cooling, and it can be effectively excluded unless one is willing to argue that solvent exchange in **2** and **3** is much more rapid than in **4** and **5**.

Scheme I. Selected Equilibria Involving Complexes **1–5**

(i) chloroform solution

$$2[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})S] \rightleftarrows \mathbf{1} + 2S$$

$$K_{1/RuS} = [\mathbf{1}][S]^2/[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})S]^2$$

(ii) DMSO, acetonitrile, or DMF solution

$$\mathbf{2} \rightleftarrows [RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})S] + C_5H_5N$$

$$K_{RuS/2} = [RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})S][C_5H_5N]/[\mathbf{2}]$$

(iii) DMF solution

$$[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})S] \rightleftarrows \mathbf{5} + S$$

$$K_{5/RuS} = [\mathbf{5}][S]/[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})S]$$

Conclusion

The dimer $[RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$ exists in two diastereoisomeric forms that interconvert by chloride bridge rupture in solutions of noncoordinating solvents ($k_{298} = (3 \pm 2) \times 10^{-1}$ s^{-1}). By a convenient preparation of the dimer, the meso form is selectively isolated. In pyridine, DMSO, MeCN, or DMF solvent, dimeric structures are not retained and solvated monomers are formed. Neither the parent dimer nor any of the solvates show dynamic behavior associated with the octadienediyl ligand. The retention of distinct ^1H NMR resonances from the syn and anti protons at the termini of the octadienediyl chain suggests that it is firmly locked in the C_2 symmetry configuration, occupying two of the equatorial coordination sites. Solution NMR studies on the pyridine and S-bound DMSO adducts indicate exclusive equatorial solvation of the $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2]$ monomer and the occurrence of solvent exchange.

For the acetonitrile and O-bound DMF adducts two structural isomers have been identified, with the solvent coordinated in either an equatorial or an axial site. The two isomers coexist in equilibrium in solution. The axially solvated isomers are favored in terms of the reaction enthalpies, yet the equatorially solvated isomers are the unique kinetic products on solvolysis of the title dimer. Subsequent isomerization to produce an equilibrium concentration of the axial solvate is faster with DMF, but is also a rapid process for acetonitrile ($k_{298} = (4.6 \pm 0.9) \times 10^{-2}$ s^{-1}). These interconversions are proposed to occur via solvent exchange rather than intramolecularly. Room-temperature isolation of the acetonitrile and DMF solvates yields exclusively the axially solvated isomer.

A series of equilibrium measurements shows that the affinities for coordination to the $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2]$ monomer fall in the sequence pyridine > DMSO > MeCN > DMF. Hence, it appears that only for relatively weakly coordinating solvents is there coexistence of both axially and equatorially solvated monomers. We are not aware of any five-coordinate system where similar phenomena have been observed, and further study of these unusual octadienediyl complexes is being pursued.

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