Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

for

Facile η^5-η^3 hapticity interconversion in pentamethylcyclopentadienyl ruthenium(II) complexes containing a phenylmethallyl ("open idenyl") ligand

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Contents

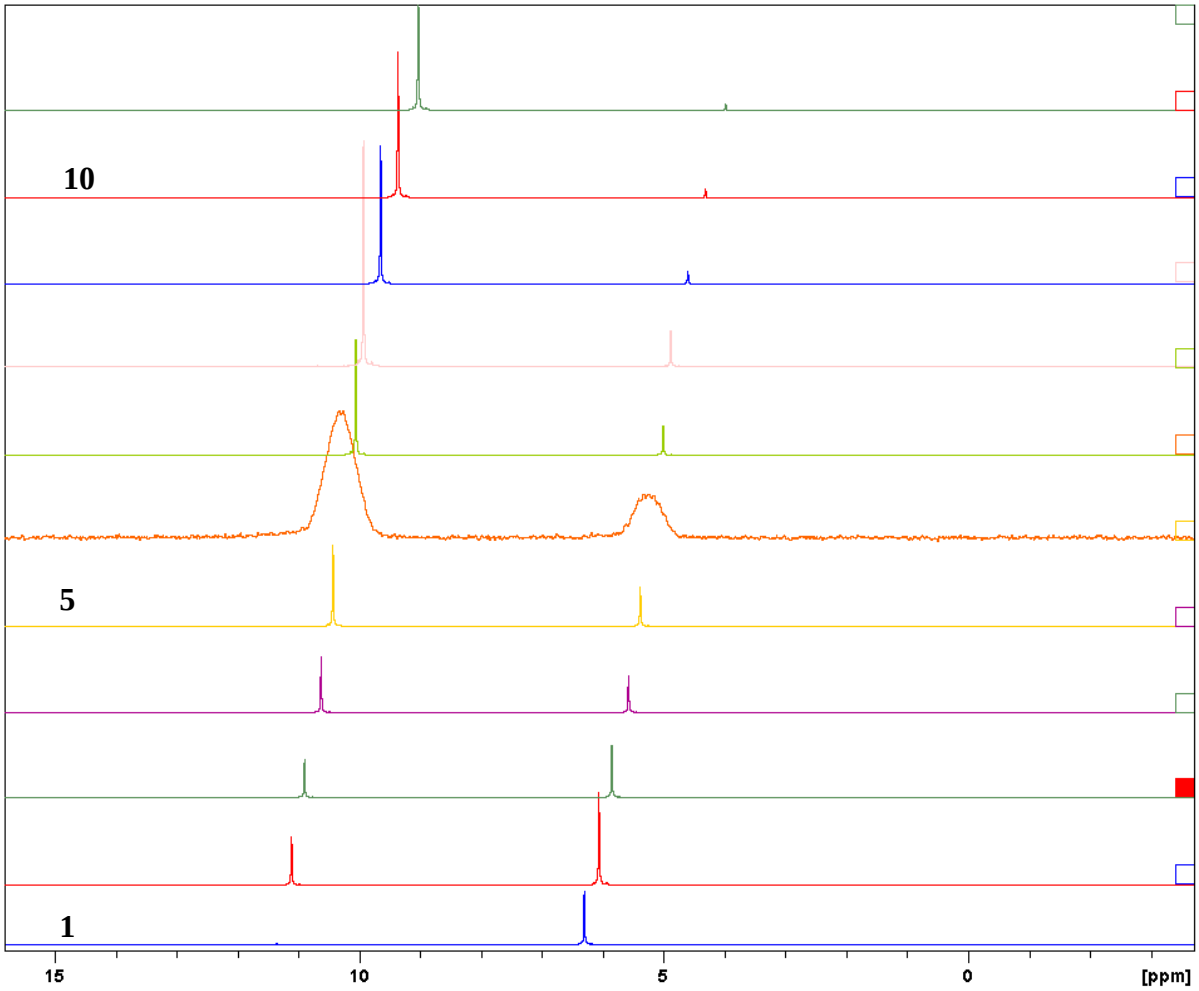
1. NMR study: Isomerization of *anti*-**2** to *syn*-**2**

A sample of freshly prepared *anti*-[(η^5-C_5Me_5)Ru(η^3-oInd^{Me})(PMe_3)] (*anti*-**2**) in C_6D_6 was sealed in an NMR tube, and the ^1H and $^{31}P\{^1H\}$ NMR spectra were measured (experiment No. 1). The NMR tube was placed in an oil bath with a constant temperature of 50° C; this time was set as the starting point of the kinetic study. For the following NMR measurements (No. 2 – No. 18), the time was stopped, and the NMR tube was cooled with an ice bath immediately after it was taken out of the oil bath.

The ratio of the *anti*- and *syn*-isomer was determined by the integration of the corresponding peaks in the ^{31}P NMR, and, as a reference, by the integration of the peaks assigned to the methyl-groups of the C_5Me_5 ligand in the ^1H NMR. Both ratios for each time are listed below.

	Time			**^{31}P NMR**		**^{1}H NMR**	
No.	days	hours	seconds	*anti*	*syn*	*anti*	*syn*
1	0.00	0.00	0	98.1%	1.9%	98.2%	1.8%
2	0.68	16.33	58800	67.4%	32.6%	68.0%	32.0%
3	0.95	22.87	82320	58.1%	41.9%	58.8%	41.2%
4	1.60	38.37	138120	41.0%	59.0%	42.1%	57.9%
5	1.94	46.62	167820	34.1%	65.9%	35.0%	65.0%
6	2.58	62.03	223320	23.7%	76.3%	24.4%	77.7%
7	2.85	68.32	245940	21.2%	78.8%	22.0%	78.0%
8	3.80	91.08	327900	13.4%	86.6%	13.9%	86.1%
9	4.75	113.95	410220	8.6%	91.4%	8.6%	91.4%
10	5.61	134.60	484560	6.0%	94.0%	6.3%	93.7%
11	6.52	156.38	562980	4.3%	95.7%	4.5%	95.5%
12	7.74	185.80	668880	3.3%	96.7%	3.5%	96.5%
13	8.73	209.57	754440	2.8%	97.2%	3.1%	96.9%
14	9.71	232.95	838620	2.5%	97.5%	2.7%	97.3%
15	11.48	275.57	992040	1.9%	98.1%	2.0%	98.0%
16	14.39	345.33	1243200	1.6%	98.4%	1.7%	98.3%
17	17.52	420.35	1513260	2.0%	98.0%	2.1%	97.9%
18	21.30	511.13	1840080	2.0%	98.0%	2.0%	98.0%

Plot of the $^{31}P\{^{1}H\}$ spectra

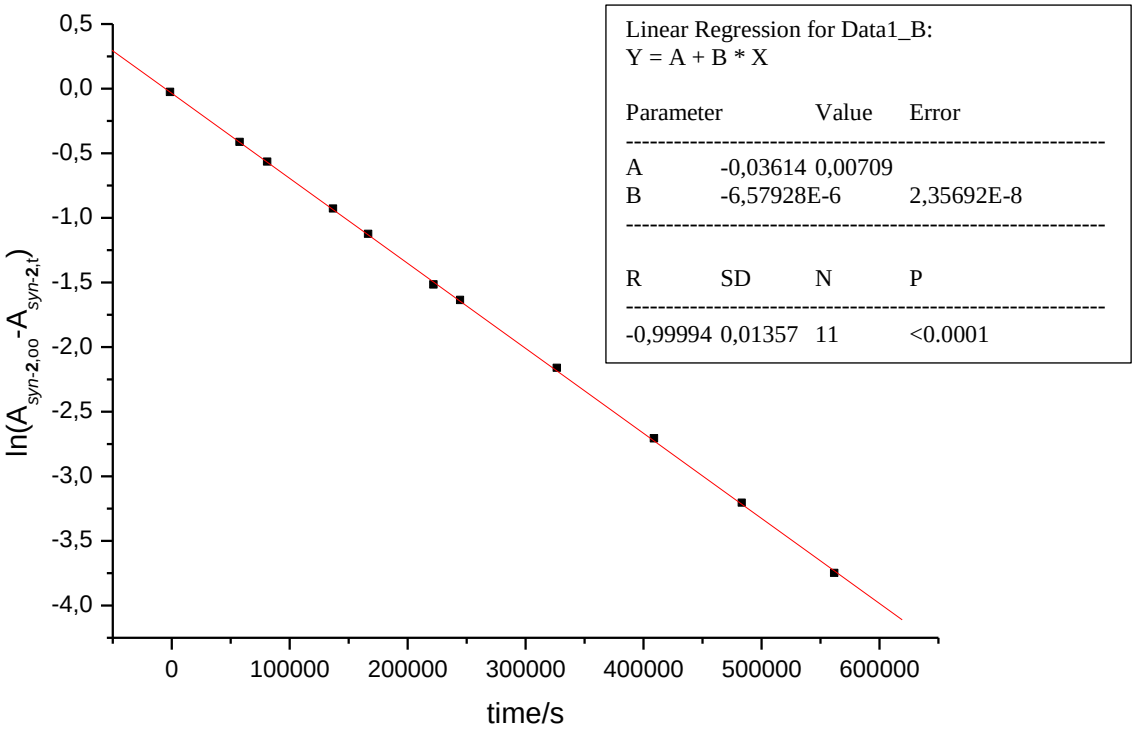


For all, except spectra 6 (Bruker DPX 200), a Bruker AV 300 spectrometer was used.

Origin Plot for the determination of the rate constant

For the calculations, the results from the first eleven $^{31}P\{^{1}H\}$ spectra were used.

In case of a first-order reaction proceeding to equilibrium, a plot of $\ln(A_{syn\text{-}\mathbf{2},\infty}-A_{syn\text{-}\mathbf{2},t})$ against the time gives the rate constant k from the slope.[1] A represents the relative integrals of the $^{31}P\{^{1}H\}$ NMR signals, with $A_{syn\text{-}\mathbf{2},\infty}$ and $A_{syn\text{-}\mathbf{2},t}$ being the relative integrals at equilibrium and at the time of the measurement, respectively.



Calculation of the half-life:

$$t_{1/2} = \frac{ln2}{k} \Rightarrow t_{1/2} = 105353s \approx 29{,}3h$$

Calculation of the free activation energy:

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT} \Leftrightarrow \Delta G^{\ddagger} = -ln\left(\frac{kh}{k_B T}\right) RT \Rightarrow \Delta G^{\ddagger} = -ln(9.69 \cdot 10^{-19}) RT = 112 kJ/mol$$

$k = 6.57 \cdot 10^{-6}\ s^{-1}$ $\quad h = 6.62 \cdot 10^{-34}\ J\ s$

$k_B = 1.38 \cdot 10^{-23}\ J\ K^{-1}$ $\quad T = 325.15\ K$

$R = 8.31\ J\ K^{-1}\ mol^{-1}$

[1] J. R. Chipperfield, *J. Organomet. Chem.*, 1989, **363**, 253.

4. Computational Details

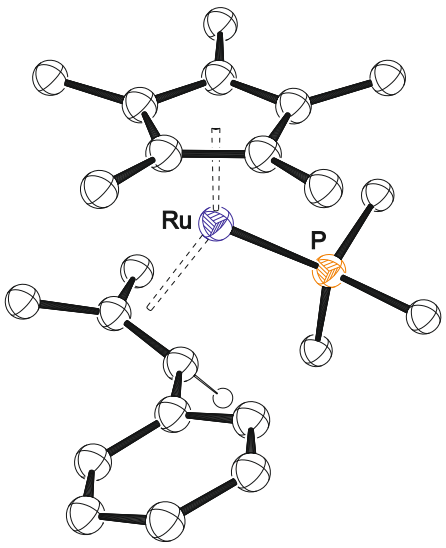
Energies for the optimized structures:

Compound			E(0 K)[a] [Ha]	H(298 K)[b] [Ha]	G(298 K)[b] [Ha]
syn	[(η^5-C_5Me_5)Ru(η^3-oInd^{Me})(PMe_3)]	(**2**)	-1332.821236	-1332.790840	-1332.876667
anti	[(η^5-C_5Me_5)Ru(η^3-oInd^{Me})(PMe_3)]	(**2**)	-1332.819061	-1332.788613	-1332.874206
syn	[(η^5-C_5Me_5)Ru(η^3-oInd^{Me})(CO)]	(**3**)	-985.210587	-985.184905	-985.262905
anti	[(η^5-C_5Me_5)Ru(η^3-oInd^{Me})(CO)]	(**3**)	-985.208179	-985.182693	-985.260128

[a]DFT energy incl. ZPE.
[b]standard conditions T = 298.15 K and p = 1 atm.

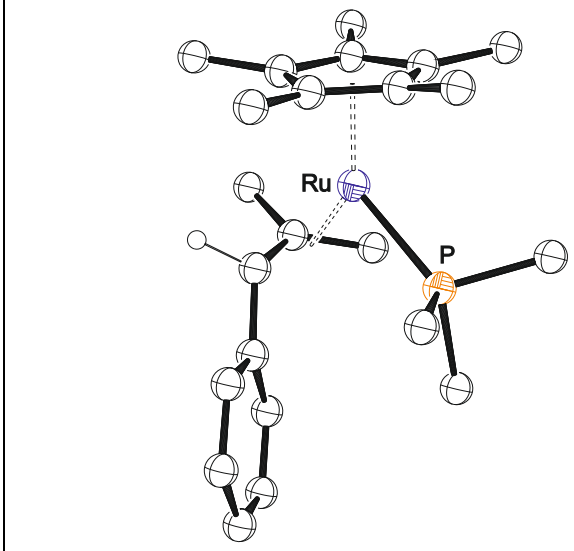
***syn*-2**

Ru	0.598300	-0.135000	-0.315300
P	1.474900	2.013500	-0.264500
C	3.304700	2.179400	-0.124600
C	1.246500	3.225400	-1.639700
C	0.906300	3.080300	1.127400
C	0.591900	0.067000	-2.501900
C	-0.725200	-0.174700	-2.005600
C	-1.260100	0.805700	-1.110200
C	-1.432000	-1.438700	-2.397500
C	-2.562300	0.690400	-0.406000
C	-2.674400	1.173000	0.902000
C	-3.718000	0.176700	-1.000300
C	-3.868500	1.107800	1.601000
C	-4.915000	0.099700	-0.300200
C	-4.996100	0.555200	1.006800
C	-0.092500	-1.952200	0.816400
C	1.009800	-2.309800	-0.028500
C	2.159300	-1.571400	0.397800
C	1.757100	-0.773000	1.514400
C	0.372500	-0.995600	1.770900
C	-1.446700	-2.576200	0.864200
C	1.057500	-3.389800	-1.055000
C	3.535900	-1.741800	-0.145600
C	2.664100	-0.035400	2.441400
C	-0.388800	-0.505300	2.952300
H	3.766100	1.657500	-0.969200
H	3.674800	1.734800	0.801200
H	3.603300	3.233700	-0.150200
H	0.199200	3.326300	-1.934700
H	1.822900	2.913300	-2.515000
H	1.612800	4.205600	-1.316500
H	1.477000	4.014500	1.185900
H	0.989800	2.547800	2.079300
H	-0.150800	3.319100	0.968100
H	1.045100	-0.733200	-3.088900
H	0.865900	1.057000	-2.853600
H	-2.054400	-1.244900	-3.282000
H	-2.087000	-1.833200	-1.619200
H	-0.712600	-2.210000	-2.684500
H	-1.785000	1.580000	1.378300
H	-3.686200	-0.159200	-2.032000
H	-3.917500	1.482100	2.620100
H	-5.794400	-0.312800	-0.787100
H	-5.931500	0.491200	1.554100
H	-1.020300	1.845100	-1.334500
H	-1.560200	-3.165100	1.783700
H	-1.614500	-3.254700	0.024200
H	-2.248500	-1.827000	0.856600
H	1.531500	-3.048600	-1.982800
H	0.062900	-3.766600	-1.307100
H	1.645900	-4.240200	-0.686300
H	4.033100	-2.629000	0.272200
H	4.167200	-0.875400	0.073800
H	3.512200	-1.857200	-1.234100
H	2.314800	0.975400	2.678700
H	3.681000	0.039700	2.047400
H	2.729600	-0.576800	3.394000
H	-0.274300	-1.188200	3.806800
H	-1.459100	-0.427900	2.737500
H	-0.044800	0.482800	3.278100



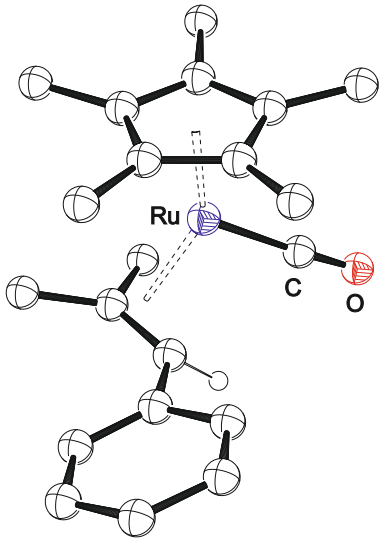
anti-2

Ru	0.622000	-0.141800	-0.183600
P	-0.710200	1.756200	-0.550600
C	0.184300	3.094700	-1.449100
C	-2.248500	1.817300	-1.562500
C	-1.342800	2.658600	0.926700
C	-0.292200	-0.901400	-2.050900
C	-0.393000	-1.841900	-0.987700
C	-1.086600	-1.473000	0.216600
C	-2.490100	-1.027000	0.297800
C	-3.414000	-1.286300	-0.717900
C	-4.742200	-0.901000	-0.595000
C	-5.184300	-0.259000	0.552900
C	-4.284800	-0.022900	1.587300
C	-2.960000	-0.405700	1.460400
C	0.262800	-3.184800	-1.111700
C	2.165600	-1.183000	1.048300
C	2.736200	-0.870900	-0.230000
C	2.771200	0.551000	-0.369000
C	2.227900	1.107900	0.830900
C	1.834100	0.047100	1.698700
C	2.096200	-2.513800	1.716700
C	3.385800	-1.810000	-1.187600
C	3.422200	1.280300	-1.494100
C	2.326800	2.535200	1.254700
C	1.333800	0.186200	3.094700
H	0.528000	2.695200	-2.408800
H	1.053900	3.437800	-0.887600
H	-0.476500	3.949800	-1.632400
H	-3.015000	1.146200	-1.173600
H	-2.036400	1.551400	-2.601700
H	-2.631800	2.843200	-1.542100
H	-1.686800	3.664200	0.658600
H	-0.578700	2.735100	1.703200
H	-2.186000	2.092900	1.334500
H	0.352500	-1.182600	-2.885400
H	-1.147900	-0.308400	-2.354100
H	-0.840300	-2.118200	1.069300
H	-3.077400	-1.802700	-1.613700
H	-5.439500	-1.111300	-1.401500
H	-6.222800	0.042700	0.648800
H	-4.622100	0.463400	2.498900
H	-2.248700	-0.212300	2.263000
H	-0.463600	-3.887500	-1.542200
H	0.564700	-3.594400	-0.144000
H	1.126900	-3.164900	-1.782800
H	2.779400	-2.542700	2.575200
H	2.382100	-3.328900	1.047400
H	1.092600	-2.733500	2.099900
H	3.075000	-1.617900	-2.220600
H	3.160400	-2.854600	-0.961300
H	4.477100	-1.694300	-1.152100
H	4.517000	1.283400	-1.393900
H	3.095300	2.323000	-1.550700
H	3.181300	0.816100	-2.456300
H	1.418400	2.915300	1.730900
H	2.577700	3.201000	0.425500
H	3.131900	2.632000	1.994500
H	2.156000	0.165600	3.825200
H	0.644200	-0.624100	3.353300
H	0.795400	1.129100	3.234300



syn-3

Ru	-0.770700	0.020600	0.527400
O	-1.263800	-1.909600	2.791200
C	-1.052000	-1.157600	1.942600
C	-0.734800	1.597000	2.084600
C	0.494400	1.577700	1.369100
C	1.253500	0.375100	1.448000
C	0.842200	2.749700	0.498300
C	2.483900	0.046400	0.696500
C	2.731100	-1.298500	0.396600
C	3.446800	0.982000	0.312400
C	3.869400	-1.688800	-0.286800
C	4.586100	0.593900	-0.382000
C	4.800600	-0.739400	-0.692800
C	-0.469600	0.217400	-1.742900
C	-1.583100	1.025500	-1.366500
C	-2.578500	0.178500	-0.783800
C	-2.071400	-1.159600	-0.813500
C	-0.765300	-1.139000	-1.404700
C	0.762000	0.645700	-2.465700
C	-1.789200	2.473400	-1.649700
C	-3.938800	0.611700	-0.361900
C	-2.823600	-2.383800	-0.415100
C	0.075500	-2.316500	-1.754700
H	-0.802200	1.143200	3.069700
H	-1.381300	2.463200	1.948900
H	-0.053000	3.328700	0.256500
H	1.345600	2.473400	-0.431100
H	1.515300	3.420500	1.048500
H	1.990100	-2.037000	0.696300
H	3.320800	2.026700	0.576200
H	4.030300	-2.739900	-0.509500
H	5.317200	1.343400	-0.671000
H	5.690900	-1.040800	-1.236000
H	1.191800	-0.163100	2.393700
H	1.670700	0.252400	-1.993400
H	0.855200	1.734200	-2.511800
H	0.745500	0.275700	-3.498500
H	-0.856500	2.988200	-1.892900
H	-2.246400	2.989500	-0.798000
H	-2.467200	2.601800	-2.503200
H	-4.628100	0.653100	-1.216400
H	-3.912700	1.608300	0.089800
H	-4.366900	-0.070100	0.577800
H	-3.524700	-2.181000	0.399800
H	-2.152400	-3.179800	-0.079000
H	-3.401000	-2.772800	-1.262700
H	-0.131000	-2.658800	-2.777900
H	-0.109100	-3.159500	-1.081600
H	1.142200	-2.075800	-1.697500



anti-3

Ru	0.469000	0.027200	-0.266200
O	-1.480700	-1.831200	-1.626800
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C	-0.340600	1.574000	-1.637400
C	-0.499500	1.961200	-0.280300
C	-1.238000	1.138000	0.626800
C	-2.581800	0.563500	0.409500
C	-3.443400	1.014200	-0.590300
C	-4.693600	0.436100	-0.765200
C	-5.118000	-0.587500	0.067100
C	-4.281400	-1.024600	1.087900
C	-3.032500	-0.455300	1.255000
C	0.250600	3.151000	0.242300
C	2.106300	0.244100	1.312600
C	2.682200	0.533300	0.040300
C	2.555500	-0.628300	-0.783900
C	1.904700	-1.638700	-0.004000
C	1.616800	-1.100600	1.291800
C	2.104500	1.116800	2.520200
C	3.408100	1.770300	-0.363400
C	3.124800	-0.780200	-2.152100
C	1.673200	-3.049100	-0.428600
C	1.040200	-1.831200	2.454400
H	-1.155500	1.149400	-2.213300
H	0.368100	2.148000	-2.233800
H	-1.053500	1.371000	1.680600
H	-3.133400	1.833300	-1.233500
H	-5.345300	0.798600	-1.555100
H	-6.095800	-1.038200	-0.071500
H	-4.605300	-1.820700	1.752300
H	-2.366500	-0.815900	2.037400
H	1.166200	3.344100	-0.325500
H	0.497500	3.052500	1.303800
H	-0.385300	4.040000	0.143200
H	1.128800	1.119400	3.018800
H	2.360400	2.151800	2.280100
H	2.838600	0.758900	3.253100
H	3.249000	2.591500	0.340400
H	3.098400	2.116900	-1.355900
H	4.488100	1.582200	-0.411800
H	4.189900	-1.047200	-2.114900
H	3.037300	0.149700	-2.723300
H	2.608000	-1.559200	-2.719300
H	1.516500	-3.129100	-1.508200
H	0.797000	-3.483600	0.061200
H	2.539000	-3.672100	-0.172700
H	1.827100	-2.260600	3.089600
H	0.391600	-2.650700	2.131500
H	0.437800	-1.166700	3.082100