Contrasting photochemical and thermal reactivity of $Ru(CO)_2(PPh_3)(dppe)$ towards hydrogen rationalised by parahydrogen NMR and DFT studies.

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Calculating the hydride signal enhancement for 3a

The procedure for calculating the enhancement provided by a given species formed by p-H_2 addition has been discussed in more detail previously (D. Blazina, S. B. Duckett, T. K. Halstead, C. M. Kozak, R. J. K. Taylor, M. S. Anwar, J. A. Jones, H. A. Carteret, *Magn. Reson. Chem.*, in the press). The raw data and a brief summary of the calculation method are provided here.

Enhancement factor for the major isomer of $Ru(CO)(PPh_3)(dppe)(H)_2$ *3**a***

The enhancement here was estimated in two steps. First of all, the sample was exposed to 300 ms of continuous wave laser irradiation and a p-H_2 spectrum was acquired using a 45° pulse, which suffers from reduced efficiency but is suitable for integration. The experiment was then repeated using a spin lock assisted coherent selective pulse; the efficiency of the detection is maximised in this experiment but it can't be integrated directly. Repeating the photolysis another 198 times enabled the thermal resonances due to **3a** to be detected. Integration of the hydride resonance (thermal or enhanced) against the internal standard provided by the CH_2 protons of the dppe ligand enabled the enhancement factor to be calculated.

However, since **1** is consumed in the reaction with hydrogen to a much greater extent than is the case when the pulsed laser is utilised, the amount of **3a** generated by each laser flash decreases as more laser flashes are applied. After 200 laser flashes, a quantitative ^{31}P NMR experiment revealed that the extent of conversion of **1** into **3a** was 12.65 %. The amount of **2** converted by each laser flash is therefore given by:

$$x = 1 - \sqrt[200]{(1 - 0.1265)} = 0.0676\%$$

If no depletion of **2** occurred during the experiment, 200 laser flashes would convert 13.5 % of the sample. It follows that the intensity of the control resonances for **3a** needs to be multiplied by a factor of 1.069 to allow for the depletion of **1**.

Integration of the CH_2 resonance of the starting material and the enhanced hydride resonance obtained by applying a 45° pulse after 300 ms of laser irradiation yielded a ratio of 1 : 1.715. The 45° read pulse is optimal for parahydrogen, but the normal signal of the CH_2 group is not at its maximum intensity; therefore, the hydride intensity should be multiplied by sin 45°, giving a corrected ratio of 1 : 1.213.

The control spectrum, acquired after a total of 60 s of laser irradiation, gave the corresponding signal integral ratio of 1 : 0.0105; to correct for the extent of conversion of **2**, this integral needs to be multiplied by 1.069, yielding a ratio of 1 : 0.0112. Since this spectrum is acquired with a 90° excitation pulse, and since neither of the resonances is parahydrogen enhanced, no correction for flip angles is necessary. However, the sample depth is 34 mm, whereas the active signal corresponds to only 12.5 mm of the sample. Therefore, the corrected integral can be calculated:

$$0.0112 \times \frac{34}{12.5} = 0.0305$$

The enhancement can now be calculated from the ratio of the hydride integrals, but it is necessary to take into account the fact that the normal hydride resonance corresponds to 200 times more laser irradiation, and hence 200 times more product, than the resonance from the enhanced spectrum:

$$\frac{1.213}{0.0305 \div 200} = 7952$$

The intensity of the enhanced hydride resonances obtained by the coherent selective pulse was a factor of 2.62 larger than that obtained using a 45° pulse. The coherent selective pulse is more efficient at capturing the available magnetisation and the final enhancement can be obtained by multiplying the above figure by 2.62. This yields an enhancement factor of 20834, corresponding to 67.1 % of the calculated maximum.

Optimised Cartesian Coordinates (QM)

1a'

Ru	-0.480950	0.085419	-0.134646
P	1.676408	0.946286	-0.193437
H	2.073034	1.932028	0.769467
H	2.829548	0.099555	-0.046157
H	2.131206	1.644430	-1.360059
C	-0.759784	0.953258	1.535226
O	-0.969917	1.531492	2.531237
C	-0.814476	0.808141	-1.862282
O	-1.052171	1.313820	-2.891434
P	-2.620582	-0.772264	-0.067071
P	0.136238	-2.169555	0.016271
C	-1.368672	-3.216517	0.466775
C	-2.612386	-2.649357	-0.215043
H	-2.593516	-2.871379	-1.302961
H	-3.546861	-3.079252	0.200305
H	-1.469824	-3.159116	1.570673
H	-1.211094	-4.279806	0.196050
H	1.083801	-2.703406	0.962094
H	0.641236	-2.942312	-1.095327
H	-3.435521	-0.564718	1.095460
H	-3.603873	-0.425201	-1.050331

1b'

Ru	0.461133	0.066998	-0.052148
P	-1.477053	1.275800	0.422111
P	-1.066336	-1.576388	-0.626411
C	-2.978068	0.415720	-0.273454
C	-2.805042	-1.088012	-0.139755
H	-1.678762	2.606062	-0.048745
H	-1.876296	1.508170	1.779485
H	-1.267677	-1.938646	-1.999003
H	-1.065408	-2.927145	-0.145426
H	-3.030771	0.705383	-1.338865
H	-3.901282	0.770645	0.217957
H	-3.551829	-1.633628	-0.742287
H	-2.934546	-1.398986	0.913157
C	1.074327	1.515319	-1.097181
O	1.438241	2.407462	-1.738265
P	1.096443	-0.056705	2.173821
H	0.215445	0.407442	3.204042
H	1.437433	-1.283007	2.832748

H	2.243644	0.655456	2.650170
C	1.901060	-1.003763	-0.625382
O	2.769190	-1.675736	-0.979571

I2a'

Ru	0.132835	-0.443597	0.405015
P	0.416159	1.849648	0.204850
P	0.175883	-0.343390	-1.934492
C	0.616322	2.367100	-1.582035
C	-0.128524	1.408652	-2.498453
H	1.428667	2.674213	0.800073
H	-0.691603	2.646438	0.624057
H	1.391550	-0.656686	-2.624581
H	-0.707845	-1.074391	-2.779605
H	1.701374	2.332285	-1.792893
H	0.285946	3.409274	-1.733280
H	0.167172	1.543263	-3.553639
H	-1.218950	1.574391	-2.430828
C	-0.981449	-1.942731	0.379641
O	-1.775406	-2.781746	0.341265
C	0.032299	-0.347286	2.278107
O	-0.015437	-0.273180	3.427679

I2b'

Ru	-0.036108	-0.383954	0.645476
P	0.166510	1.968876	0.582535
P	-0.074326	-0.350196	-1.547748
C	0.555418	2.345049	-1.211934
C	-0.207585	1.411104	-2.143029
H	1.161979	2.796281	1.197509
H	-0.905543	2.898088	0.798535
H	1.043942	-0.852716	-2.277738
H	-1.116258	-0.985856	-2.284407
H	1.644425	2.198705	-1.329732
H	0.333185	3.399547	-1.449019
H	0.149221	1.490439	-3.186227
H	-1.285404	1.658372	-2.140511
C	-1.798087	-1.083649	0.657372
O	-2.835994	-1.599363	0.635489
C	1.628315	-1.295732	0.597310
O	2.596356	-1.929193	0.533448

I3a'

Ru	0.099538	-0.407533	0.325725
P	0.344714	1.868742	0.137323
P	0.247431	-0.332012	-1.937663
C	0.649535	2.390326	-1.638448
C	-0.010505	1.403355	-2.587910
H	1.257090	2.780306	0.780809
H	-0.830178	2.620514	0.457050
H	1.504403	-0.665974	-2.545206
H	-0.581663	-1.077189	-2.828524
H	1.746866	2.380914	-1.776939
H	0.303575	3.423132	-1.816669
H	0.371623	1.507208	-3.618757
H	-1.103707	1.564192	-2.614948
C	-1.130559	-1.784453	0.235108

O	-2.014998	-2.534205	0.154057
P	0.159928	-0.513017	2.621074
H	1.366382	-1.043510	3.184323
H	0.080965	0.630928	3.478035
H	-0.743691	-1.324158	3.371586

I3b'

Ru	0.118986	-0.408457	0.371212
P	0.409625	1.816587	0.252164
P	0.383929	-0.282931	-1.938539
C	0.648038	2.442767	-1.503060
C	0.058472	1.465494	-2.508621
H	1.394366	2.631433	0.908471
H	-0.711656	2.599558	0.678385
H	1.701902	-0.531825	-2.438574
H	-0.325015	-1.008959	-2.949654
H	1.739013	2.532501	-1.654972
H	0.214457	3.450611	-1.624711
H	0.447977	1.637241	-3.527194
H	-1.041898	1.562622	-2.549687
C	0.282175	-0.410819	2.227933
O	0.499481	-0.439847	3.365859
P	-1.590104	-1.892492	0.335684
H	-1.508521	-3.330494	0.360463
H	-2.616997	-1.810864	1.326917
H	-2.460845	-1.841255	-0.799060

I3c'

Ru	-0.069309	-0.503032	0.494787
P	0.186526	1.711948	0.592649
P	0.210230	-0.623482	-1.724126
C	0.818100	2.100236	-1.138252
C	0.182435	1.202761	-2.201945
H	1.098413	2.534850	1.333809
H	-0.920098	2.624364	0.665711
H	1.432562	-1.028567	-2.349666
H	-0.645553	-1.102982	-2.776526
H	1.911020	1.931775	-1.104862
H	0.659928	3.166327	-1.384286
H	0.672895	1.352970	-3.181052
H	-0.884096	1.468463	-2.330915
C	1.728659	-0.822970	0.846312
O	2.818866	-1.093238	1.134682
P	-2.391508	-0.606592	0.652944
H	-3.251867	0.450264	1.102981
H	-3.296941	-1.088054	-0.351323
H	-2.715425	-1.562516	1.664341

2a'

Ru	-0.443139	0.019015	-0.488877
C	-0.303215	-0.176892	-2.360433
C	-1.001226	-1.777448	-0.106270
O	-0.250790	-0.232541	-3.505496
O	-1.397548	-2.833797	0.114502
H	-1.980190	0.432394	-0.766249
H	-0.229604	1.623739	-0.822716
P	1.825640	-0.003718	0.123481

P	-0.752331	0.948816	1.613377
C	1.979545	0.527493	1.911498
C	0.892244	1.533029	2.270544
H	2.731830	0.892517	-0.516610
H	2.693480	-1.138766	0.130830
H	-1.561261	2.105821	1.768688
H	-1.261396	0.206101	2.722795
H	1.864769	-0.390792	2.516992
H	2.983862	0.934537	2.120554
H	1.090472	2.504710	1.782405
H	0.849304	1.706857	3.359873

2b'

Ru	-0.546164	-0.000130	-0.546878
P	-0.420075	-0.006272	1.794671
P	1.795025	0.006488	-0.418249
C	-0.836234	-1.856540	-0.853617
C	-0.852880	1.856121	-0.837444
O	-1.119805	2.941222	-1.098612
O	-1.097386	-2.941535	-1.121143
H	-0.557792	-0.000448	-2.170181
H	-2.169421	-0.000335	-0.561499
C	2.320997	-0.325183	1.348413
C	1.346049	0.325535	2.322359
H	2.643034	-0.903888	-1.116344
H	2.542160	1.187850	-0.710177
H	-1.119012	0.904130	2.641972
H	-0.712811	-1.187762	2.541523
H	2.311559	-1.423911	1.475172
H	3.354816	0.017230	1.528935
H	1.472707	1.424271	2.313026
H	1.525475	-0.016865	3.356361

2c'

Ru	-0.304988	-0.176900	-0.407558
P	1.955907	-0.118754	0.182609
P	-0.600192	0.707931	1.738446
C	2.167582	0.997071	1.656020
C	1.031386	0.758395	2.641007
H	2.656351	-1.289291	0.602346
H	2.944654	0.383536	-0.709526
H	-1.437488	0.092424	2.712792
H	-1.074512	2.041997	1.901735
H	1.150176	-0.224027	3.133510
H	1.015833	1.526625	3.433321
H	3.152164	0.847505	2.132255
H	2.132596	2.030572	1.266190
C	0.075178	-0.876859	-2.111972
O	0.311431	-1.297270	-3.155102
H	-0.050255	1.395804	-0.922295
H	-0.438152	-1.693874	0.273681
C	-2.149133	-0.103512	-0.773068
O	-3.275783	-0.053259	-0.994639

3a'

Ru	-0.410350	0.079338	-0.407632
P	-0.284419	-0.052417	-2.691057

C	-1.078524	-1.679637	-0.127646
O	-1.534794	-2.726853	0.040287
H	-0.727785	1.066016	-3.451016
H	-1.024250	-1.046960	-3.399186
H	0.947668	-0.246538	-3.392636
H	-1.908446	0.611331	-0.732572
H	-0.055484	1.678092	-0.689672
P	-0.706649	0.921813	1.680716
P	1.819237	-0.144113	0.230457
C	0.948869	1.361024	2.425764
C	1.980000	0.306459	2.044093
H	-1.298744	0.162284	2.738396
H	-1.437165	2.124529	1.888731
H	2.605076	-1.340772	0.221943
H	2.824427	0.693722	-0.345660
H	1.796295	-0.626595	2.608661
H	3.004186	0.640086	2.284772
H	0.878016	1.478600	3.521412
H	1.226213	2.342163	1.998609

3b'

Ru	-0.515784	0.036659	-0.375722
P	-1.330263	1.572362	1.170944
C	-2.082292	-0.985846	-0.486332
O	-3.030916	-1.624621	-0.627792
H	-1.166298	0.983539	-1.524168
H	-0.071227	-0.818209	-1.682899
H	-1.382406	1.354538	2.588012
H	-2.680047	2.019205	1.049546
H	-0.748984	2.877225	1.259499
P	0.797646	-1.375770	0.923745
P	1.497239	1.053240	-0.887024
C	2.572165	-0.768556	0.916325
C	2.898850	-0.082173	-0.403781
H	0.976946	-2.739750	0.536838
H	0.659304	-1.640615	2.325963
H	1.831773	1.359043	-2.234840
H	1.931705	2.294004	-0.314097
H	3.276669	-1.592505	1.123978
H	2.656485	-0.047785	1.751019
H	2.980549	-0.829452	-1.214084
H	3.858586	0.460996	-0.350415

3c'

Ru	-0.397093	-0.123386	-0.608954
P	1.868418	-0.131989	-0.066244
P	-0.670776	0.640443	1.573450
C	2.115653	0.851744	1.510631
C	0.972948	0.574029	2.479119
H	2.607318	-1.318806	0.249753
H	2.876897	0.458038	-0.887526
H	-1.505763	0.008452	2.550235
H	-1.085102	1.977156	1.864141
H	3.096204	0.641586	1.972472
H	2.111634	1.916906	1.212113
H	1.065131	-0.448568	2.891618
H	0.989029	1.272874	3.333499
C	-0.419739	1.510741	-1.508847

O	-0.501128	2.484212	-2.120574
H	-0.149314	-0.712952	-2.104684
H	-1.987017	-0.094243	-0.962156
P	-1.091973	-2.296405	-0.231536
H	-0.255498	-3.431778	0.030715
H	-1.863847	-2.901771	-1.259394
H	-2.008391	-2.540357	0.837931

3d'

Ru	-0.461247	0.058872	0.043832
P	1.203994	-1.572160	-0.101971
P	1.304854	1.498478	-0.011737
C	2.874763	-0.777423	0.140739
C	2.871904	0.607909	-0.487890
H	1.298437	-2.671918	0.802216
H	1.420246	-2.324879	-1.298417
H	1.730451	2.204152	1.156981
H	1.338267	2.609762	-0.905111
H	3.026648	-0.703564	1.233078
H	3.680410	-1.411095	-0.268834
H	3.763545	1.188855	-0.193717
H	2.867456	0.532062	-1.590539
P	-2.186023	-1.450323	-0.093545
H	-3.394969	-1.043875	-0.729870
H	-2.792172	-2.037638	1.060014
H	-2.015845	-2.667415	-0.820938
H	-0.516764	0.111719	-1.631770
H	-0.329908	-0.150731	1.696572
C	-1.660027	1.471102	0.258942
O	-2.392832	2.352709	0.399814

TSa

Ru	0.475785	0.052174	0.393224
P	-1.145610	-1.568762	-0.049653
P	-1.316195	1.460443	0.138104
C	-2.863213	-0.812295	-0.233643
C	-2.744060	0.618875	-0.744069
H	-1.510708	-2.688213	0.790659
H	-1.035196	-2.366612	-1.247573
H	-2.024854	2.048318	1.254973
H	-1.207686	2.677129	-0.614083
H	-2.488988	0.630529	-1.823512
H	-3.687911	1.185699	-0.604126
H	-3.496805	-1.438777	-0.893306
H	-3.319694	-0.827350	0.778327
C	1.557849	1.445889	-0.238846
P	2.123366	-1.374511	-0.392102
O	2.230455	2.303896	-0.668330
H	0.755689	-0.518492	2.083355
H	0.624977	0.343060	2.131127
H	1.780771	-2.414469	-1.328384
H	3.232208	-0.847689	-1.133973
H	2.916318	-2.226061	0.460770

TSb

Ru	0.488859	0.052480	0.397645
P	-1.310813	1.470631	0.151927

P	-1.124955	-1.571959	-0.044254
C	-2.840841	-0.812494	-0.246982
C	-2.721216	0.621015	-0.752418
H	-2.449216	0.635835	-1.827707
H	-3.671180	1.180857	-0.626817
H	-3.309379	-0.831025	0.759380
H	-3.466298	-1.437509	-0.915595
H	-1.506079	-2.681225	0.803269
H	-1.004157	-2.381694	-1.232601
H	-2.036001	2.034842	1.268110
H	-1.204612	2.694274	-0.587805
C	1.526405	1.470001	-0.253997
P	2.097170	-1.389631	-0.394018
O	2.148402	2.358331	-0.697760
H	0.271630	-0.085515	2.208299
H	1.146880	-0.048839	2.072030
H	3.208325	-0.882973	-1.147584
H	2.889072	-2.253159	0.451399
H	1.726894	-2.426378	-1.323098