Electronic Supplementary Material (ESI) for Dalton Transactions


# Reversible binding of water, methanol, and ethanol to a five-coordinate ruthenium(II) complex†

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## SUPPLEMENTARY MATERIAL



**Figure S1.** ORTEP diagram of *trans*-$RuCl_2(P–N)(P(p\text{-tolyl})_3)(H_2O)$ (**2b**) with 50% probability thermal ellipsoids.

**Figure S2.** TGA spectrum of **2a**, depicting the loss of acetone and $H_2O$ from 80 to 110 °C.

**Figure S3.** $^{31}P\{^1H\}$ NMR spectra (202.5 MHz) of *trans*-$RuCl_2(P–N)(PPh_3)(H_2O)$ (**2a**) in $CD_2Cl_2$ at various temperatures. An unidentified, trace species is seen at $\delta$ 49. 8 and $\delta$ 59.0 from –50 to –80 °C .

**Figure S4**. $^{31}P\{^1H\}$ NMR spectra (121.4 MHz, 20 °C) of $RuCl_2(P–N)(PPh_3)$ (**1a**) in $d_6$-acetone with added $H_2O$ to form **2a**.

**Figure S5.** $^1H$ NMR spectra (500 MHz) of *trans*-$RuCl_2(P–N)(PPh_3)(H_2O)$ (**2a**) in $CD_2Cl_2$ at various temperatures.

**Figure S6.** Spectral changes observed upon addition of $H_2O$ to $RuCl_2(P–N)(PPh_3)$ (**1a**) ($1.21 \times 10^{-3}$ M) in $C_6H_6$ at 25 °C. Added [$H_2O$] = (a) 0.0, (b) 0.0056, (c) 0.0111, (d) 0.0222, (e) 0.0333, (f) 0.0444, (g) 0.0776 M.

**Figure S7.** Spectral changes observed upon addition of $H_2O$ to $RuCl_2(P–N)(PPh_3)$ (**1a**) ($1.12 \times 10^{-3}$ M) in acetone at 25 °C. Added [$H_2O$] = (a) 0.0, (b) 0.0089, (c) 0.2652, (d) 0.9171, (e) 1.9702, (f) 3.9591 M.

**Figure S8.** Spectral changes observed upon addition of $H_2O$ to $RuCl_2(P–N)(PPh_3)$ (**1a**) ($1.19 \times 10^{-3}$ M) in THF at 25 °C. Added [$H_2O$] = (a) 0.0, (b) 0.0444, (c) 0.1110, (d) 0.2220, (e) 0.9992, (f) 4.330 M.

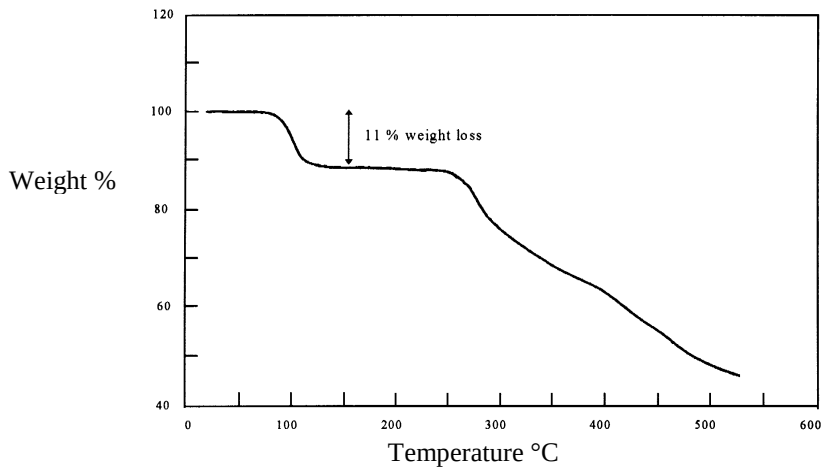


**Fig S1** TGA spectrum of **2a**, depicting the loss of acetone and $H_2O$ from 80 to 110 °C.

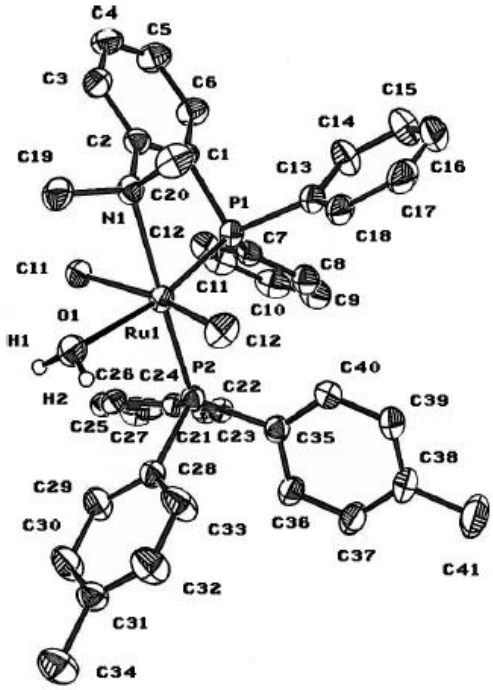


**Fig S2** ORTEP diagram of *trans*-$RuCl_2$(P–N)(P(*p*-tolyl)$_3$)($OH_2$) (2b) with 50% probability thermal ellipsoids.

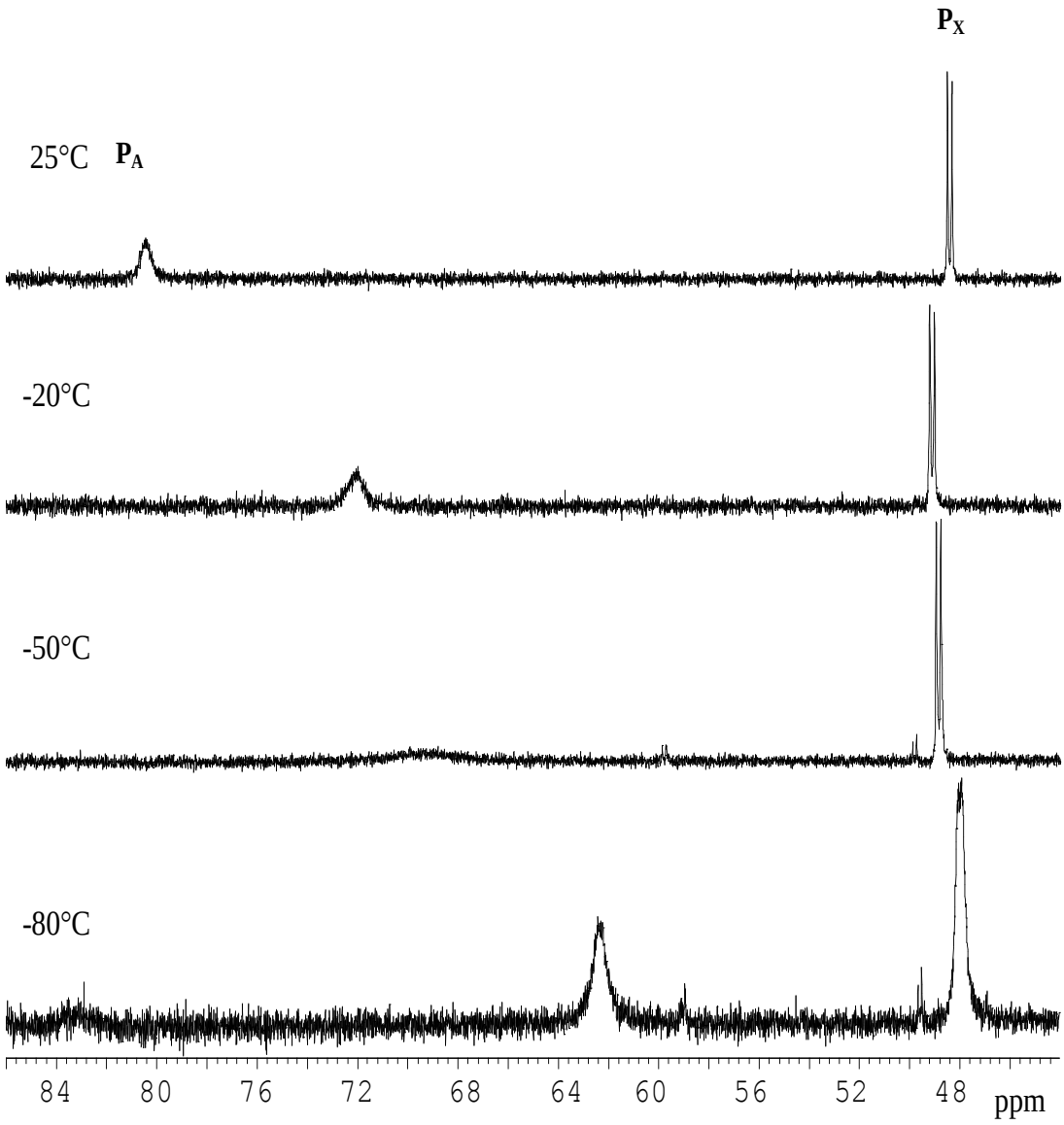


**Fig S3** $^{31}P\{^{1}H\}$ NMR spectra (202.5 MHz) of *trans*-$RuCl_2(P{-}N)(PPh_3)(H_2O)$ (**2a**) in $CD_2Cl_2$ at various temperatures. An unidentified, trace species is seen at $\delta$ 49. 8 and $\delta$ 59.0 from –50 to –80 °C .

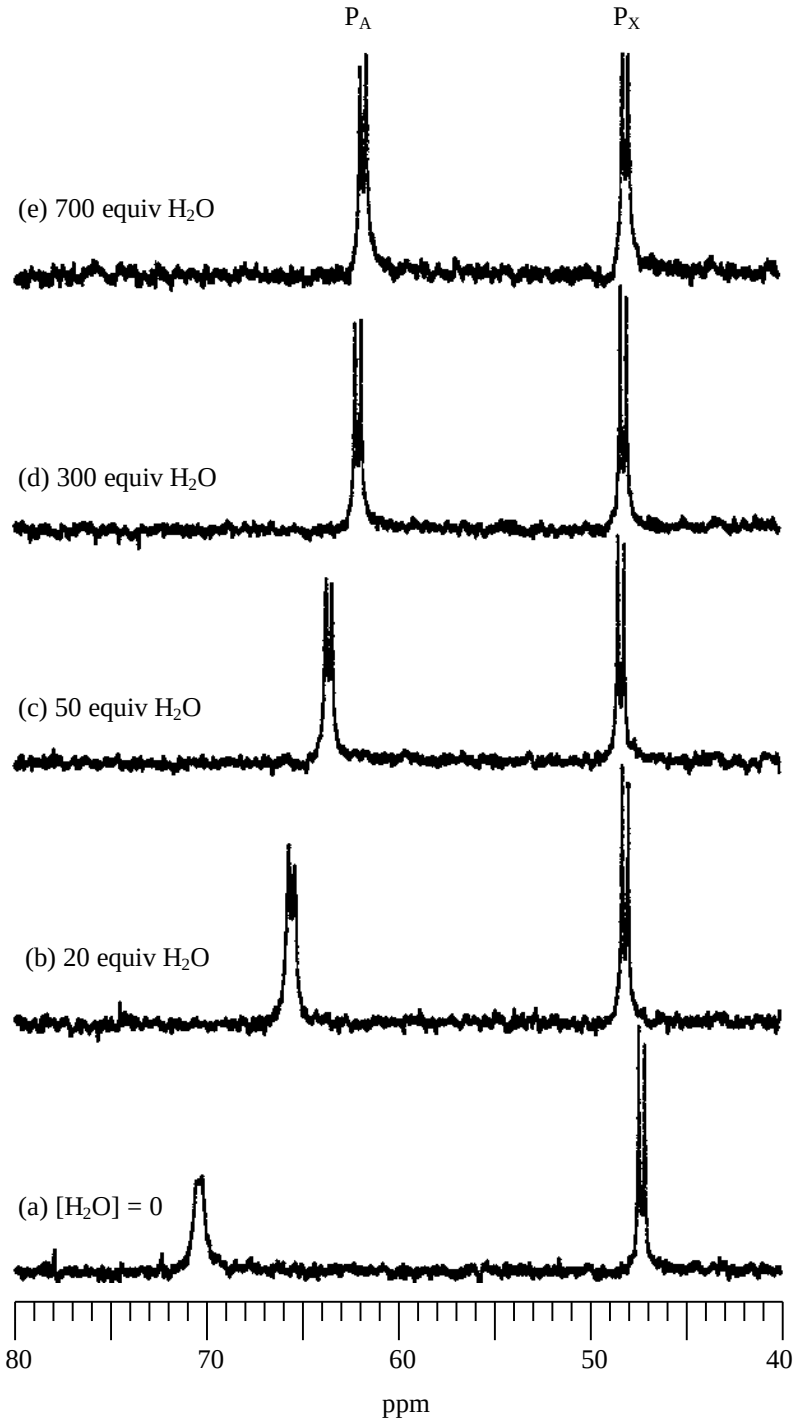


**Fig S4** $^{31}P\{^{1}H\}$ NMR spectra (121.4 MHz, 20 °C) of $RuCl_2(P–N)(PPh_3)$ (**1a**) in $d_6$-acetone with added $H_2O$ to form **2a**.

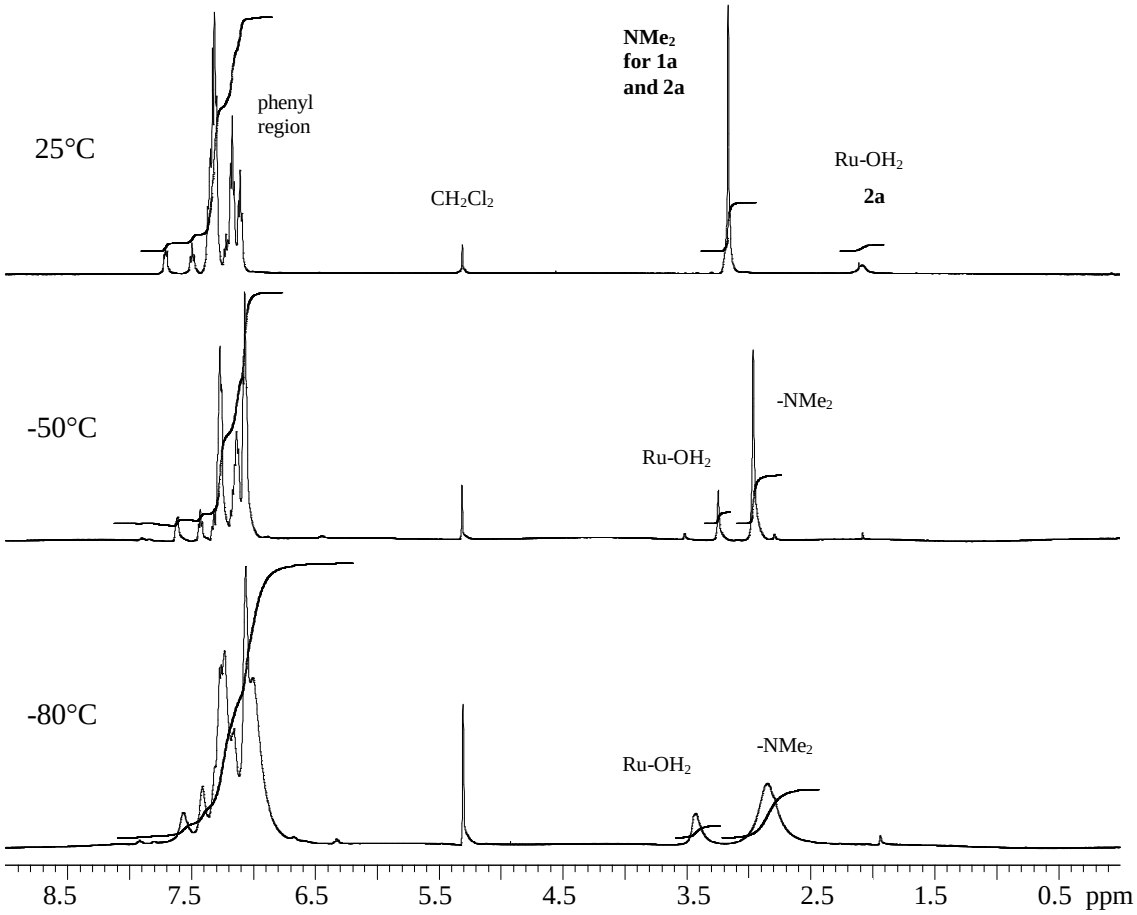


**Fig S5** $^{1}$H NMR spectra (500 MHz) of *trans*-$RuCl_2(P–N)(PPh_3)(H_2O)$ (**2a**) in $CD_2Cl_2$ at various temperatures.

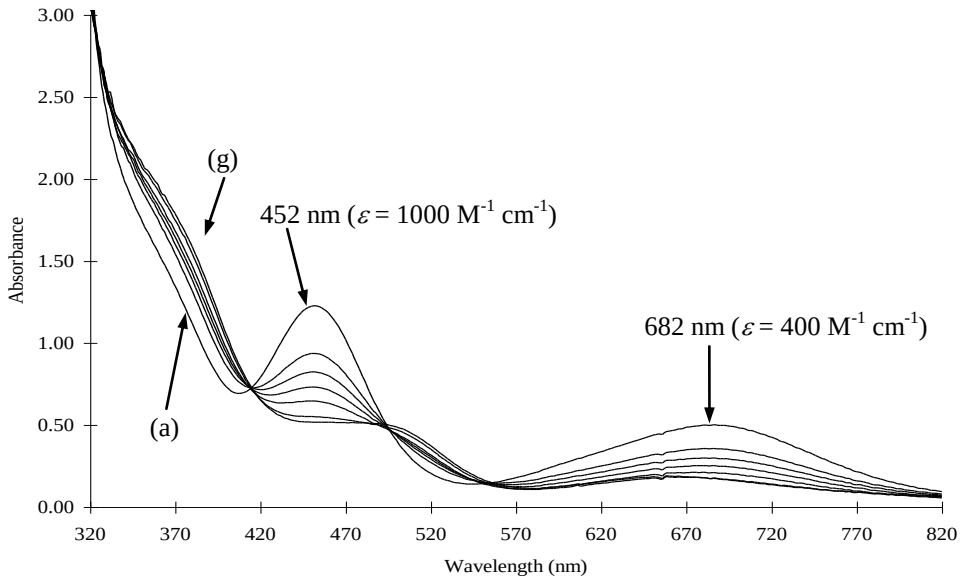


**Fig S6** Spectral changes observed upon addition of $H_2O$ to $RuCl_2(P–N)(PPh_3)$ (**1a**) (1.21 x $10^{-3}$ M) in $C_6H_6$ at 25 °C. Added [$H_2O$] = (a) 0.0, (b) 0.0056, (c) 0.0111, (d) 0.0222, (e) 0.0333, (f) 0.0444, (g) 0.0776 M.

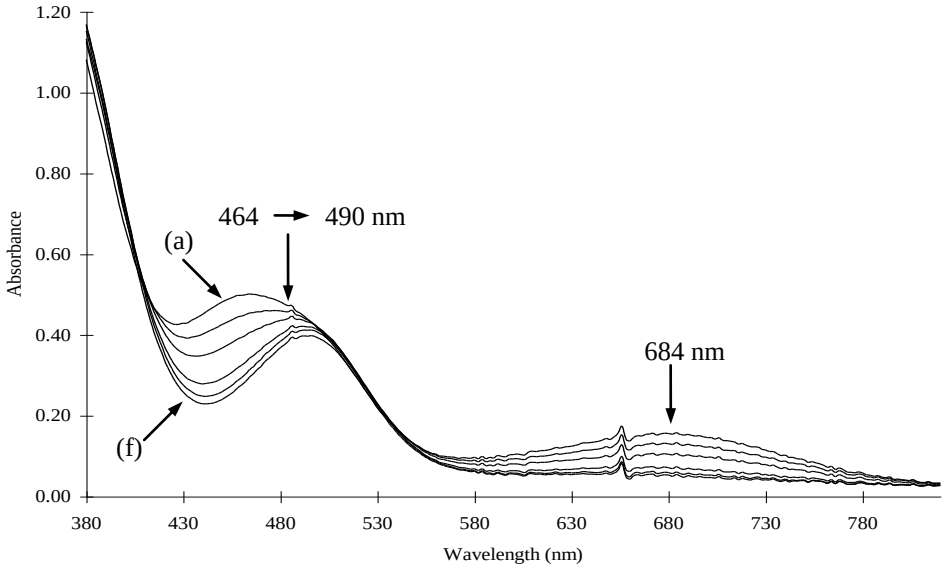


**Fig S7** Spectral changes observed upon addition of $H_2O$ to $RuCl_2(P–N)(PPh_3)$ (**1a**) (1.12 x $10^{-3}$ M) in acetone at 25 °C. Added [$H_2O$] = (a) 0.0, (b) 0.0089, (c) 0.2652,
(d) 0.9171, (e) 1.9702, (f) 3.9591 M.

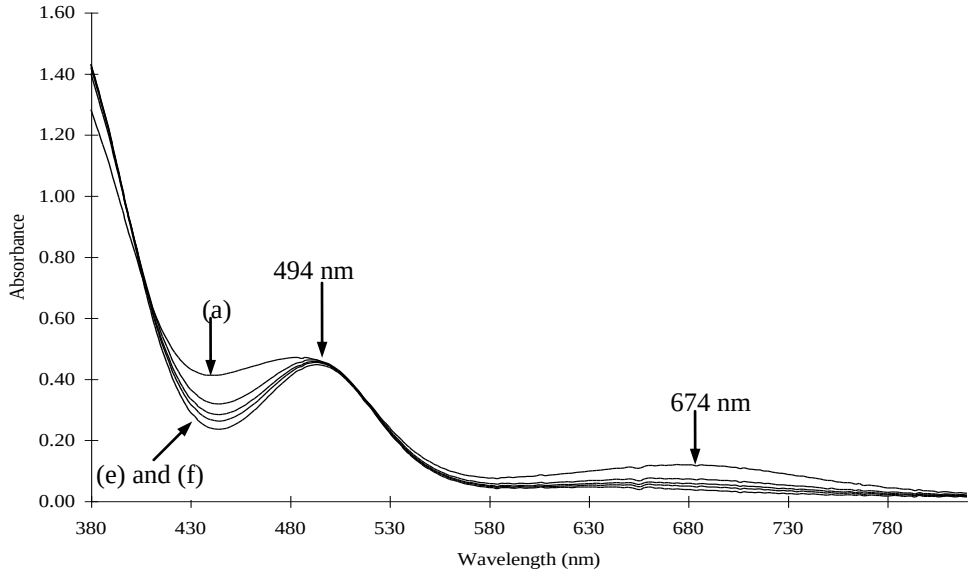


**Fig S8** Spectral changes observed upon addition of $H_2O$ to $RuCl_2(P–N)(PPh_3)$ (**1a**) (1.19 x $10^{-3}$ M) in THF at 25 °C. Added [$H_2O$] = (a) 0.0, (b) 0.0444, (c) 0.1110, (d) 0.2220, (e) 0.9992, (f) 4.330 M.

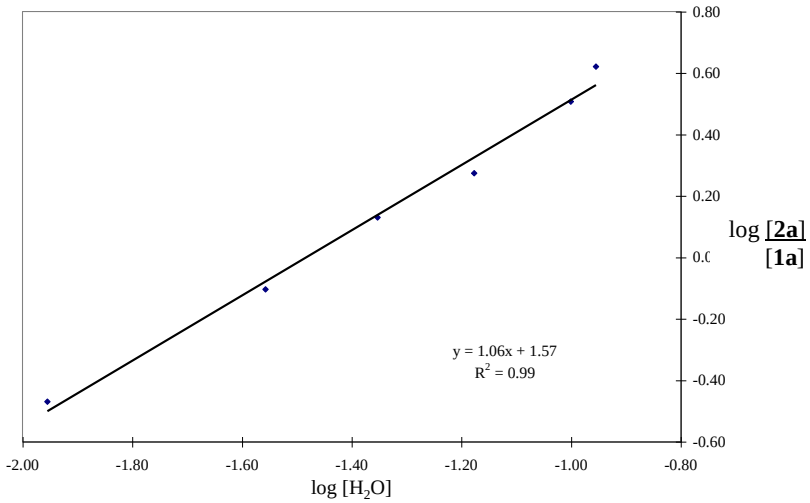


**Fig S9** Determination of K for reversible binding of $H_2O$ to **1a** at 25 °C. Concentrations obtained by absorbance at 678 nm (Fig. 4). Data at higher [$H_2O$] omitted due to solubility limit of $H_2O$ in $CH_2Cl_2$: 0.128 M at 25 °C (IUPAC Solubility Data Series, Vol. 60, *Halogenated Methanes with Water*; A. L. Horváth, F. W. Getzen, eds.; Oxford Univ. Press: Oxford, 1995, p. 153).

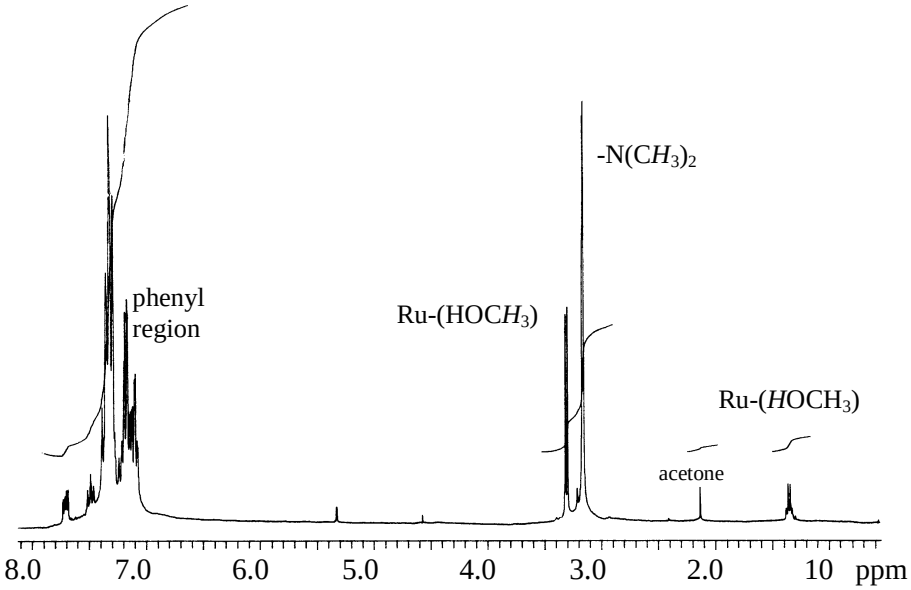


**Fig S10** $^1$H NMR spectrum (300 MHz) of *trans*-$RuCl_2(P–N)(PPh_3)(MeOH)$ (**3**) in $CD_2Cl_2$ at room temperature.

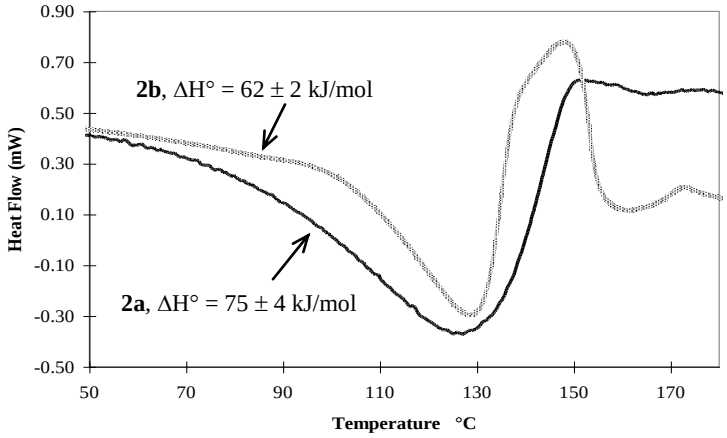


**Figure S11.** DSC curves for the *trans*-$RuCl_2(P–N)(PR_3)(H_2O)$ complexes **2a** (R = Ph) and **2b** (R = *p*-tolyl).

**Table S1** $^{31}P\{^{1}H\}$ NMR data for $RuCl_2(P–N)(PPh_3)$ (**1a**) and *trans*-$RuCl_2(P–N)(PPh_3)(H_2O)$ (**2a**) in various solvents at 20 °C.

| Solvent | $\delta_{P_A}$ [a] | | $\delta_{P_B}$ [a] | | $^2J_{PP}$ (Hz) | |
|---|---|---|---|---|---|---|
| | **1a** | **2a** | **1a** | **2a** | **1a** | **2a** |
| $CD_2Cl_2$ | 80.51 | 80.1 br[b] | 47.00 | 48.40[b] | 36.54 | 37.39[b] |
| $CDCl_3$ | 83.23 | 68.5 br[b] | 48.41 | 45.70[b] | 34.82 | 37.76[b] |
| $C_6D_6$ | 83.69 | 73.52[b] | 48.87 | 49.30[b] | 36.54 | 38.00[b] |
| $d_6$-acetone | 70.5 br | 61.78[c] | 47.27 | 48.03[c] | 38.36 | 38.12[c] |

[a] All doublets unless specified as br. [b] Data for isolated samples of **2a** in the absence of added $H_2O$. [c] Data for fully formed **2a** in the presence of added $H_2O$.

# Appendix A

Crystal data for *trans*-$RuCl_2(P–N)(P(p\text{-tolyl}_3)(OH_2)$(**2b**)



## EXPERIMENTAL

### DATA COLLECTION

A red prism crystal of $C_{41}H_{43}Cl_2NOP_2Ru$ having approximate dimensions of 0.100 X 0.180 X 0.200 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Cu Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 22.26 < 2θ < 56.17° corresponded to a triclinic cell with dimensions:

| | | | |
|---|---|---|---|
| a = | 11.232 (3)Å | α = | 102.22 (2)° |
| b = | 15.717 (4)Å | β = | 102.91 (2)° |
| c = | 11.056 (2)Å | γ = | 86.30 (3)° |
| V = | 1858.9 (9)Å$^3$ | | |

For Z = 2 and F.W. = 799.72, the calculated density is 1.429 g/cm$^3$. Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$P\bar{1}$ (#2)

The data were collected at a temperature of 21 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 155.4°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.33° with a take-off angle of 6.0°. Scans of (0.94 + 0.20 tan θ)° were made at a speed of 16.0°/min (in omega). The weak reflections (I < 40.0σ(I)) were rescanned (maximum of 8 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 285.0 mm.

### DATA REDUCTION

Of the 7989 reflections which were collected, 7573 were unique ($R_{int}$ = .039); equivalent reflections were merged. The intensities of three representative reflections which

# Appendix A



were measured after every 200 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Cu Kα is 59.3 $cm^{-1}$. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.68 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.86(5) E-06).

## STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by the Patterson method. The non-hydrogen atoms were refined anisotropically. The water hydrogen atoms were refined with isotropic thermal parameters and the remaining hydrogen atoms were fixed in calculated positions with C-H = 0.98 Å. The final cycle of full-matrix least-squares refinement[4] was based on 4964 observed reflections ($I > 3.00\sigma(I)$) and 442 variable parameters and converged (largest parameter shift was 0.09 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.035$$

$$R_w = [( \Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2 )]^{1/2} = 0.034$$

The standard deviation of an observation of unit weight[5] was 1.61. The weighting scheme was based purely on counting statistic (p = 0.00). Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.45 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[6]. Anomalous dispersion effects were included in Fcalc[7]; the values for Δf′ and Δf" were those of Cromer[8]. All calculations were performed using the TEXSAN[9] crystallographic software package of Molecular Structure Corporation.

# Appendix A



## References

(1) PLUTO:
Motherwell,S. & Clegg,W.; PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England (1978).

(2) ORTEP:
Johnson,C.K.; ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee (1976).

(3) Structure Solution Methods:
PHASE
Calbrese,J.C.; PHASE - Patterson Heavy Atom Solution Extractor. Univ. of Wisconsin-Madison, Ph.D. Thesis (1972).

(4) Least-Squares:
Function minimized: $\Sigma\, w\, (|Fo| - |Fc|)^2$
where: $w = 4Fo^2/\sigma^2(Fo^2)$
$\sigma^2(Fo^2) = [S^2(C+R^2B) + (pFo^2)^2]/Lp^2$
S = Scan rate
C = Total Integrated Peak Count
R = Ratio of Scan Time to background counting time.
B = Total Background Count
Lp = Lorentz-polarization factor
p = p-factor

(5) Standard deviation of an observation of unit weight:

$$[\Sigma\, w(|Fo| - |Fc|)^2/(No - Nv)]^{1/2}$$

where: No = number of observations
Nv = number of variables

(6) Cromer,D.T. & Waber,J.T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers,J.A. & Hamilton,W.C.; Acta Crystallogr., 17, 781 (1964).

(8) D.T. Cromer, "International Tables for X-ray Crystallography", Vol/ IV, The Kynoch Press, Birmingham, England, Table 2.3.1 (1974).

(9) TEXSAN - TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).

# Appendix A



## EXPERIMENTAL DETAILS

### A. Crystal Data

| | |
|---|---|
| Empirical Formula | $C_{41}H_{43}Cl_2NOP_2Ru$ |
| Formula Weight | 799.72 |
| Crystal Color, Habit | red, prism |
| Crystal Dimensions (mm) | 0.100 X 0.180 X 0.200 |
| Crystal System | triclinic |
| No. Reflections Used for Unit Cell Determination (2θ range) | 25 ( 22.3 - 56.2°) |
| Omega Scan Peak Width at Half-height | 0.33 |
| Lattice Parameters: | |
| | a = 11.232 (3)Å |
| | b = 15.717 (4)Å |
| | c = 11.056 (2)Å |
| | α = 102.22 (2)° |
| | β = 102.91 (2)° |
| | γ = 86.30 (3)° |
| | V = 1858.9 (9)Å$^3$ |
| Space Group | $P\bar{1}$ (#2) |
| Z value | 2 |
| $D_{calc}$ | 1.429 g/cm$^3$ |
| $F_{000}$ | 824 |
| $\mu$(CuKα) | 59.26 cm$^{-1}$ |

### B. Intensity Measurements

| | |
|---|---|
| Diffractometer | Rigaku AFC6S |
| Radiation | CuKα (λ = 1.54178 Å) |
| Temperature | 21°C |
| Take-off Angle | 6.0° |

# Appendix A



| | |
|---|---|
| Detector Aperture | 6.0 mm horizontal<br>6.0 mm vertical |
| Crystal to Detector Distance | 285 mm |
| Scan Type | $\omega$-2$\theta$ |
| Scan Rate | 16.0°/min (in omega)<br>(8 rescans) |
| Scan Width | (0.94 + 0.20 tan$\theta$)° |
| $2\theta_{max}$ | 155.4° |
| No. of Reflections Measured | Total: 7989<br>Unique: 7573 ($R_{int}$ = .039) |
| Corrections | Lorentz-polarization<br>Absorption<br>(trans. factors: 0.68 - 1.00)<br>Secondary Extinction<br>(coefficient: 0.86(5) E-06) |

C. Structure Solution and Refinement

| | |
|---|---|
| Structure Solution | Patterson Method |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\Sigma\ w\ (\lvert Fo\rvert - \lvert Fc\rvert)^2$ |
| Least-squares Weights | $4Fo^2/\sigma^2(Fo^2)$ |
| p-factor | 0.00 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($I>3.00\sigma(I)$) | 4964 |
| No. Variables | 442 |
| Reflection/Parameter Ratio | 11.23 |
| Residuals: R; $R_w$ | 0.035; 0.034 |
| Goodness of Fit Indicator | 1.61 |
| Max Shift/Error in Final Cycle | 0.09 |
| Maximum Peak in Final Diff. Map | 0.34 $e^-/Å^3$ |
| Minimum Peak in Final Diff. Map | -0.45 $e^-/Å^3$ |

# Appendix A

Table . Final atomic coordinates (fractional) and $B_{eq}$ ($Å^2$)*

| atom | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| Ru(1) | 0.05149(3) | 0.21639(2) | 0.07921(3) | 3.03(1) |
| Cl(1) | 0.11309(10) | 0.08469(7) | 0.15857(10) | 4.01(4) |
| Cl(2) | -0.01142(11) | 0.31700(8) | -0.05781(9) | 4.51(5) |
| P(1) | 0.15569(10) | 0.29625(7) | 0.25700(9) | 3.07(4) |
| P(2) | -0.13618(10) | 0.23037(7) | 0.12966(10) | 3.22(4) |
| O(1) | -0.0200(4) | 0.1202(3) | -0.1012(3) | 4.5(2) |
| N(1) | 0.2451(3) | 0.2047(2) | 0.0340(3) | 3.6(1) |
| C(1) | 0.3072(3) | 0.2444(3) | 0.2659(4) | 3.3(2) |
| C(2) | 0.3346(4) | 0.2000(3) | 0.1524(4) | 3.5(2) |
| C(3) | 0.4456(4) | 0.1565(3) | 0.1517(4) | 4.3(2) |
| C(4) | 0.5279(4) | 0.1551(3) | 0.2653(5) | 4.9(2) |
| C(5) | 0.5014(4) | 0.1985(4) | 0.3774(5) | 5.2(2) |
| C(6) | 0.3926(4) | 0.2440(3) | 0.3781(4) | 4.6(2) |
| C(7) | 0.1182(4) | 0.2938(3) | 0.4083(3) | 3.4(2) |
| C(8) | 0.0559(4) | 0.3644(3) | 0.4675(4) | 4.4(2) |
| C(9) | 0.0256(5) | 0.3616(4) | 0.5814(5) | 5.7(3) |
| C(10) | 0.0541(5) | 0.2904(4) | 0.6350(4) | 5.7(3) |
| C(11) | 0.1135(5) | 0.2202(4) | 0.5762(4) | 5.4(2) |
| C(12) | 0.1436(4) | 0.2204(3) | 0.4604(4) | 4.4(2) |
| C(13) | 0.1996(4) | 0.4119(3) | 0.2841(4) | 3.7(2) |
| C(14) | 0.2715(5) | 0.4508(3) | 0.3994(4) | 5.2(2) |
| C(15) | 0.3124(5) | 0.5345(4) | 0.4170(5) | 6.1(3) |
| C(16) | 0.2862(5) | 0.5791(3) | 0.3209(7) | 6.3(3) |
| C(17) | 0.2152(5) | 0.5418(3) | 0.2076(6) | 5.5(2) |
| C(18) | 0.1718(4) | 0.4583(3) | 0.1874(4) | 4.2(2) |

# Appendix A

Table . Final atomic coordinates (fractional) and $B_{eq}$ ($Å^2$)* (cont.)

| atom | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| C(19) | 0.2486(4) | 0.1256(3) | -0.0651(4) | 5.0(2) |
| C(20) | 0.2802(4) | 0.2781(3) | -0.0138(4) | 4.8(2) |
| C(21) | -0.1550(4) | 0.1776(3) | 0.2571(4) | 3.3(2) |
| C(22) | -0.1800(4) | 0.2259(3) | 0.3706(4) | 3.8(2) |
| C(23) | -0.1880(4) | 0.1850(3) | 0.4681(4) | 4.0(2) |
| C(24) | -0.1733(4) | 0.0956(3) | 0.4572(4) | 4.1(2) |
| C(25) | -0.1375(4) | 0.0883(3) | 0.2477(4) | 3.5(2) |
| C(26) | -0.1481(4) | 0.0483(3) | 0.3447(4) | 3.9(2) |
| C(27) | -0.1831(5) | 0.0524(4) | 0.5638(4) | 5.9(3) |
| C(28) | -0.2590(4) | 0.1849(3) | -0.0081(4) | 3.5(2) |
| C(29) | -0.3052(5) | 0.1050(3) | -0.0301(5) | 5.3(2) |
| C(30) | -0.3957(5) | 0.0743(3) | -0.1372(5) | 6.0(2) |
| C(31) | -0.4413(4) | 0.1244(3) | -0.2246(4) | 4.3(2) |
| C(32) | -0.3949(5) | 0.2047(4) | -0.2030(5) | 5.8(2) |
| C(33) | -0.3042(5) | 0.2349(3) | -0.0981(5) | 5.7(2) |
| C(34) | -0.5408(5) | 0.0906(4) | -0.3388(5) | 6.4(3) |
| C(35) | -0.2082(4) | 0.3375(3) | 0.1691(4) | 3.6(2) |
| C(36) | -0.3287(4) | 0.3439(3) | 0.1836(5) | 4.5(2) |
| C(37) | -0.3892(4) | 0.4233(3) | 0.2016(5) | 5.1(2) |
| C(38) | -0.3323(5) | 0.4996(3) | 0.2047(5) | 5.0(2) |
| C(39) | -0.2134(5) | 0.4933(3) | 0.1896(5) | 4.7(2) |
| C(40) | -0.1514(4) | 0.4140(3) | 0.1739(4) | 4.0(2) |
| C(41) | -0.3986(6) | 0.5864(4) | 0.2219(7) | 7.8(3) |

$*B_{eq} = (8/3)\pi^2 \Sigma\Sigma U_{ij} a_i * a_j * (a_i \cdot a_j)$

# Appendix A

Hydrogen atom coordinates (fractional) and $B_{iso}$ ($Å^2$)

| atom | x | y | z | $B_{iso}$ |
|---|---|---|---|---|
| H(1) | -0.044(6) | 0.067(4) | -0.086(6) | 11(2) |
| H(2) | -0.069(6) | 0.141(4) | -0.133(6) | 9(2) |
| H(3) | 0.4659 | 0.1267 | 0.0714 | 5.1 |
| H(4) | 0.6055 | 0.1228 | 0.2652 | 5.8 |
| H(5) | 0.5600 | 0.1973 | 0.4573 | 6.3 |
| H(6) | 0.3752 | 0.2764 | 0.4584 | 5.5 |
| H(7) | 0.0340 | 0.4155 | 0.4289 | 5.2 |
| H(8) | -0.0171 | 0.4114 | 0.6239 | 6.8 |
| H(9) | 0.0323 | 0.2894 | 0.7157 | 6.9 |
| H(10) | 0.1350 | 0.1695 | 0.6158 | 6.5 |
| H(11) | 0.1825 | 0.1690 | 0.4166 | 5.2 |
| H(12) | 0.2933 | 0.4189 | 0.4685 | 6.3 |
| H(13) | 0.3610 | 0.5621 | 0.4997 | 7.4 |
| H(14) | 0.3181 | 0.6376 | 0.3333 | 7.5 |
| H(15) | 0.1946 | 0.5745 | 0.1391 | 6.7 |
| H(16) | 0.1215 | 0.4321 | 0.1050 | 5.1 |
| H(17) | 0.2262 | 0.0751 | -0.0364 | 6.0 |
| H(18) | 0.1908 | 0.1325 | -0.1432 | 6.0 |
| H(19) | 0.3313 | 0.1166 | -0.0813 | 6.0 |
| H(20) | 0.3629 | 0.2677 | -0.0295 | 5.8 |
| H(21) | 0.2227 | 0.2834 | -0.0929 | 5.8 |
| H(22) | 0.2782 | 0.3321 | 0.0494 | 5.8 |
| H(23) | -0.1918 | 0.2892 | 0.3814 | 4.5 |
| H(24) | -0.2047 | 0.2204 | 0.5470 | 4.8 |
| H(25) | -0.1171 | 0.0528 | 0.1705 | 4.2 |

# Appendix A

Hydrogen atom coordinates (fractional) and $B_{iso}$ ($Å^2$) (cont.)

| atom | x | y | z | $B_{iso}$ |
|---|---|---|---|---|
| H(26) | -0.1376 | -0.0151 | 0.3335 | 4.7 |
| H(27) | -0.2643 | 0.0646 | 0.5833 | 7.0 |
| H(28) | -0.1711 | -0.0106 | 0.5385 | 7.0 |
| H(29) | -0.1205 | 0.0752 | 0.6391 | 7.0 |
| H(30) | -0.2747 | 0.0673 | 0.0307 | 6.4 |
| H(31) | -0.4270 | 0.0156 | -0.1499 | 7.2 |
| H(32) | -0.4264 | 0.2426 | -0.2634 | 7.0 |
| H(33) | -0.2711 | 0.2929 | -0.0872 | 6.8 |
| H(34) | -0.5667 | 0.0336 | -0.3329 | 7.7 |
| H(35) | -0.6107 | 0.1314 | -0.3415 | 7.7 |
| H(36) | -0.5095 | 0.0850 | -0.4161 | 7.7 |
| H(37) | -0.3714 | 0.2909 | 0.1809 | 5.4 |
| H(38) | -0.4736 | 0.4257 | 0.2125 | 6.1 |
| H(39) | -0.1717 | 0.5463 | 0.1899 | 5.6 |
| H(40) | -0.0661 | 0.4121 | 0.1660 | 4.8 |
| H(41) | -0.4666 | 0.5871 | 0.1491 | 9.4 |
| H(42) | -0.3420 | 0.6329 | 0.2285 | 9.4 |
| H(43) | -0.4303 | 0.5956 | 0.2995 | 9.4 |

# Appendix A

Table . Selected bond lengths (Å) and angles (°).

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| Ru(1) | Cl(1) | 2.418(1) | P(1) | C(13) | 1.859(4) |
| Ru(1) | Cl(2) | 2.385(1) | P(2) | C(21) | 1.835(4) |
| Ru(1) | P(1) | 2.220(1) | P(2) | C(28) | 1.861(4) |
| Ru(1) | P(2) | 2.284(1) | P(2) | C(35) | 1.831(4) |
| Ru(1) | O(1) | 2.252(4) | N(1) | C(2) | 1.474(5) |
| Ru(1) | N(1) | 2.326(4) | N(1) | C(19) | 1.477(5) |
| P(1) | C(1) | 1.830(4) | N(1) | C(20) | 1.475(5) |
| P(1) | C(7) | 1.822(4) | | | |

| atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|
| Cl(1) | Ru(1) | Cl(2) | 162.91(4) | Ru(1) | P(1) | C(13) | 127.2(1) |
| Cl(1) | Ru(1) | P(1) | 90.73(4) | C(1) | P(1) | C(7) | 104.5(2) |
| Cl(1) | Ru(1) | P(2) | 96.26(5) | C(1) | P(1) | C(13) | 99.3(2) |
| Cl(1) | Ru(1) | O(1) | 82.2(1) | C(7) | P(1) | C(13) | 100.6(2) |
| Cl(1) | Ru(1) | N(1) | 83.7(1) | Ru(1) | P(2) | C(21) | 116.7(1) |
| Cl(2) | Ru(1) | P(1) | 104.30(5) | Ru(1) | P(2) | C(28) | 111.9(1) |
| Cl(2) | Ru(1) | P(2) | 89.74(5) | Ru(1) | P(2) | C(35) | 121.2(2) |
| Cl(2) | Ru(1) | O(1) | 81.6(1) | C(21) | P(2) | C(28) | 104.8(2) |
| Cl(2) | Ru(1) | N(1) | 90.8(1) | C(21) | P(2) | C(35) | 102.7(2) |
| P(1) | Ru(1) | P(2) | 98.04(5) | C(28) | P(2) | C(35) | 96.7(2) |
| P(1) | Ru(1) | O(1) | 168.8(1) | Ru(1) | N(1) | C(2) | 107.7(2) |
| P(1) | Ru(1) | N(1) | 80.20(9) | Ru(1) | N(1) | C(19) | 107.8(3) |
| P(2) | Ru(1) | O(1) | 91.4(1) | Ru(1) | N(1) | C(20) | 115.3(3) |
| P(2) | Ru(1) | N(1) | 178.24(9) | C(2) | N(1) | C(19) | 112.1(3) |
| O(1) | Ru(1) | N(1) | 90.3(1) | C(2) | N(1) | C(20) | 106.9(3) |
| Ru(1) | P(1) | C(1) | 101.1(1) | C(19) | N(1) | C(20) | 107.1(3) |
| Ru(1) | P(1) | C(7) | 120.1(1) | | | | |

# Appendix A

Table . Bond lengths (Å) with estimated standard deviations.

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| Ru(1) | Cl(1) | 2.418(1) | C(13) | C(14) | 1.387(6) |
| Ru(1) | Cl(2) | 2.385(1) | C(13) | C(18) | 1.387(5) |
| Ru(1) | P(1) | 2.220(1) | C(14) | C(15) | 1.382(6) |
| Ru(1) | P(2) | 2.284(1) | C(15) | C(16) | 1.363(7) |
| Ru(1) | O(1) | 2.252(4) | C(16) | C(17) | 1.361(7) |
| Ru(1) | N(1) | 2.326(4) | C(17) | C(18) | 1.386(6) |
| P(1) | C(1) | 1.830(4) | C(21) | C(22) | 1.398(5) |
| P(1) | C(7) | 1.822(4) | C(21) | C(25) | 1.391(5) |
| P(1) | C(13) | 1.859(4) | C(22) | C(23) | 1.390(6) |
| P(2) | C(21) | 1.835(4) | C(23) | C(24) | 1.387(6) |
| P(2) | C(28) | 1.861(4) | C(24) | C(26) | 1.385(6) |
| P(2) | C(35) | 1.831(4) | C(24) | C(27) | 1.506(6) |
| N(1) | C(2) | 1.474(5) | C(25) | C(26) | 1.383(5) |
| N(1) | C(19) | 1.477(5) | C(28) | C(29) | 1.344(6) |
| N(1) | C(20) | 1.475(5) | C(28) | C(33) | 1.385(6) |
| C(1) | C(2) | 1.390(5) | C(29) | C(30) | 1.397(6) |
| C(1) | C(6) | 1.389(5) | C(30) | C(31) | 1.365(6) |
| C(2) | C(3) | 1.383(6) | C(31) | C(32) | 1.351(6) |
| C(3) | C(4) | 1.386(6) | C(31) | C(34) | 1.512(6) |
| C(4) | C(5) | 1.368(7) | C(32) | C(33) | 1.382(6) |
| C(5) | C(6) | 1.376(6) | C(35) | C(36) | 1.393(6) |
| C(7) | C(8) | 1.395(6) | C(35) | C(40) | 1.383(6) |
| C(7) | C(12) | 1.381(6) | C(36) | C(37) | 1.380(6) |
| C(8) | C(9) | 1.386(6) | C(37) | C(38) | 1.387(6) |
| C(9) | C(10) | 1.362(7) | C(38) | C(39) | 1.377(6) |
| C(10) | C(11) | 1.371(7) | C(38) | C(41) | 1.507(6) |
| C(11) | C(12) | 1.396(6) | C(39) | C(40) | 1.385(6) |

**Appendix B.** Thermodynamic calculations and UV-Vis spectroscopic data for the reversible formation of *trans*-$RuCl_2(P–N)(PR_3)(H_2O)$.

***NOTE:*** *The complexes numbered* ***1a*** *and* ***2a*** *in the manuscript are here labelled* ***6a*** *and* ***33a****, respectively, and the Tables are numbered* ***XII.1.1–XII.1.9****, and* ***XII.2.1****.*

**Thermodynamic Calculations and Data for the Reversible Formation of**

***Trans*-RuCl$_2$(P-N)(PPh$_3$)(OH$_2$) (33a) (UV-Vis Spectroscopic Data)**

For the equilibrium:

$$\underset{\mathbf{6a}}{RuCl_2(P\text{-}N)(PPh_3)} + H_2O \overset{K}{\rightleftharpoons} \underset{\mathbf{33a}}{\textit{cis}\text{-}RuCl_2(P\text{-}N)(PPh_3)(OH_2)} \quad (1)$$

$$K = \frac{[\mathbf{33a}]}{[\mathbf{6a}][H_2O]} \quad (2)$$

$$\log\left(\frac{[\mathbf{33a}]}{[\mathbf{6a}]}\right) = \log K + n\log[H_2O] \quad (3)$$

where n = 1 (slope)

plot of $\log\left(\frac{[\mathbf{33a}]}{[\mathbf{6a}]}\right)$ versus log $[H_2O]$ gives intercept = log K

$$A = \varepsilon c \ell \quad (4)$$

where A=absorbance
$\varepsilon$ = molar absortivity ($M^{-1}$ $cm^{-1}$)
c = concentration (M)
$\ell$ = pathlength = 1 cm

$$A = A_{6a} + A_{33a} = \varepsilon_{6a}[\mathbf{6a}] + \varepsilon_{33a}[\mathbf{33a}] \quad (5)$$

$$[Ru]_{total} = [\mathbf{6a}] + [\mathbf{33a}] \quad (6)$$

$$\varepsilon_{6a} = \frac{A_0}{[Ru]_{total}} \quad (7)$$

$$\varepsilon_{33a} = \frac{A_\infty}{[Ru]_{total}} \quad (8)$$

Solve for [**6a**] and [**33a**] by substitution of equations (6) and (7) into (5), and equations (6) and (8) into (5), respectively:

$$\left|\frac{[\mathbf{33a}]}{[\mathbf{6a}]}\right| = \left|\frac{A - A_0}{A - A_\infty}\right| \quad (9)$$

## XII.1 Calculations in $CH_2Cl_2$

Trial 1 at 25°C

**Table XII.1.1** Calculation of K at T = 25°C; 5.2 x $10^{-6}$ mol **6a** dissolved in 5.0 mL $CH_2Cl_2$ ($[Ru]_{total}$ = 1.04 x $10^{-3}$ M); absorbances monitored at $\lambda_{max}$ = 678 nm; $A_0$ = 0.52, $A_\infty$ = 0.078 (estimated from a flat baseline between λ =550 to 820 nm).

| $H_2O$ added (μL) | $[H_2O]$ (M) | log $[H_2O]$ | A at $\lambda_{max}$ = 678 nm | $\frac{[33a]}{[6a]}$ | log $\frac{[33a]}{[6a]}$ |
|---|---|---|---|---|---|
| 0.0 | 0.0000 | - | 0.52 | -0.00052 | - |
| 0.5 | 0.0056 | -2.26 | 0.47 | 0.11119 | -0.95 |
| 1.0 | 0.0111 | -1.95 | 0.41 | 0.33838 | -0.47 |
| 2.5 | 0.0278 | -1.56 | 0.33 | 0.78687 | -0.10 |
| 4.0 | 0.0444 | -1.35 | 0.27 | 1.34657 | 0.13 |
| 6.0 | 0.0666 | -1.18 | 0.23 | 1.87686 | 0.27 |
| 9.0 | 0.0999 | -1.00 | 0.18 | 3.21073 | 0.51 |
| 10.0 | 0.1110 | -0.95 | 0.16 | 4.17443 | 0.62 |
| 17.0 | 0.1887 | -0.72 | 0.15 | 5.22535 | 0.72 |

Plot of plot of $\log(\frac{[33a]}{[6a]})$ versus log $[H_2O]$ (see Figure 59) gives y = 1.06x + 1.57; K = 37 $M^{-1}$.

Trial 2 at 25°C

**Table XII.1.2** Calculation of K at T = 25°C; 3.0 x $10^{-6}$ mol **6a** dissolved in 5.0 mL $CH_2Cl_2$ ($[Ru]_{total}$ = 6.0 x $10^{-4}$ M); absorbances monitored at $\lambda_{max}$ = 678 nm; $A_0$ = 0.30, $A_\infty$ = 0.045 (estimated from a flat baseline between λ =550 to 820 nm).

| $H_2O$ added (μL) | $[H_2O]$ (M) | log $[H_2O]$ | A at $\lambda_{max}$ = 678 nm | $\frac{[33a]}{[6a]}$ | log $\frac{[33a]}{[6a]}$ |
|---|---|---|---|---|---|
| 0.0 | 0.0000 | - | 0.30 | 0.00252 | -2.60 |
| 0.1 | 0.0006 | -3.26 | 0.25 | 0.26758 | -0.57 |
| 1.0 | 0.0111 | -1.95 | 0.20 | 0.69199 | -0.16 |
| 1.5 | 0.0167 | -1.78 | 0.15 | 1.46377 | 0.17 |
| 3.5 | 0.0389 | -1.41 | 0.12 | 2.40864 | 0.38 |
| 6.5 | 0.0722 | -1.14 | 0.10 | 3.54626 | 0.55 |
| 8.5 | 0.0944 | -1.03 | 0.09 | 5.07432 | 0.71 |
| 12.0 | 0.1332 | -0.88 | 0.08 | 6.55556 | 0.82 |
| 17.0 | 0.1887 | -0.72 | 0.08 | 6.92910 | 0.84 |

Plot of plot of $\log(\frac{[33a]}{[6a]})$ versus log $[H_2O]$ gives y = 0.83x + 1.54; K = 35 $M^{-1}$.

Trial 1 at 10°C

**Table XII.1.3** Calculation of K at T = 10°C; 4.0 x $10^{-6}$ mol **6a** dissolved in 5.0 mL $CH_2Cl_2$ ($[Ru]_{total}$ = 8.1 x $10^{-4}$ M); absorbances monitored at $\lambda_{max}$ = 678 nm; $A_0$ = 0.39, $A_\infty$ = 0.07 (estimated from a flat baseline between λ =550 to 820 nm).

| $H_2O$ added (μL) | $[H_2O]$ (M) | log $[H_2O]$ | A at $\lambda_{max}$ = 678 nm | $\frac{[33a]}{[6a]}$ | log $\frac{[33a]}{[6a]}$ |
|---|---|---|---|---|---|
| 0.0 | 0.0000 | - | 0.39 | 0.00000 | - |
| 0.5 | 0.0056 | -2.26 | 0.35 | 0.14286 | -0.85 |
| 1.0 | 0.0111 | -1.95 | 0.31 | 0.33333 | -0.48 |
| 1.5 | 0.0167 | -1.78 | 0.27 | 0.60000 | -0.22 |
| 2.0 | 0.0222 | -1.65 | 0.25 | 0.77778 | -0.11 |
| 3.0 | 0.0333 | -1.48 | 0.21 | 1.28571 | 0.11 |
| 4.0 | 0.0444 | -1.35 | 0.20 | 1.46154 | 0.16 |
| 6.0 | 0.0666 | -1.18 | 0.18 | 1.90909 | 0.28 |

Plot of plot of $\log(\frac{[33a]}{[6a]})$ versus log $[H_2O]$ gives y = 1.07x + 1.62; K = 42 $M^{-1}$.

Trial 2 at 10°C

**Table XII.1.4** Calculation of K at T = 10°C; 4.1 x $10^{-6}$ mol **6a** dissolved in 5.0 mL $CH_2Cl_2$ ($[Ru]_{total}$ = 8.2 x $10^{-4}$ M); absorbances monitored at $\lambda_{max}$ = 678 nm; $A_0$ = 0.40, $A_\infty$ = 0.07 (estimated from a flat baseline between λ =550 to 820 nm).

| $H_2O$ added (μL) | $[H_2O]$ (M) | log $[H_2O]$ | A at $\lambda_{max}$ = 678 nm | $\frac{[33a]}{[6a]}$ | log $\frac{[33a]}{[6a]}$ |
|---|---|---|---|---|---|
| 0.0 | 0.0000 | - | 0.40 | 0.00000 | - |
| 0.5 | 0.0056 | -2.26 | 0.34 | 0.22222 | -0.65 |
| 1.0 | 0.0111 | -1.95 | 0.30 | 0.43478 | -0.36 |
| 1.5 | 0.0167 | -1.78 | 0.25 | 0.83333 | -0.08 |
| 2.0 | 0.0222 | -1.65 | 0.22 | 1.20000 | 0.08 |
| 3.0 | 0.0333 | -1.48 | 0.19 | 1.75000 | 0.24 |
| 4.0 | 0.0444 | -1.35 | 0.16 | 2.66667 | 0.43 |
| 6.0 | 0.0666 | -1.18 | 0.12 | 5.60000 | 0.75 |

Plot of plot of $\log(\frac{[33a]}{[6a]})$ versus log $[H_2O]$ gives y = 1.28x + 2.18; K = 151 $M^{-1}$.

Trial 1 at 35°C

**Table XII.1.5** Calculation of K at T = 35°C; 4.5 x $10^{-6}$ mol **6a** dissolved in 5.0 mL $CH_2Cl_2$ ($[Ru]_{total}$ = 9.0 x $10^{-4}$ M); absorbances monitored at $\lambda_{max}$ = 678 nm; $A_0$ = 0.43, $A_\infty$ = 0.08 (estimated from a flat baseline between λ =550 to 820 nm).

| $H_2O$ added (μL) | $[H_2O]$ (M) | log $[H_2O]$ | A at $\lambda_{max}$ = 678 nm | $\left\|\frac{[33a]}{[6a]}\right\|$ | log $\left\|\frac{[33a]}{[6a]}\right\|$ |
|---|---|---|---|---|---|
| 0.0 | 0.0000 | - | 0.42 | 0.02609 | - |
| 1.0 | 0.0111 | -1.95 | 0.34 | 0.32180 | -0.49 |
| 2.0 | 0.0222 | -1.65 | 0.30 | 0.60860 | -0.22 |
| 3.0 | 0.0333 | -1.48 | 0.25 | 1.08694 | 0.04 |
| 4.0 | 0.0444 | -1.35 | 0.23 | 1.37176 | 0.14 |
| 6.0 | 0.0666 | -1.18 | 0.21 | 1.60359 | 0.21 |
| 9.0 | 0.0999 | -1.00 | 0.20 | 1.91569 | 0.28 |
| 12.0 | 0.1332 | -0.88 | 0.19 | 2.14861 | 0.33 |

Plot of plot of $\log(\frac{[33a]}{[6a]})$ versus log $[H_2O]$ gives y = 0.84x + 1.20; K = 16 $M^{-1}$.

Trial 2 at 35°C

**Table XII.1.6** Calculation of K at T = 35°C; 4.8 x $10^{-6}$ mol **6a** dissolved in 5.0 mL $CH_2Cl_2$ ($[Ru]_{total}$ = 9.7 x $10^{-4}$ M); absorbances monitored at $\lambda_{max}$ = 678 nm; $A_0$ = 0.43, $A_\infty$ = 0.075 (estimated from a flat baseline between λ =550 to 820 nm).

| $H_2O$ added (μL) | $[H_2O]$ (M) | log $[H_2O]$ | A at $\lambda_{max}$ = 678 nm | $\left\|\frac{[33a]}{[6a]}\right\|$ | log $\left\|\frac{[33a]}{[6a]}\right\|$ |
|---|---|---|---|---|---|
| 0.0 | 0.0000 | - | 0.43 | -0.00591 | - |
| 1.0 | 0.0111 | -1.95 | 0.37 | 0.20433 | -0.69 |
| 2.0 | 0.0222 | -1.65 | 0.32 | 0.43649 | -0.36 |
| 3.0 | 0.0333 | -1.48 | 0.28 | 0.70044 | -0.15 |
| 4.0 | 0.0444 | -1.35 | 0.26 | 0.94755 | -0.02 |
| 6.0 | 0.0666 | -1.18 | 0.23 | 1.36100 | 0.13 |
| 9.0 | 0.0999 | -1.00 | 0.20 | 1.89962 | 0.28 |
| 12.0 | 0.1332 | -0.88 | 0.19 | 2.12886 | 0.33 |

Plot of plot of $\log(\frac{[33a]}{[6a]})$ versus log $[H_2O]$ gives y = 1.03x + 1.34; K = 22 $M^{-1}$.

Trial 1 at 38°C

**Table XII.1.7** Calculation of K at T = 38°C; $5.4 \times 10^{-6}$ mol **6a** dissolved in 5.0 mL $CH_2Cl_2$ ($[Ru]_{total}$ = $1.08 \times 10^{-3}$ M); absorbances monitored at $\lambda_{max}$ = 678 nm; $A_0 = 0.48$, $A_\infty = 0.08$ (estimated from a flat baseline between $\lambda$ =550 to 820 nm).

| $H_2O$ added (μL) | $[H_2O]$ (M) | log $[H_2O]$ | A at $\lambda_{max}$ = 678 nm | $\left\|\frac{[33a]}{[6a]}\right\|$ | log $\left\|\frac{[33a]}{[6a]}\right\|$ |
|---|---|---|---|---|---|
| 0.0 | 0.0000 | - | 0.48 | 0.00000 | - |
| 1.0 | 0.0111 | -1.95 | 0.37 | 0.37931 | -0.42 |
| 2.0 | 0.0222 | -1.65 | 0.34 | 0.53846 | -0.27 |
| 3.0 | 0.0333 | -1.48 | 0.27 | 1.10526 | 0.04 |
| 5.0 | 0.0555 | -1.26 | 0.25 | 1.35294 | 0.13 |
| 7.0 | 0.0777 | -1.11 | 0.22 | 1.85714 | 0.27 |
| 10.0 | 0.1110 | -0.95 | 0.18 | 3.00000 | 0.48 |
| 12.0 | 0.1332 | -0.88 | 0.15 | 4.71429 | 0.67 |

Plot of plot of $\log(\frac{[33a]}{[6a]})$ versus log $[H_2O]$ gives y = 0.89x + 1.29; K = 20 $M^{-1}$.

Trial 2 at 38°C

**Table XII.1.8** Calculation of K at T = 38°C; $6.2 \times 10^{-6}$ mol **6a** dissolved in 5.0 mL $CH_2Cl_2$ ($[Ru]_{total}$ = $1.25 \times 10^{-3}$ M); absorbances monitored at $\lambda_{max}$ = 678 nm; $A_0 = 0.60$, $A_\infty = 0.085$ (estimated from a flat baseline between $\lambda$ =550 to 820 nm).

| $H_2O$ added (μL) | $[H_2O]$ (M) | log $[H_2O]$ | A at $\lambda_{max}$ = 678 nm | $\left\|\frac{[33a]}{[6a]}\right\|$ | log $\left\|\frac{[33a]}{[6a]}\right\|$ |
|---|---|---|---|---|---|
| 0.0 | 0.0000 | - | 0.60 | 0.00000 | - |
| 1.0 | 0.0111 | -1.95 | 0.55 | 0.10753 | -0.97 |
| 2.0 | 0.0222 | -1.65 | 0.47 | 0.33766 | -0.47 |
| 3.0 | 0.0333 | -1.48 | 0.44 | 0.45070 | -0.35 |
| 5.0 | 0.0555 | -1.26 | 0.39 | 0.68852 | -0.16 |
| 7.0 | 0.0777 | -1.11 | 0.38 | 0.74576 | -0.13 |
| 10.0 | 0.1110 | -0.95 | 0.37 | 0.80702 | -0.09 |
| 12.0 | 0.1332 | -0.88 | 0.36 | 0.87273 | -0.06 |

Plot of plot of $\log(\frac{[33a]}{[6a]})$ versus log $[H_2O]$ gives y = 0.78x + 0.70; K = 5 $M^{-1}$.

**Table XII.1.9** Equilibrium constants for the reversible formation of **33a** at various temperatures (K obtained from Tables XII.1.1 - XII.1.9).

| Temp (°C) | 1/T (K) | K | ln K |
|---|---|---|---|
| 10 | 0.003532 | 42 | 3.74 |
| 10 | 0.003532 | 151 | 5.02 |
| 25 | 0.003354 | 37 | 3.61 |
| 25 | 0.003354 | 35 | 3.56 |
| 35 | 0.003245 | 16 | 2.77 |
| 35 | 0.003245 | 22 | 3.09 |
| 38 | 0.003214 | 20 | 3.00 |
| 38 | 0.003214 | 5 | 1.61 |

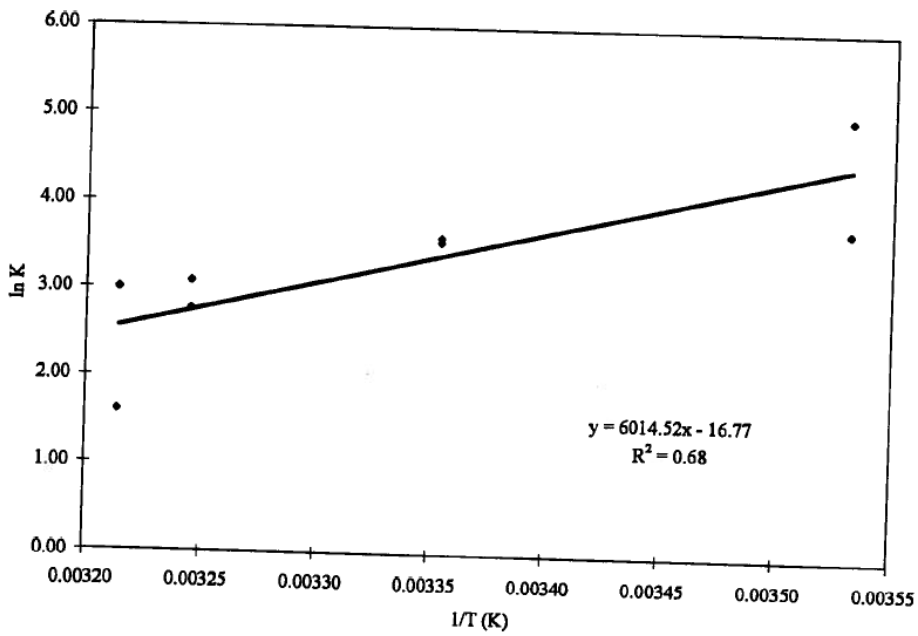


**Figure XII.1** Van't Hoff plot for the reversible formation of $RuCl_2(P\text{-}N)(PPh_3)(OH_2)$ **33a**.

Estimated thermodyanmic parameters from the above plot are:
$\Delta H° = -50 \pm 20$ kJ/mol; $\Delta S° = -140 \pm 40$ J/mol K; $\Delta G° = -8.9 \pm 0.2$ kJ/mol (25°C, based on $K = 37 \pm 2\ M^{-1}$).

## XII.2 Calculations in $C_6H_6$

**Table XII.2.1** Calculation of K at T = 25°C; $6.0 \times 10^{-6}$ mol **6a** dissolved in 5.0 mL $C_6H_6$ ($[Ru]_{total}$ = $1.20 \times 10^{-3}$ M); absorbances monitored at $\lambda_{max}$ = 682 nm; $A_0 = 0.50$, $A_\infty = 0.090$ (estimated from a flat baseline between $\lambda$ =550 to 820 nm).

| $H_2O$ added (μL) | $[H_2O]$ (M) | log $[H_2O]$ | A at $\lambda_{max}$ = 682 nm | $\frac{[33a]}{[6a]}$ | log $\frac{[33a]}{[6a]}$ |
|---|---|---|---|---|---|
| 0.0 | 0.0 | - | 0.50 | 0.00001 | -5.00 |
| 0.5 | 0.0056 | -2.26 | 0.35 | 0.50333 | -0.30 |
| 1.0 | 0.0111 | -1.95 | 0.30 | 0.88328 | -0.05 |
| 2.0 | 0.0222 | -1.65 | 0.25 | 1.37334 | 0.14 |
| 3.0 | 0.0333 | -1.48 | 0.21 | 2.08413 | 0.32 |
| 4.0 | 0.0444 | -1.35 | 0.18 | 3.04990 | 0.48 |
| 7.0 | 0.0776 | -1.11 | 0.17 | 3.4629 | 0.54 |

Plot of plot of $\log(\frac{[33a]}{[6a]})$ versus log $[H_2O]$ gives y = 0.77x + 1.45; K = 28 $M^{-1}$.*

*Determination of K in $C_6H_6$ is more difficult and less accurate than in $CH_2Cl_2$ because water has a lower solubility in $C_6H_6$ (0.0356 M. 25°C)[1] than in $CH_2Cl_2$ (0.128 M, 25°C).[2]

1. IUPAC Solubility Data Series, Volume 37, Hydrocarbons with Water and Seawater Part I: Hydrocarbons $C_5$ to $C_7$; Kertes, A. S., Ed. Pergamon Press: Toronto, 1989, p. 95.
2. IUPAC Solubility Data Series, Volume 60, Halogentated Methanes with Water; Horváth, A. L.; Getzen, F. W., Eds.; Oxford University Press: Oxford, 1995, p. 153.