Supporting Information to

Cyclopentadienyl and Pentamethylcyclopentadienyl Ruthenium Complexes as Catalysts for the Total Deoxygenation of 1,2-Hexanediol and Glycerol

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Details of the catalytic deoxygenation reactions of the 1,2-hexanediol model system.

Table S1 shows the product distribution for catalysts **1**–**3** after 24 h across the temperature range 125–225 °C in the presence of HOTf as the co-catalyst and in sulfolane solvent.

In general, the yield of 1-hexanol was < 20% and the yield of hexane traceable by GC in the sulfolane was less than 5%, except for catalyst **3**. While the yields of 1-hexanol with **3** were comparable to those obtained with **1** and **2**, at higher temperatures substantial amounts of hexane were formed by this catalyst. Furthermore, after 24 h at $T \geq 150$ °C two layers were noticed in the reactor upon cooling. GC/GC-MS and ^{13}C NMR spectroscopy of the top layer identified it as hexane. As hexane has a limited solubility in sulfolane, the amount of hexane quantified by GC (max. ~ 17 % yield) reflects its solubility limit in sulfolane, not its actual yield. Thus, **3** is much more active than it appears from the quantitative GC analysis of the sulfolane layer alone. We previously observed the same behaviour and phase separation with $[Ru(H_2O)_3$(4'-phenyl-2,2':6',2''-terpyridine)]$(OTf)_2$ as the catalysts under similar conditions.[1] Due to the overall small amounts involved and its volatility,[2] a quantification of the hexane separated from the sulfolane is not meaningful. Tracking the conversion of the primary substrate 1,2-hexanediol and the secondary substrate 1-hexanol allows the indirect establishment of the mass balance and therefore an assessment of the true catalyst activity. The increased production of 1-hexanol and its subsequent dehydration to hexene and hydrogenation to hexane observed with **3** suggests that the absence of the bulky methyl groups does in fact result in a more active catalyst compared to the cp^* complexes **1** and **2**.

For all catalysts complete conversion of 1,2-hexanediol was seen at temperatures above 150 °C after 1 h. Other products detected by GC/GC-MS over the course of the reactions were hexanal, *cis*/*trans*-2-pentyl-4-butyl-1,3-dioxolane, traces of hexanoic acid, di-*n*-hexyl ether, 2,5(6)-dibutyl-1,4-dioxane, hexyl hexanoate, and 1,1′-oxy(dihexanol) (or the 1,2′ or 2,2′ isomer) in varying amounts. The amount of the condensation products hexanal and 1,3-dioxolane was often fairly high in the initial samples (about 25%), but decreases or disappears altogether over the course of the reaction. The other products were generally present in < 5% yield total. However, the sum of the products does not come close to equalling the mass balance. We hypothesize that in cases when no hexane layer was observed (i.e., with catalysts **1** and **2**), higher condensates or oligomers are forming under the acidic conditions, and these are not volatile enough for GC analysis, while at the same time being very difficult to isolate and quantify from the sulfolane solution.

Table S1: Deoxygenation of 1,2-Hexanediol by [cp*Ru(OH_2)(bipy)](OTf) (**1**), [cp*Ru(OH_2)(phen)](OTf) (**2**), and [cpRu(CH_3CN)(bipy)](OTf) (**3**) as a function of temperature.[a]

Catalyst **T [°C]**	**Recovery/Yield of Identified Products**[b]	**1** **[%]**	**2** **[%]**	**3** **[%]**
125	1,2-hexanediol	36	42	n/d
	1-hexanol	0	0	n/d
	hexane	0	0	n/d
150	1,2-hexanediol	0	0	0
	1-hexanol	7	16	17
	hexane	0	1	7[c]
175	1,2-hexanediol	0	0	0
	1-hexanol	6	12	2
	hexane	0	1	3[c]
200	1,2-hexanediol	0	0	0
	1-hexanol	3	0	3
	hexane	0	3	4[c]
225	1,2-hexanediol	0	n/d	0
	1-hexanol	0	n/d	0
	hexane	2	n/d	17[c]

[a] Reaction conditions: 500 mmol/L substrate in sulfolane, 100 mmol/L dimethylsulfone as internal standard, 0.5 mol % catalyst, 4 equivalents of HOTf with respect to Ru (10 mmol/L), 4.83 MPa of $H_{2\,(g)}$ (cold), 24 h. [b] By quant. GC and GC-MS. [c] Hexane content of the sulfolane phase; a hexane layer separates from the sulfolane solution.

Figure S1 shows a representative time/temperature profile using catalyst **1**. At high enough temperatures the yield of 1-hexanol shortly reaches a maximum albeit at still low overall yields < 10 %), and then begins to decrease as it forms small amounts of hexene, hexane and dihexyl ether. Very similar 1-hexanol time-concentration profiles are obtained with catalysts **2** and **3**. Moreover, the catalysts are stable to at least 200 °C with no sign of decomposition. This was confirmed by an experiment in which 1,2-hexanediol was hydrogenated at 225 °C using **1**. After 24 h, the reaction solution was recharged with the same amount of substrate, the reactor re-pressurized, and the mixture hydrogenated for another 24 h. The catalyst was still active and after a total of 48 h reaction time, substantial amounts of hexane and hexenes (by GC/GC-MS) were observed floating on top of the sulfolane upon completion of this particular experiment, indicating that with longer reaction times and higher temperatures **1** also is capable of totally deoxygenating the substrate, but the fact that hexenes were present in the product layer suggest a lower activity of **1** and **2** vs **3** as a function of steric bulk of the cp* vs the cp ligand. Also this experiment suggests that the higher condensates or oligomers formed in this reaction and that must be present in the reused solution (as discussed above) do eventually react to fully deoxygenated products. Reuse of a solution of catalyst **3** also gives complete conversion of 1,2-hexanediol to hexane with phase separation as in the first run with no visually apparent decomposition of the clear red catalyst solution.

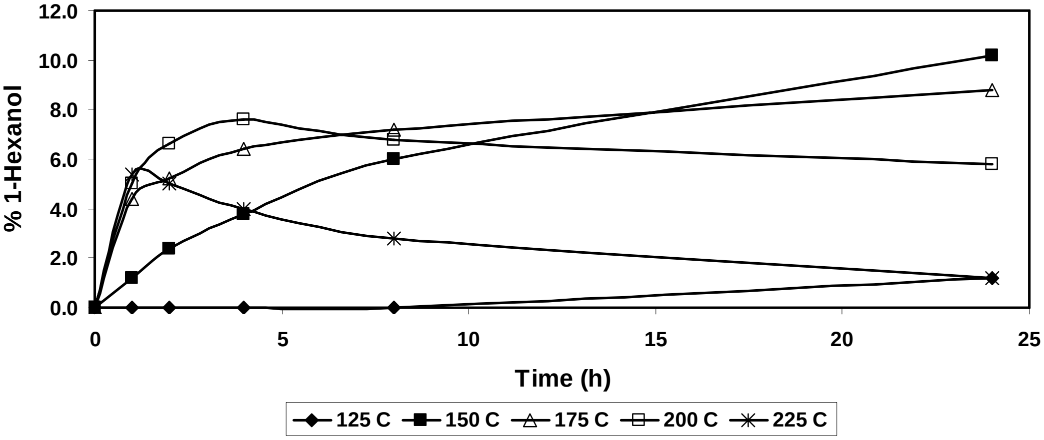


Figure S1: Time/Temperature Profile of 1,2-Hexanediol Deoxygenation to 1-hexanol Using Catalyst **1**.

To probe the possible effects of different acid and water concentrations on the dehydration and condensation equilibria preceding the hydrogenations themselves and therefore the selectivity of the reaction overall, the acid- and water-concentrations in the reactions were systematically varied using a 24-well parallel reactor (24 × 2 mL glass test tubes) with both [cp*Ru(N–N)](OTf) catalysts (**1** and **2**). Reaction conditions were [1,2-hexanediol] = 500 mmol/L, 6.89 MPa H_2 (cold), 0.5 mol % catalyst, [dimethyl sulfone] = 100 mmol/L (internal GC standard), in sulfolane. The concentration of water ranged from 0 to 20 v/v %, while the amount of acid added was between 4 and 16 equivalents with respect to catalyst (10 – 40 mmol/L). This allowed for an array of 20 samples, each with a different acid and water content, and 4 blanks containing only 100 mmol/L dimethyl sulfone in sulfolane. Figures S2 and S3, respectively, summarize the results at 150 °C after 24 h and 2 h for catalyst **1**.

No clear trend in the yield of 1-hexanol across increasing acid or water concentrations or ideal combination of acid and H_2O for the maximization of the 1-hexanol yield emerges from the reaction carried out at 150 °C for 24 h. With 20 % H_2O, 5–50 % of the 1,2-hexanediol was still present, as well as 5–10 % of *cis/trans*-2-pentyl-4-butyl-1,3-dioxolane. Small quantities of hexanol and hexanoic acid were observed in some of the other samples, but in general, the bulk of the 1,2-hexanediol was unaccounted for, i.e., as with the 1,2-hexanediol temperature profiles the mass balances by GC are incomplete due to the formation of non-volatile oligomers with these catalysts at this temperature.

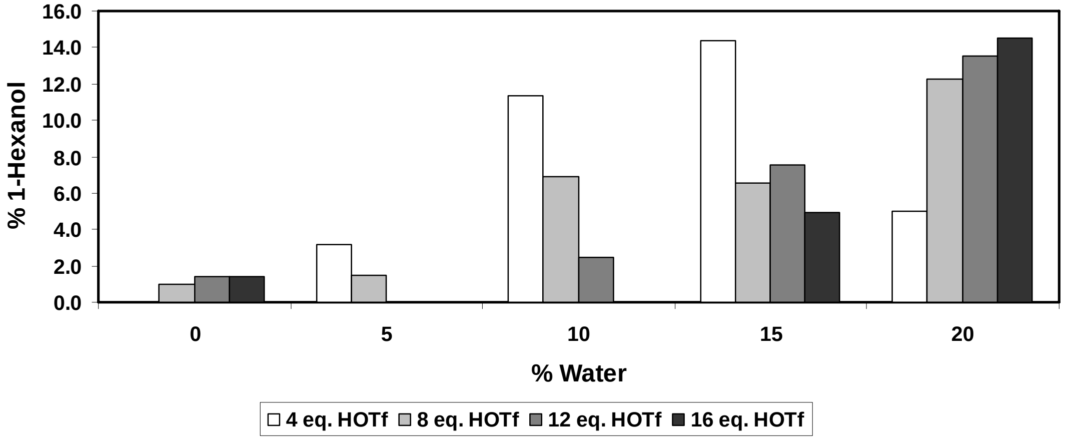


Figure S2: 1,2-Hexanediol Acid/Water Series, Catalyst **1**, 150 °C, 24 h

When the hydrogenation was stopped after 2 h instead of 24 h, a different pattern emerged. The highest yields of 1-hexanol were at lower water concentrations, though again there was not a clear trend. Little, if any, diol remained at 0–5 % H_2O, though some hexanal and traces of hexanoic acid were present. Only a trace of 1-hexanol formed with 15–20 % H_2O, but the mass balance was good at higher water concentrations, consisting of varying amounts of 1,2-hexanediol, hexanal, and 2-pentyl-4-butyl-1,3-dioxolane.

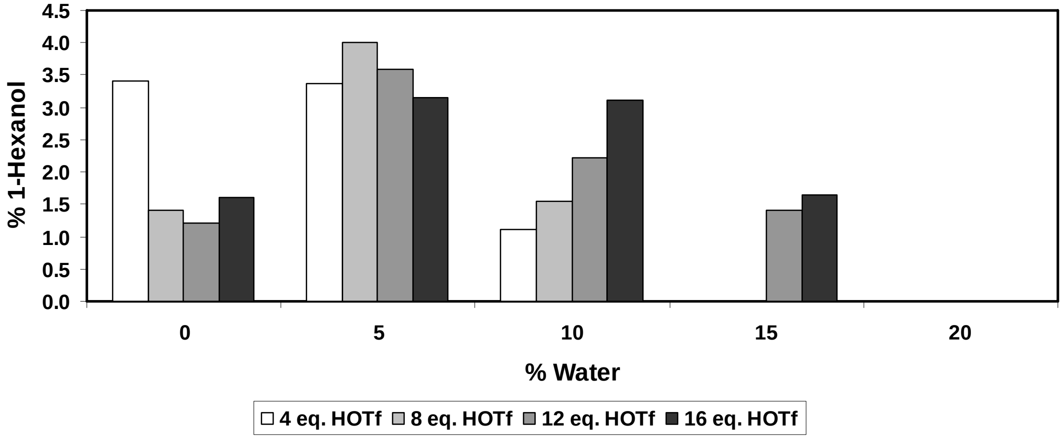


Figure S3: 1,2-Hexanediol Acid/Water Series, Catalyst **1**, 150 °C, 2 h

Upon increasing the temperature to 175 °C for 24 h, formation of non-volatile condensation products is the dominant reaction, though there is some 1-hexanol formation with 20 % H_2O. After 24 h at 200 °C, no volatile products were observed. Acid/H_2O parallel experiments were also conducted using **2** at 175 °C for 2 and 24 h, but the results were not significantly different from those obtained with **1**. In general, the parallel acid/H_2O experiments indicated that a high water content is necessary to reduce the degree of condensation reactions. At higher temperatures, these reactions dominate to the extent that either the desired product (hexanol, in this case) does not form, or it is consumed over 24 h. This is particularly apparent when comparing results after 2 h with those after 24 h. As noted above under more forcing conditions catalyst **1** also produces hexene and hexane, the presence of which could however not be proven when using parallel reactor due to the small reaction volume (< 1.5 mL in each well). As we did not anticipate better selectivities to 1-hexanol with catalyst **3** (it generates a hexane layer even at T = 150 °C; see Table 1), an acid/water concentration study was not carried out with this system.

1,2-Hexanediol Hydrogenation in MeOH

Common to all of the hexanediol hydrogenation experiments was the complete lack of a mass balance. Generally less than 25% of the products could be quantified; the remainder was either not volatile enough to be analyzed by GC or was present as a hexane layer phase separated from the aqueous sulfolane reaction solution and hence also not reliably quantifiable. In an attempt to obtain better mass balances, a hydrogenation experiment using **1** as the catalyst was performed in a 50 mL minireactor using MeOH as the solvent instead of sulfolane. Under these conditions 1,2-hexanediol or its derivatives were anticipated to preferentially form methyl ethers, dimethyl acetals or ketals, which should be volatile enough to analyze by GC and GC-MS, rather than non-volatile self-condensation products.

Table S2 summarizes the results of the MeOH experiment. Approximately 50% of the substrate was consumed as methyl ethers, lending support to the hypothesis that 1,2-hexanediol can dimerize or oligomerize to non-volatile products. In addition, two layers were observed after hydrogenation. ^1H NMR spectroscopy and GC-MS analysis of the top layer indicated that it was a mixture of one or more of dihexyl ether, methoxyhexanes, 1-hexanol, and hexane, while the bottom layer was aqueous MeOH.

Table S2: Product Distribution from Hydrogenation of 1,2-Hexanediol in MeOH Using Catalyst **1**.[a]

Compound[b]	**Yield [%]**
1,2-Hexanediol	2
Hexenes	< 1
OMe-hexanes	22
3-Hexanone	1
2-Hexanone	< 1
Hexanal	< 1
1-Hexanol	34
1,1-$(OMe)_2$-hexane	< 1
1,2-$(OMe)_2$-hexane	9
1-OMe-2-hexanol	12
2-OMe-1-hexanol	7
Dihexyl ether	< 1
2-Pentyl-4-butyl-1,3-dioxolane	0
2-Butyl-2-octenal	< 1
Product Loss (%)	2

[a]Conditions: [1,2-Hexanediol] = 500 mmol/L, 200 °C, 4.83 MPa H_2 (cold), 8 HOTf with respect to [Ru], 0.5 mol% [cp*Ru(OH_2)(bipy)](OTf) (**1**), [dimethyl sulfone] = 100 mmol/L ISTD, in MeOH, 12 h. [b] Identified by GC-MS against authentic samples or by database match of fragmentation pattern.

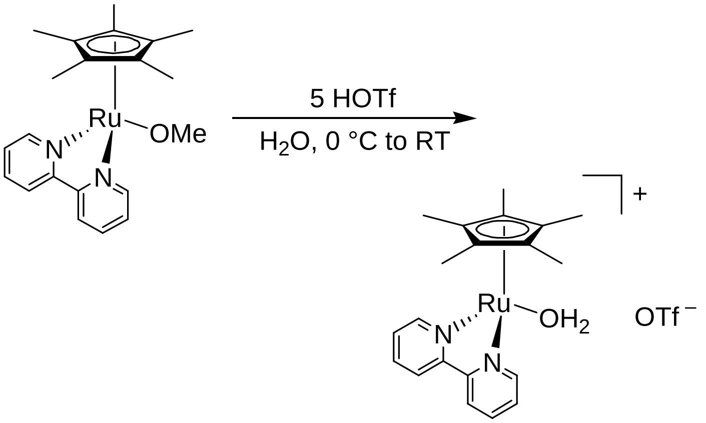
Conclusions from the Deoxygenation Reactions of 1,2-Hexanediol

With catalyst **1** and **2** condensation reactions dominate at reaction temperatures greater than 150 °C and reaction times ≤ 24 h. The addition of water alleviates this problem to a certain extent, but also results in decreased catalytic activity. Either the increased water content inhibits displacement of the aqua ligand by dihydrogen, or more likely the high water content pushes the dehydration equilibrium between 1,2-hexanediol and hexanal towards the former. In contrast, under the same conditions the more active and promiscuous catalyst **3** completely deoxygenates 1,2-hexanediol to hexane in ≤ 24 h, which appears as a separate product layer, indicating that for this catalyst hydrogenation of the reactive intermediates hexanal and hexene competes effectively with reactions leading to oligomeric non-volatile products.

Compound Name: Aqua(2,2′-bipyridine)(η^5-pentamethylcyclopentadienyl)-ruthenium(II) triflate (**1**)

MW: 559.60 g/mol

Synthesis and Structure:



Appearance:
Red-brown powder

Lit. and/or notebook # and page:
MT-3-260, p. 150

First made on date:
November 13, 2006

Made by:
Michelle Thibault

Chromatography conditions:

^{1}H: (300 MHz, CD_3OD): 1.60 (s, 15H), 7.69 (t, J = 5.7 Hz, 2H), 8.03 (t, J = 7.2 Hz, 2H), 8.37 (d, J = 7.5 Hz, 2 H), 9.45 (d, J = 4.2 Hz, 2H).

^{13}C: (75 MHz, CD_3OD): 9.6 (*C*H_3), 78.0 (*C*), 123.4 (*C*H), 127.5 (*C*H), 137.9 (*C*H), 154.0 (*C*H), 157.9 (*C*).

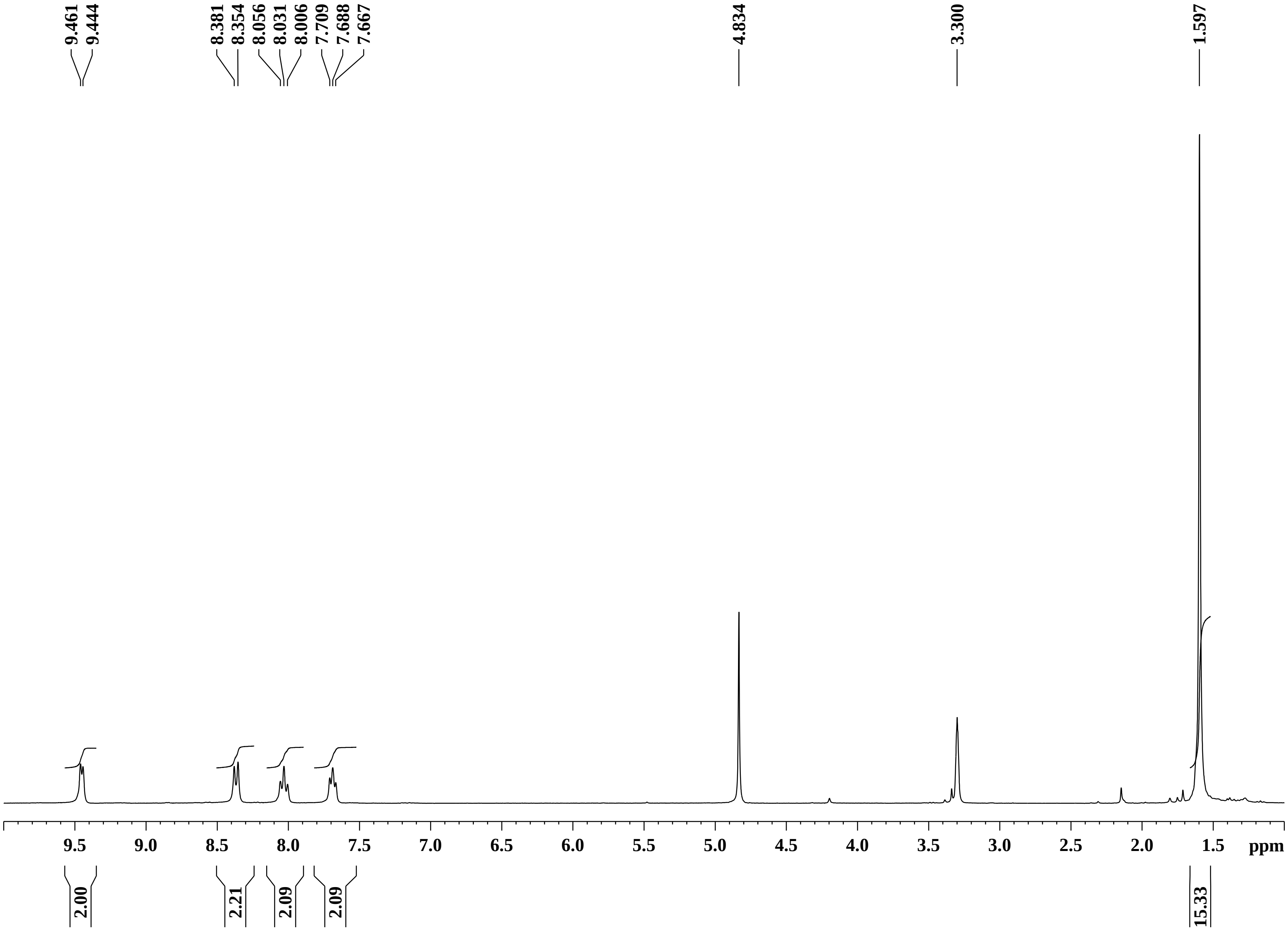
Heteronuclei (^{31}P, ^{29}Si, etc.):

IR:

UV:

MS: (+ESI) *m/e* calc. for $C_{20}H_{23}N_2{}^{102}Ru$: 393.0937, found 393.0869 $[(C_5Me_5)^{102}Ru(bipy)]^+$.

EA:	**C%**	**H%**	**N%**	**_%**	**_%**
Theory:	45.08	4.50	5.01		
Found:	45.26	4.59	5.19		



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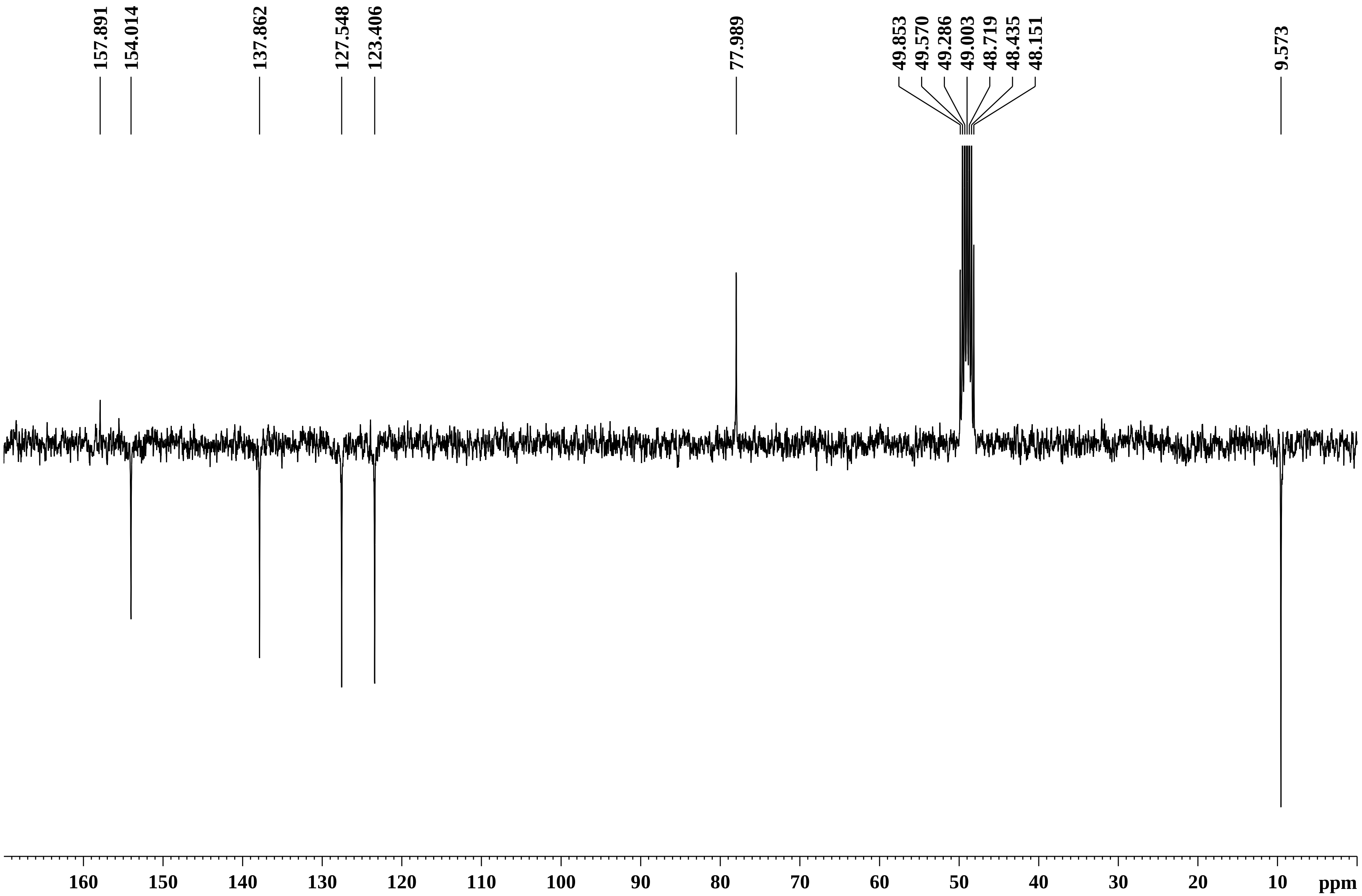
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9.573
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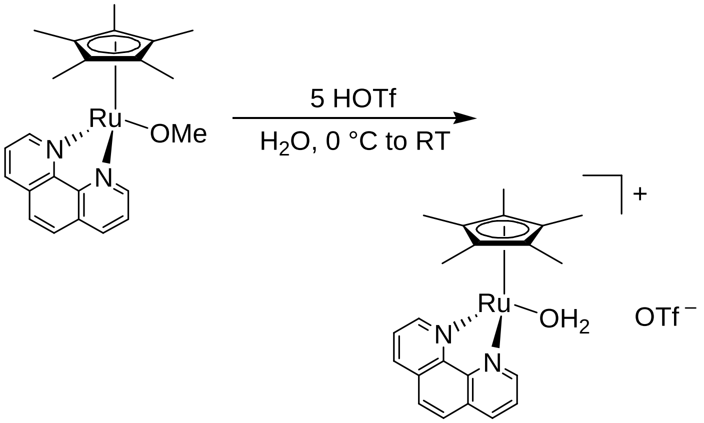
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound Name: Aqua(η^5-pentamethylcyclopentadienyl)(1,10-phenanthroline)-ruthenium(II) triflate (**2**)

MW: 583.63 g/mol

Synthesis and Structure:



Appearance:
Dark yellow powder

Lit. and/or notebook # and page:
MT-5-427 (best), p. 37

First made on date:
January 11, 2007

Made by:
Michelle Thibault

Chromatography conditions:

^{1}H: (300 MHz, dmso-*d*$_6$): 1.56 (s, 15H), 8.09 (dd, J = 5.1, 8.1 Hz, 2H), 8.25 (s, 2H), 8.79 (d, J = 7.8 Hz, 2 H), 9.38 (d, J = 5.1 Hz, 2H).

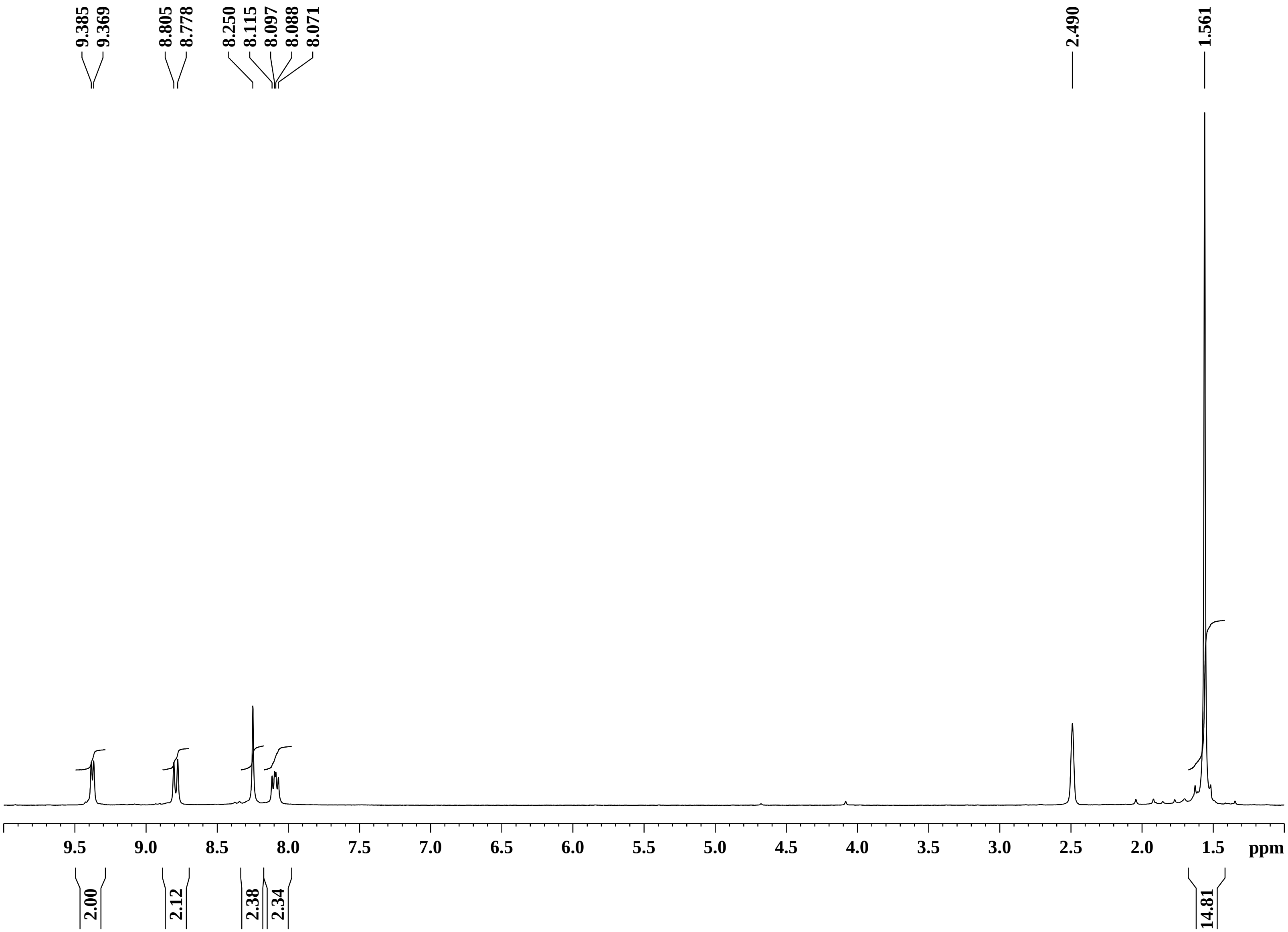
^{13}C: (75 MHz, dmso-*d*$_6$): 8.7 (*C*H$_3$), 86.5 (*C*), 126.1 (*C*H), 127.5 (*C*H), 129.8 (*C*), 1.36.5 (*C*H), 146.4 (*C*), 154.2 (*C*H).

Heteronuclei (^{31}P, ^{29}Si, etc.):

IR:

UV:

MS: (+ESI) *m/e* calc. for $C_{22}H_{23}N_2{}^{102}Ru$: 417.0937, found 417.0879 $[(C_5Me_5)^{102}Ru(phen)]^+$.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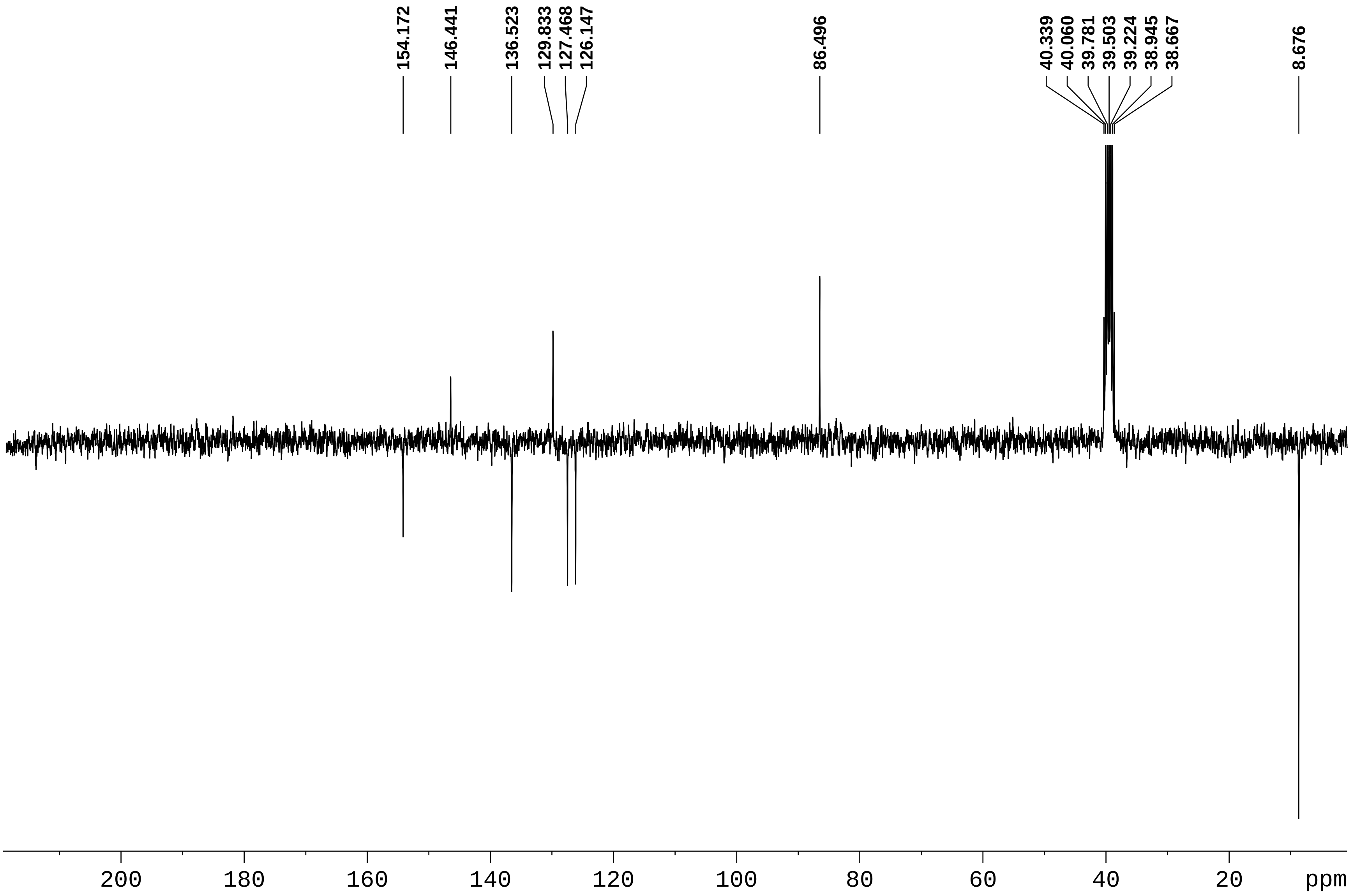
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200
180
160
140
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40
20
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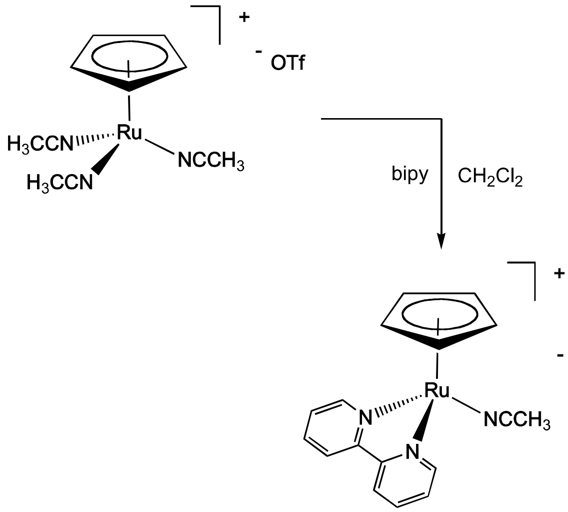
Compound Name: (2,2-bipyridine)(η^5-cyclopentadienyl)(acetonitrile))ruthenium(II) triflate **[6]**

MW: 514 g/mol

Synthesis and Structure:



Appearance:
Red powder

Lit. and/or notebook # and page:

DD1-41, Pg73
DD2-56, Pg1

Lacour, J.; et al. *Angew. Chem. Int. Ed.* **2007**, 46, 8979 –8982

First made on date:
July 29, 2008

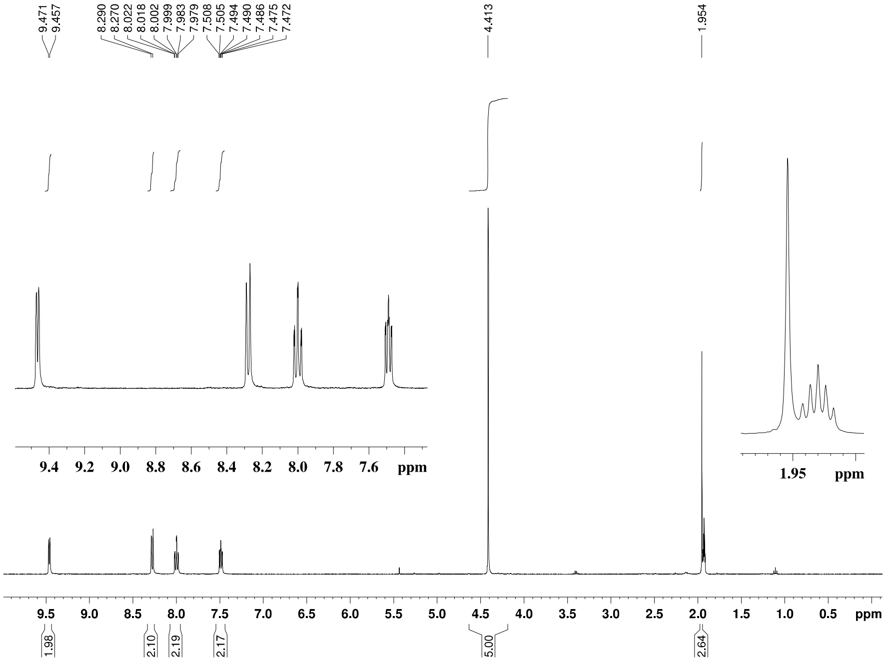
Made by:
Domenic Di Mondo

Experimental Data:

^{1}**H NMR** (400 MHz, acetonitrile-*d*$_3$): δ = 1.95 (s, 3H), 4.41 (s, 5H), 7.49 (td, J = 6.6, 1.2 Hz, 2H), 8.00 (td, J = 7.6, 1.6 Hz, 2H), 8.28 (d, J = 7.2 Hz, 2H), 9.46 (d, J = 7.6 Hz, 2H).

^{13}**C NMR** (75 MHz, acetonitrile-*d*$_3$): δ = 72.1 (*C*H), 123.8 (*C*H), 126.8 (*C*H), 138.0 (*C*H), 156.9 (*C*H), 157.1 (*C*).

MS (MALDI) *m/e* calc. for $C_{15}H_{13}N_2{}^{102}Ru$: 323.1815, found 322.9991 $[cp^{102}Ru(bipy)]^+$.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7.486
7.475
7.472
4.413
1.954
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 ppm
1.95 ppm
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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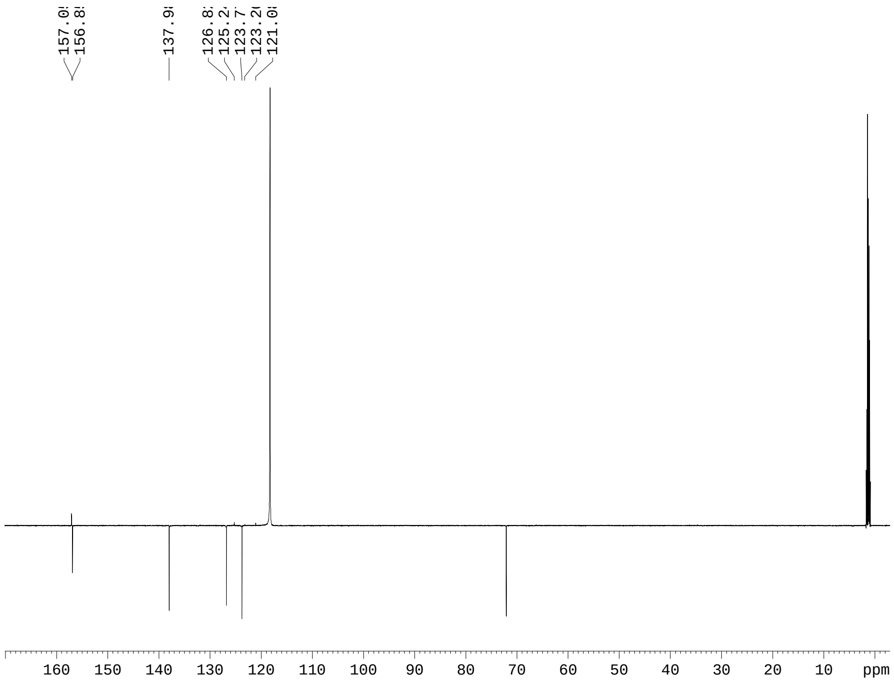
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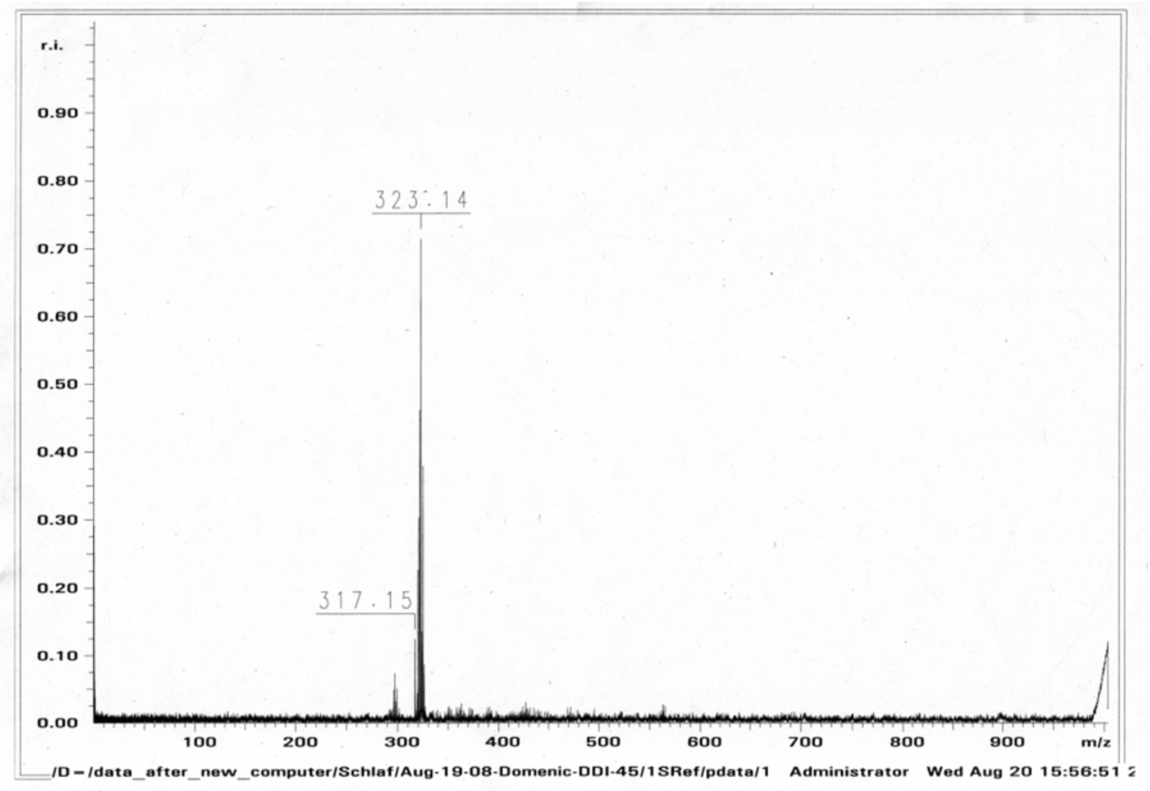
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0.30
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317.15
100
200
300
400
500
600
700
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m/z
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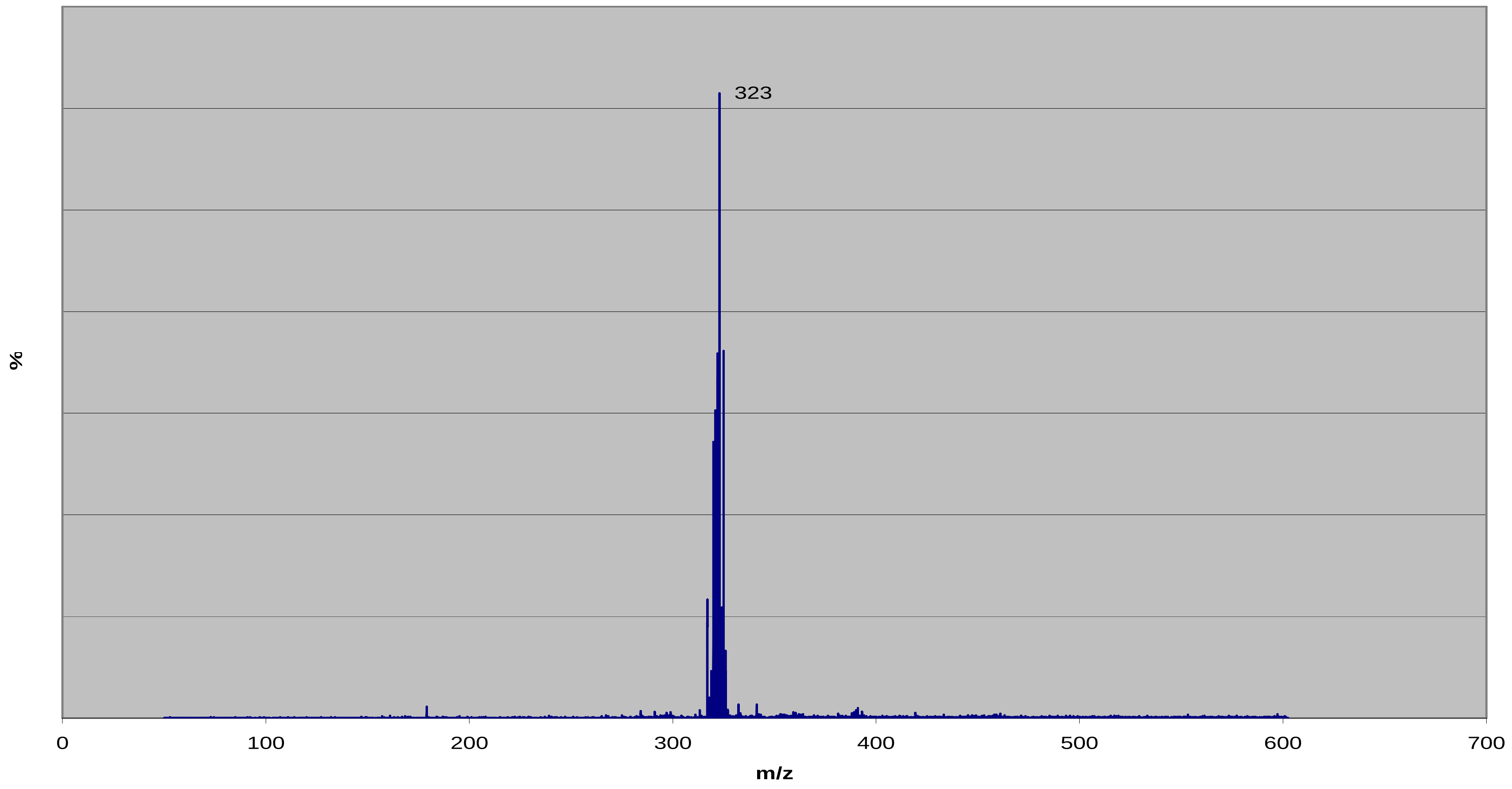
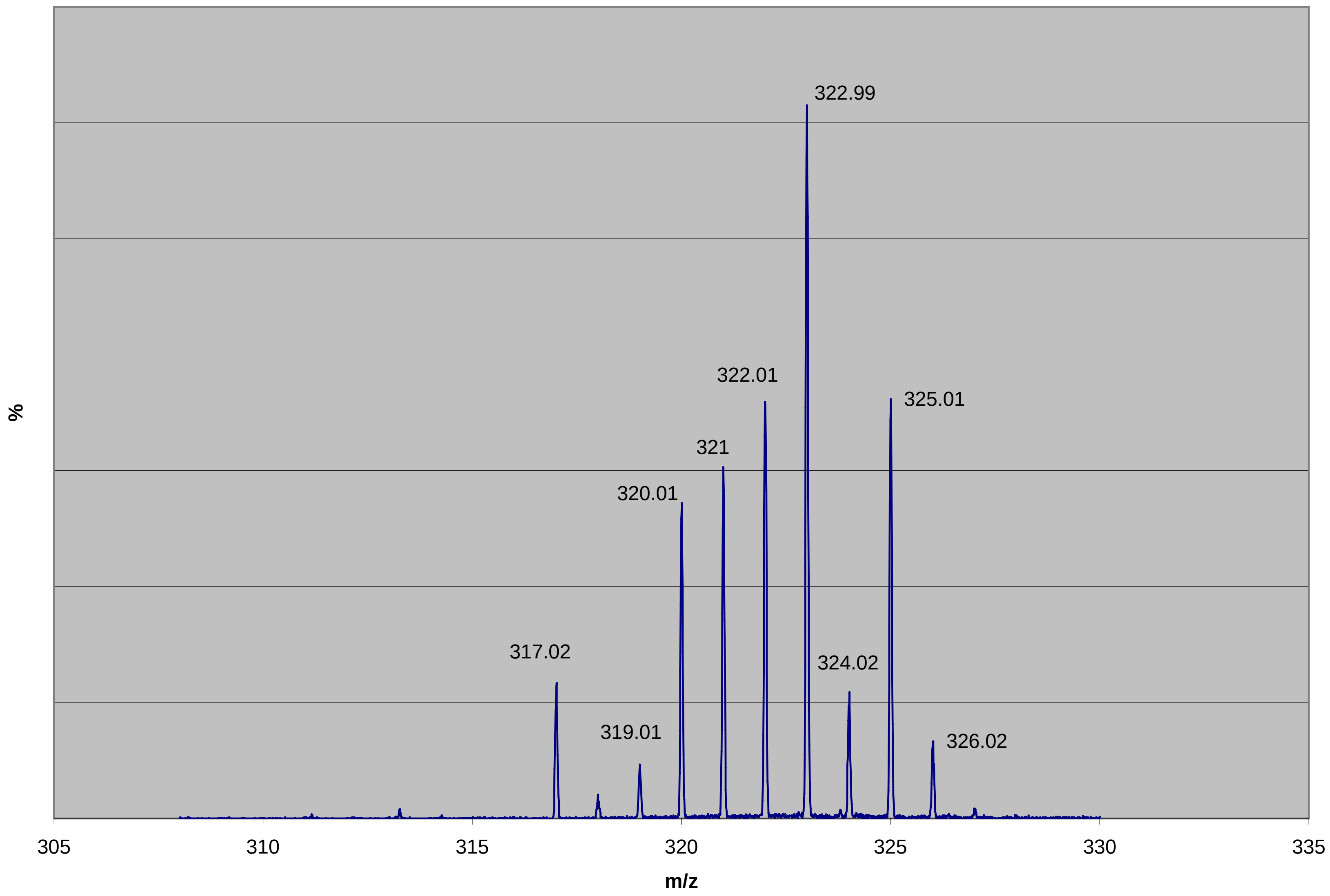
Mass Spectrometry
Q-Tof: 317.0068
TOF MS ES+ 1.37e4
Parent peak = 322.9991 m/z corresponds to cation with loss of CH_3CN

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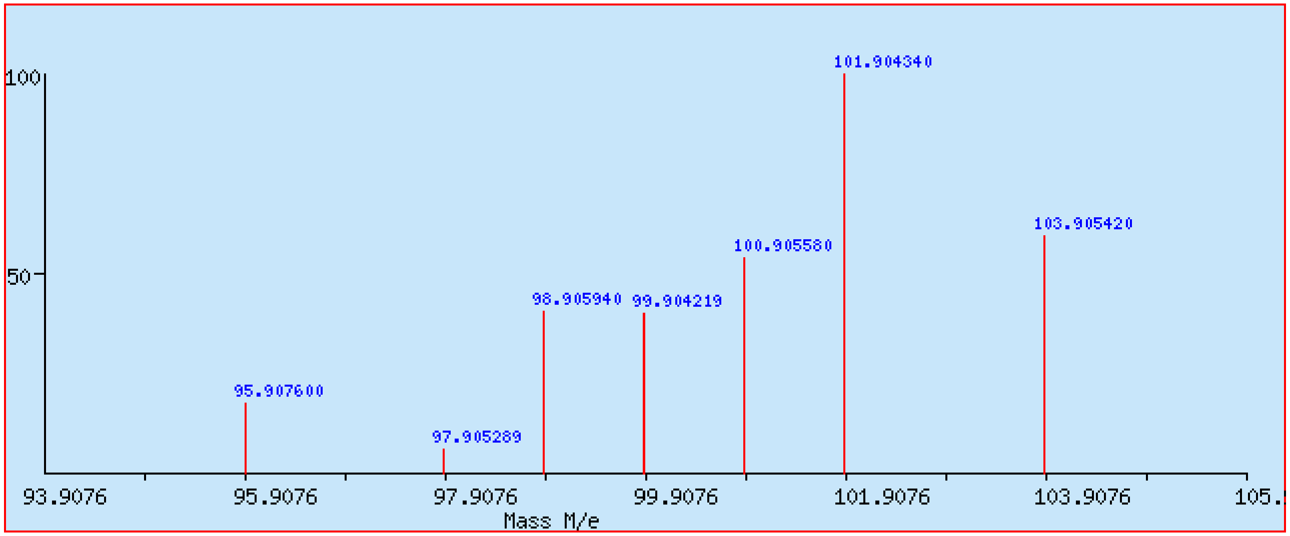
335
m/z

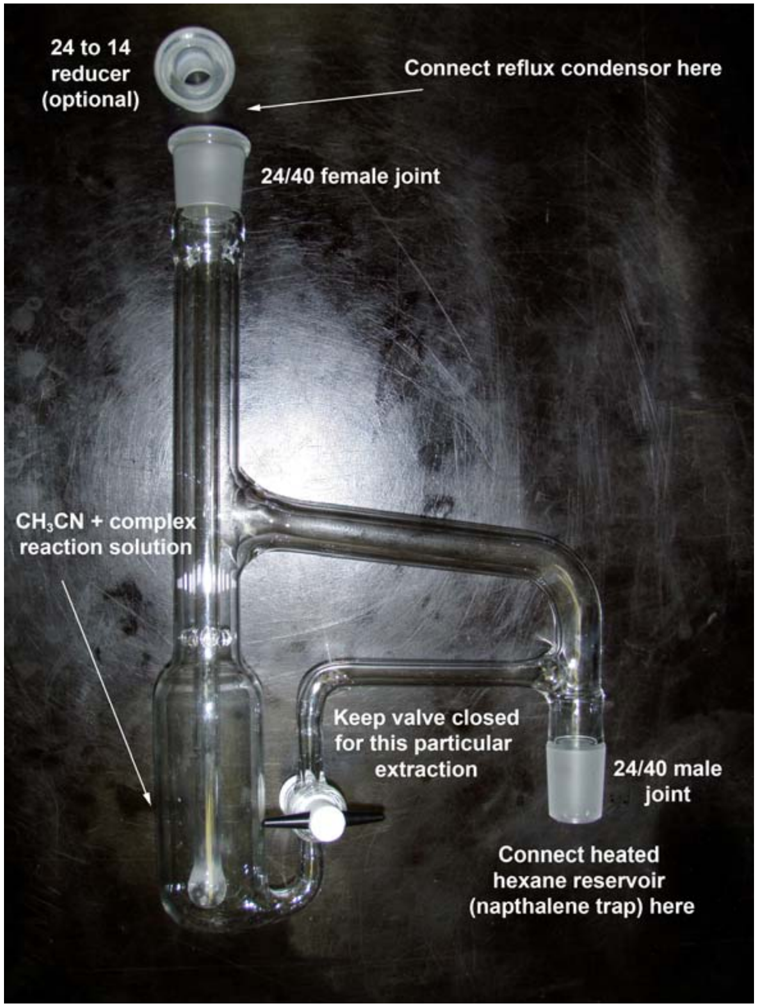
Isotope Distribution for Ruthenium metal in Mass Spec Plot

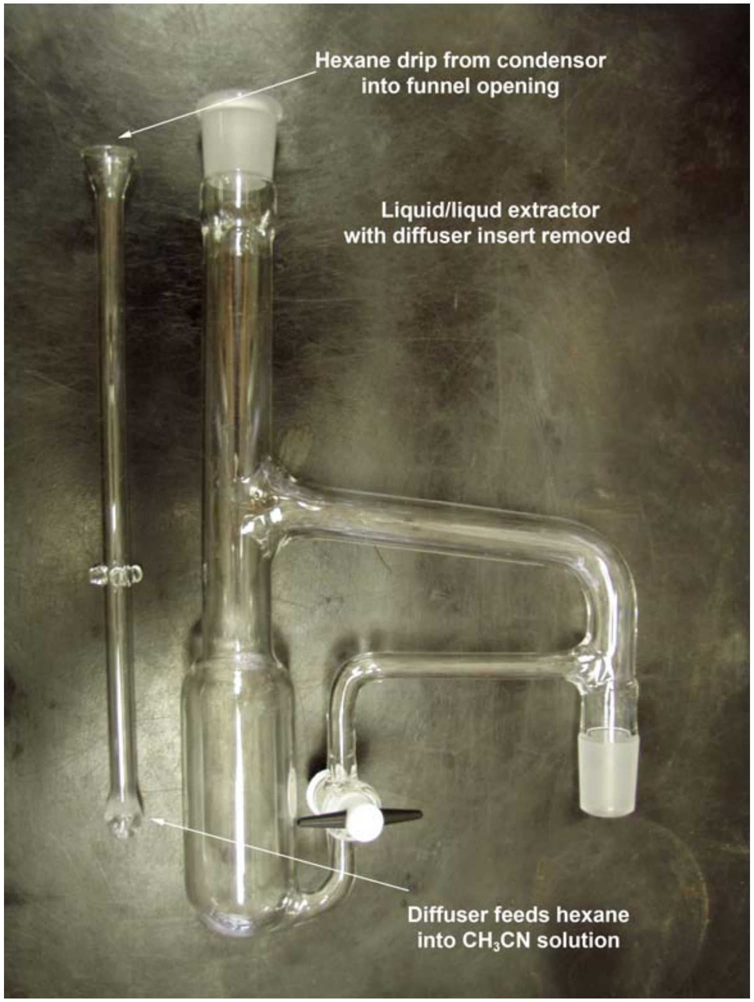


Reference

Isotope Distribution Calculator, Scientific Instrument Services. Available online: http://www2.sisweb.com/mstools/isotope.htm

Images of the liquid/liquid extractor used in the optimized synthesis of [(cp)Ru(CH_3CN)$_3$](OTf):





Experimental Conditions for single crystal X-ray analysis of Complex 3.

Crystals of [cpRu(NCMe)(μ-bipy)][F_3CSO_3] were grown from a concentrated aqueous solution. An orange plate was mounted on a glass fibre. Data were collected at low temperature (-123 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski & Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The crystal data and refinement parameters for [cpRu(NCMe)(μ-bipy)][F_3CSO_3] are listed in Table I. Interatomic distances and angles are listed in Table III. The reflection data were consistent with a triclinic space group: P-1.

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. Independent molecules were formed. The cation and anion were both very well ordered. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

The largest residue electron density peak (0.674 e/Å^3) was associated with the ruthenium-nitrogen bridging unit. Full-matrix least squares refinement on F^2 gave $R_1 = 3.95$ for 2σ data and $wR_2 = 9.20$ for all data (GOOF = 1.053). The final solution was submitted to the IUCR checkCIF program and had no Alert level A's or B's.

CIF file for [cpRu(NCCH$_3$)(bipy)](OTf) (**3**)

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 on F, with F set to zero for negative F^2^. The threshold expression
of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
 not relevant to the choice of reflections for refinement.  R-factors
based
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and R-
 factors based on ALL data will be even larger.
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O32 O 1.3051(3) 0.8131(3) 1.3321(3) 0.0340(6) Uani 1 1 d . . .
O33 O 1.0680(3) 0.7788(2) 1.1095(3) 0.0316(6) Uani 1 1 d . . .
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C35 C 1.0649(5) 0.5872(4) 1.2138(4) 0.0297(8) Uani 1 1 d . . .
F36 F 1.1393(3) 0.5302(2) 1.1518(2) 0.0417(6) Uani 1 1 d . . .
F37 F 0.9004(3) 0.5257(2) 1.1336(3) 0.0456(6) Uani 1 1 d . . .
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C3 0.029(2) 0.041(2) 0.024(2) 0.0110(17) 0.0184(17) 0.0131(17)
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C18 0.028(2) 0.038(2) 0.024(2) 0.0065(16) 0.0151(17) 0.0056(17)
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angles
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only
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planes.
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C8 H8C 0.9800 . ?
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C12 N11 C16 118.3(3) . . ?
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C21 N22 C17 117.9(3) . . ?
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C17 N22 Ru 117.2(2) . . ?
O32 S34 O33 115.40(16) . . ?
O32 S34 O31 114.98(16) . . ?
O33 S34 O31 114.98(15) . . ?
O32 S34 C35 102.58(16) . . ?
O33 S34 C35 103.27(16) . . ?
O31 S34 C35 103.02(16) . . ?
F36 C35 F37 107.9(3) . . ?
F36 C35 F38 107.0(3) . . ?
F37 C35 F38 107.0(3) . . ?
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F37 C35 S34 112.0(2) . . ?
F38 C35 S34 110.8(3) . . ?
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C3 Ru C1 C5 -80.7(2) . . . . ?
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Ru C2 C3 C4 -61.4(2) . . . . ?
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C5 Ru C4 C3 -118.2(3) . . . . ?
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Ru C4 C5 C1 -61.0(2) . . . . ?
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C12 N11 C16 C17 -178.8(3) . . . . ?
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C18 C19 C20 C21 -0.6(6) . . . . ?
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C18 C17 N22 C21 -1.6(5) . . . . ?
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_refine_diff_density_rms    0.111
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References

(1) Taher, D.; Thibault, M. E.; Mondo, D. D.; Jennings, M.; Schlaf, M. *Chem. Eur. J.* **2009**, 10132.
(2) Even with cooling by an ice-bath, substantial amounts of hexane are lost upon venting the reactor at the end of the reaction.