Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Hydrogenation of CO_2 to Formic Acid with Iridium^{III}(bisMETAMORPhos)(Hydride): the Role of a Dormant *fac*-Ir^{III}(trihydride) and an Active *trans*-Ir^{III}(dihydride) Species

S. Oldenhof,[a] J. I. van der Vlugt,[a*] J. N.H. Reek[a*]

[a] Dr. S. Oldenhof, Dr. Ir. J. I. van der Vlugt, Prof. Dr. J. N. H. Reek
Homogeneous, Bioinspired & Supramolecular Catalysis, van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH, Amsterdam, The Netherlands.
j.i.vandervlugt@uva.nl ; j.n.h.reek@uva.nl

Table of contents

General procedures

All reactions were carried out in dry glassware under nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. Pentane was distilled from sodium under dinitrogen, CH_2Cl_2 and diethylether were collected from an MB SPS-800. DMF, triethylamine and DBU were all degassed by purging with N_2. H_2 (5.0) and CO_2 (4.6) from Praxair were used as received. NMR spectra were measured on a Varian Mercury 300 (^{1}H: 300.1 MHz) spectrometer. BisMETAMORPhos and complex **1** were prepared as previously described.[S1]

General procedure for catalytic CO_2 hydrogenation

Complex **1** (1.04 mg, 0.001 mmol) was added to a solution of DMSO-d_6, DMF (77 µL, 1.0 mmol) and appropriate base (1.0 mmol) in a high-pressure sapphire NMR tube under a flow of N_2 (total volume of 2 mL). The high pressure NMR tube was pressurized and flushed at least three times with 10 bar CO_2, where after the tube was pressurized with CO_2 and H_2 to the preferred partial pressures. The high pressure NMR tube was carefully shaken and heated inside the NMR probe.

Note: It has to be taken into account that the applied experimental set-up suffers from a significant pressure drop in the NMR tube during turnover. The total gaseous volume of the sapphire NMR tube used is 4.5 mL (taking 2 mL solvent into account). Once 0.5 mmol of $HDBU^+ \cdot HCOO^-$ is produced, 1 mmol of gas is consumed (0.5 mmol CO_2 and 0.5 mmol H_2). This corresponds to a pressure drop of approximately 11 bars.

Complex 3

Complex **1** (20 mg) was added to a high-pressure sapphire NMR tube under a flow of N_2. Degassed DMSO-d_6 was added (2 mL) and a yellow suspension formed that was slightly heated and shaken to generate a saturated solution. The NMR tube was pressurized and flushed three times with 10 bar CO_2, where after the tube was pressurized with CO_2 and H_2 to 50 bar (1:1). The tube was heated inside the NMR probe.

^{1}H NMR Spectroscopy during Catalysis

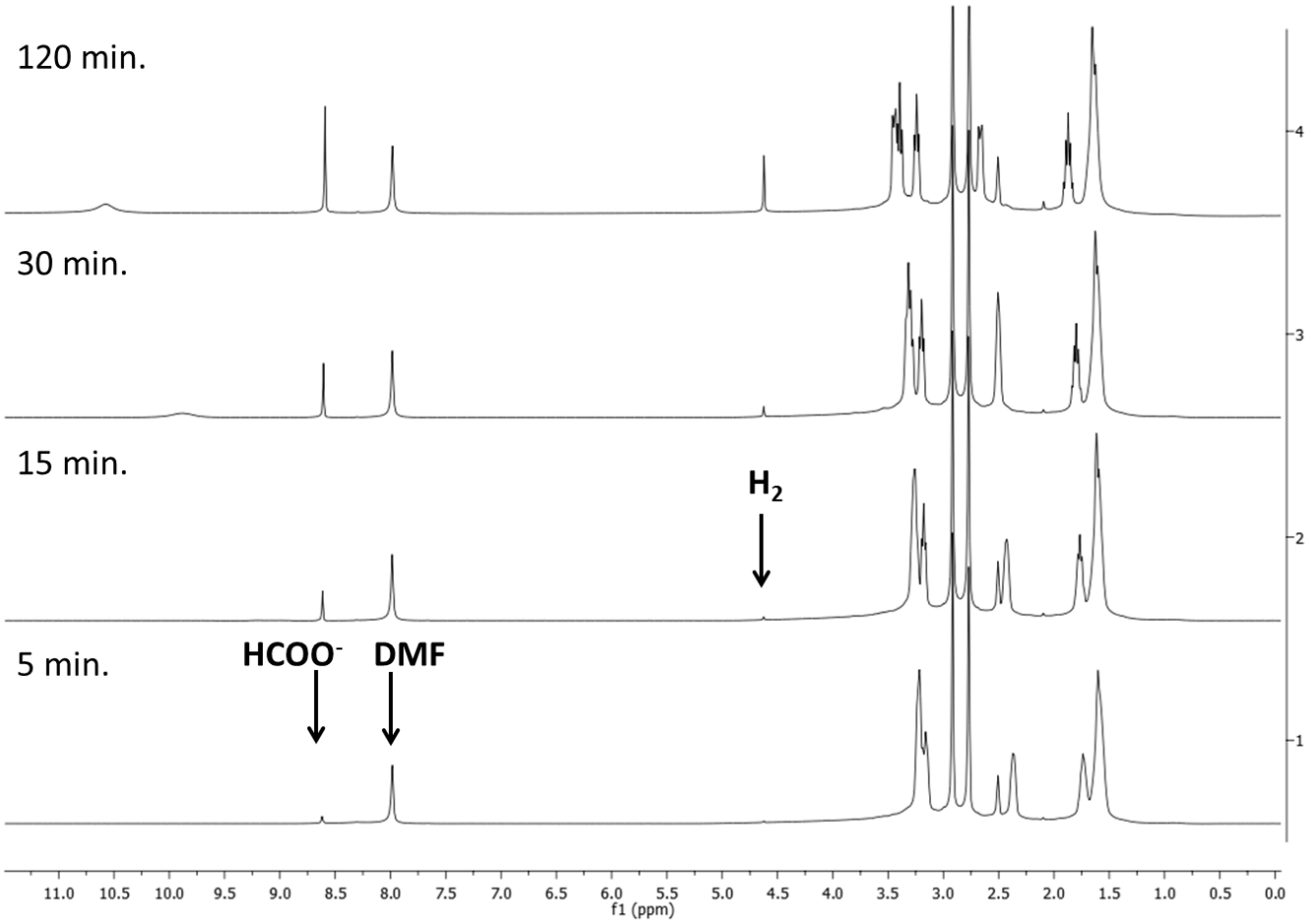

Figure S1. In situ ^{1}H NMR studies in DMSO-d_6 on the hydrogenation of CO_2 with complex **1**, showing the formation of $HDBU^+ \cdot HCOO^-$.

Computational details

Geometry optimizations were carried out with the Turbomole program package,[S2] coupled to the PQS Baker optimizer[S3] via the BOpt package,[S4] at the spin unrestricted ri-DFT level using the BP86 functional, the resolution-of-identity (ri) method, and the def2-TZVP basis set for the geometry optimizations.

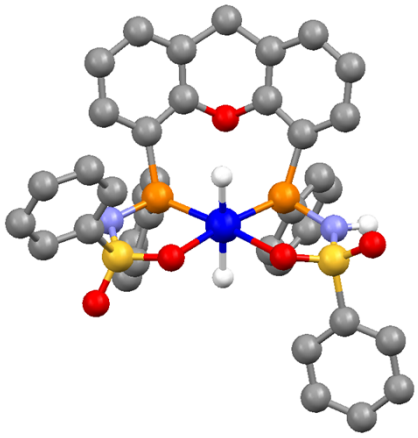

Figure S2. DFT optimized structure of complex **2** [BP86, SV(P)], ΔG°_{298K}: 0.0 kcal mol^{-1}.

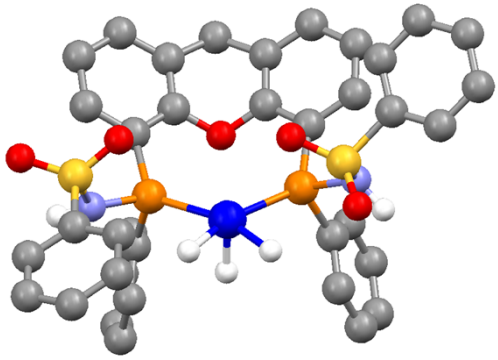

Figure S3. DFT optimized structure of complex **3** [BP86, SV(P)] ΔG°_{298K}: 4.0 kcal mol^{-1}.

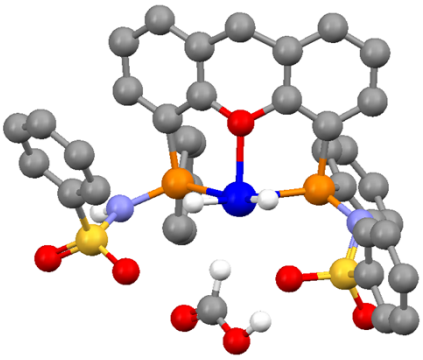

Figure S4. Transition state, axial CO_2 insertion [BP86, SV(P)], ΔG°_{298K}: 61.6 kcal mol^{-1} imaginary frequency -526.950012.

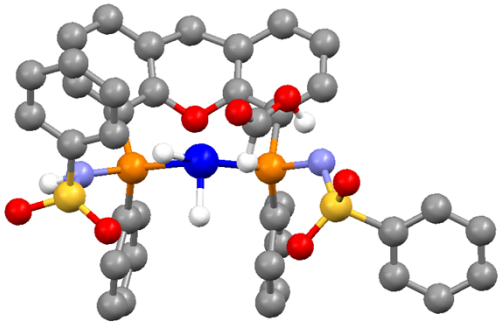

Figure S4. Transition state, equatorial CO_2 insertion [BP86, SV(P)], ΔG°_{298K}: 40.2 kcal mol^{-1}, imaginary frequency -277.260010.

Energies and imaginairy frequencies of calculated structures

Structure	SCF	imaginairy frequency
2	-3498,95775	
2-TS	-3687,63084	-163,179993
3	-3500,15013	
3TS-ax	-3685,72123	-526,950012
3TS-eq	-3685,77405	-129,240005

Cartesian Coordinates for Optimized Structures

Complex **2**

atom	X	Y	Z
O	-1.4745208	-2.7797705	-0.9185767
O	0.0143876	-1.0815781	1.2141124
P	0.2157951	-1.6049617	-3.0906001
P	1.9114623	0.1998136	-0.6117331
C	1.4544627	-2.7531268	-3.8221791
C	3.6177022	-4.4392721	-4.4623495
C	2.7832250	-2.3619600	-3.6474688
C	1.2213408	-4.0222488	-4.3677228
C	2.3006556	-4.8506187	-4.6957155
C	3.8820438	-3.1754831	-3.9235805
H	0.2024063	-4.3907048	-4.4896148
H	2.1098293	-5.8412090	-5.1094568
H	4.4466939	-5.1129645	-4.6888618
C	3.6254004	-0.4117892	-0.9151578
C	6.0798558	-1.7560942	-1.2604838
C	4.6091513	-0.3627991	0.0832728
C	3.9414042	-1.0957398	-2.0887519
C	5.1264738	-1.8091070	-2.2820462
C	5.8313719	-1.0163675	-0.0993169
H	4.3844643	0.1559008	1.0153690
H	6.5850309	-0.9767175	0.6878846
H	7.0184714	-2.3034651	-1.3710136
C	0.0478492	-0.2805248	-4.3472838
C	-0.3647266	1.7228053	-6.2618764
C	0.5008296	-0.4569923	-5.6645799
C	-0.6047281	0.9101794	-3.9931525
C	-0.8105605	1.9048037	-4.9494133
C	0.2926102	0.5426780	-6.6179083
H	1.0221313	-1.3730600	-5.9464128
H	-0.9337861	1.0447252	-2.9606931
H	-1.3114843	2.8306752	-4.6642863
H	0.6490080	0.3991189	-7.6390814
H	-0.5229223	2.5047670	-7.0062889
O	2.9776939	-1.1082642	-3.0948319
C	5.2457005	-2.6237524	-3.5571930
H	5.9788084	-3.4335623	-3.4375045
H	5.6142288	-1.9801468	-4.3778395
N	-1.2800522	-2.4724469	-3.3705962
N	1.9122549	0.6106942	0.9913319
C	1.8327894	1.8105971	-1.4885611
C	1.6305527	4.3287195	-2.7100687
C	0.9110087	2.7578606	-1.0127997

C	2.6516482	2.1369905	-2.5777019
C	2.5485683	3.3912626	-3.1864183
C	0.8129231	4.0091610	-1.6204393
H	0.2889444	2.5160198	-0.1496930
H	3.3807984	1.4198358	-2.9533690
H	0.1034326	4.7426440	-1.2337688
H	1.5576804	5.3110026	-3.1799122
S	-2.1838532	-3.1465998	-2.1563132
S	0.8144150	-0.0050709	1.9377747
O	-2.4375352	-4.5421119	-2.4489943
H	-6.9637196	-2.7410864	-3.1701523
C	-6.0882610	-2.2608493	-2.7317512
C	-3.8413798	-1.0292799	-1.5775238
C	-4.8600646	-2.9249932	-2.7398140
C	-6.1961032	-0.9936502	-2.1523781
C	-5.0777028	-0.3832322	-1.5748639
C	-3.7502251	-2.2956768	-2.1668696
H	-4.7602498	-3.9240446	-3.1625879
H	-7.1594657	-0.4818833	-2.1427789
H	-5.1670059	0.5998451	-1.1115118
H	-2.9570860	-0.5693478	-1.1295198
O	0.0023644	0.9896115	2.6218780
C	1.6980757	-0.9123445	3.2074042
C	3.1010368	-2.2997124	5.1670278
C	2.1977413	-2.1872468	2.9210299
C	1.8848715	-0.3270089	4.4617954
C	2.5941499	-1.0267602	5.4413826
C	2.8990595	-2.8788726	3.9095619
H	2.0223365	-2.6304006	1.9399593
H	1.4644065	0.6583580	4.6604194
H	2.7430161	-0.5774731	6.4243999
H	3.2838910	-3.8776529	3.6983280
H	3.6484297	-2.8459910	5.9367596
Ir	0.2406507	-1.2541306	-0.9209699
H	-0.9055350	-0.0197013	-1.0799451
H	3.1946580	3.6362276	-4.0308775
H	1.3057401	-2.5120304	-0.6292708
H	-1.5949642	-2.7024180	-4.3132655

Complex **2TS**

atom	X	Y	Z
O	-1.6213871	-2.5881156	-0.5393510
O	0.1668542	-1.2452210	1.3670222
P	0.1588848	-1.8788592	-2.9301173
P	2.0131618	0.0491222	-0.5040634
C	1.4747402	-2.7902607	-3.8504588
C	3.7013821	-4.1808927	-4.8787680

C	2.7785209	-2.3095482	-3.7205049
C	1.2973691	-3.9719044	-4.5900783
C	2.4034514	-4.6496271	-5.1077054
C	3.9102191	-2.9920575	-4.1762732
H	0.3009366	-4.3854034	-4.7434540
H	2.2512939	-5.5726860	-5.6673192
H	4.5589904	-4.7472602	-5.2473188
C	3.7116579	-0.5227368	-0.9010382
C	6.1977422	-1.6930990	-1.5133001
C	4.7536166	-0.4980758	0.0370545
C	3.9736045	-1.1082262	-2.1368507
C	5.1808940	-1.7224786	-2.4724950
C	5.9894022	-1.0701101	-0.2773942
H	4.5693954	-0.0577408	1.0169345
H	6.7919138	-1.0543667	0.4606105
H	7.1567473	-2.1679129	-1.7309304
C	-0.4716065	-0.6825537	-4.1676850
C	-1.4181631	1.1638262	-6.0503738
C	-0.6056607	-1.0524062	-5.5174484
C	-0.8090912	0.6179725	-3.7720471
C	-1.2788106	1.5379812	-4.7131450
C	-1.0830229	-0.1342969	-6.4512865
H	-0.3321330	-2.0572178	-5.8409442
H	-0.6996301	0.9014496	-2.7244827
H	-1.5314168	2.5502196	-4.3957547
H	-1.1869085	-0.4295664	-7.4964062
H	-1.7836061	1.8833712	-6.7847684
O	2.9293600	-1.1090959	-3.0569978
C	5.2600357	-2.3963573	-3.8285863
H	6.0412529	-3.1691036	-3.8389363
H	5.5416988	-1.6511809	-4.5960877
N	-1.0462557	-3.1957277	-2.9793986
N	2.0940417	0.3993529	1.1098503
C	1.8638363	1.6843725	-1.3342249
C	1.5457382	4.2333322	-2.4683076
C	1.0223436	2.6321043	-0.7272886
C	2.5476549	2.0282400	-2.5083563
C	2.3870758	3.2972789	-3.0722391
C	0.8650536	3.8974049	-1.2934360
H	0.5103525	2.3828470	0.2038700
H	3.2126181	1.3136035	-2.9908074
H	0.2179153	4.6283715	-0.8060265
H	1.4278994	5.2262408	-2.9053375
S	-2.2234442	-3.1413420	-1.7796435
S	0.9375112	-0.1099708	2.0479073
O	-2.8301385	-4.4514508	-1.7038047
H	-5.6215667	-1.5266010	-4.9127454
C	-5.0837994	-1.3370462	-3.9833817

C	-3.7066868	-0.8420576	-1.5868068
C	-4.0909707	-2.2220997	-3.5679232
C	-5.3937776	-0.2145542	-3.2068688
C	-4.7101778	0.0307223	-2.0141064
C	-3.4102137	-1.9580294	-2.3735052
H	-3.8478037	-3.1075654	-4.1545497
H	-6.1756023	0.4715412	-3.5353722
H	-4.9542344	0.9046664	-1.4096557
H	-3.1568348	-0.6667865	-0.6630966
O	0.0888733	0.9437391	2.5873966
C	1.7387018	-0.9116570	3.4317288
C	3.0039510	-2.1203082	5.5881478
C	2.3013979	-2.1819461	3.2683652
C	1.7927852	-0.2419825	4.6564420
C	2.4346697	-0.8529449	5.7364116
C	2.9328597	-2.7829726	4.3581165
H	2.2323414	-2.7032786	2.3127661
H	1.3263669	0.7377899	4.7530180
H	2.4819703	-0.3384674	6.6972078
H	3.3643692	-3.7780371	4.2433455
H	3.4983467	-2.5975856	6.4356989
Ir	0.2830735	-1.3773384	-0.7592845
H	-0.6201516	-0.0220965	-0.8663709
H	2.9287277	3.5542900	-3.9838820
H	1.1790105	-2.8854033	-0.5735150
C	1.4170669	-4.3865008	-0.4289515
H	-0.5379836	-4.0767326	-2.7621531
O	0.8019369	-4.9253316	-1.3196647
O	2.1517428	-4.4793263	0.5148113

Complex **3**

atom	X	Y	Z
O	-1.6615000	0.6040210	-1.9523809
O	0.1749968	-4.0175283	1.8953573
P	1.6717672	-1.3120271	-2.7003851
P	2.8783249	-3.0739845	0.5260099
C	1.7539326	-2.7663599	-3.8516932
C	1.7290078	-5.1356370	-5.3928747
C	2.4959961	-3.8969631	-3.4870451
C	1.0141260	-2.8462537	-5.0442887
C	1.0058472	-4.0131820	-5.8097473
C	2.4882516	-5.0906161	-4.2226802
H	0.4116962	-1.9916978	-5.3509578
H	0.4168159	-4.0543633	-6.7265767
H	1.7023002	-6.0562478	-5.9798445
C	3.0902099	-4.7935410	-0.1562240
C	3.1821468	-7.3588164	-1.3455195

C	3.0581540	-5.9566063	0.6297558
C	3.1938751	-4.9714064	-1.5403869
C	3.2282927	-6.2251449	-2.1599064
C	3.1082684	-7.2230361	0.0431578
H	2.9538965	-5.8771315	1.7117749
H	3.0700657	-8.1099942	0.6762012
H	3.2013040	-8.3508473	-1.8019388
C	2.8047520	-0.1030020	-3.5102217
C	4.5619051	1.7894150	-4.6174121
C	3.5916662	-0.4299173	-4.6243917
C	2.9125862	1.1835923	-2.9509746
C	3.7774036	2.1246659	-3.5093577
C	4.4703023	0.5105489	-5.1694369
H	3.5215512	-1.4230216	-5.0689463
H	2.3265863	1.4319483	-2.0642709
H	3.8489876	3.1196866	-3.0675048
H	5.0823194	0.2402543	-6.0314303
H	5.2467651	2.5229761	-5.0453884
O	3.2477769	-3.8266132	-2.3276441
C	3.2943626	-6.2454791	-3.6708615
H	2.9319517	-7.2037505	-4.0684037
H	4.3476373	-6.1458859	-3.9956170
N	0.1426228	-0.6193317	-3.2775212
N	2.6016668	-3.4268871	2.2161377
C	4.6410566	-2.5500385	0.7550098
C	7.2662435	-1.5931849	1.0821986
C	4.8946966	-1.4079326	1.5375293
C	5.7187681	-3.2049853	0.1439162
C	7.0227359	-2.7245893	0.3022064
C	6.1978655	-0.9396069	1.7048628
H	4.0619767	-0.8839918	2.0085754
H	5.5462376	-4.0976992	-0.4573932
H	6.3782800	-0.0545516	2.3170605
H	8.2842284	-1.2206030	1.2060852
S	-1.2321107	-0.7309082	-2.3248138
S	1.1585354	-3.8541496	2.9469541
O	-0.9585080	-1.7652755	-1.3288953
H	-3.6440625	-4.3048734	-4.7056183
C	-3.5303171	-3.2303278	-4.5583954
C	-3.2619482	-0.4706046	-4.1617241
C	-2.5860752	-2.7555119	-3.6460643
C	-4.3299385	-2.3354316	-5.2758850
C	-4.1981074	-0.9584747	-5.0747869
C	-2.4570803	-1.3757976	-3.4622669
H	-1.9628850	-3.4406356	-3.0721794
H	-5.0648862	-2.7125129	-5.9885417
H	-4.8308521	-0.2601057	-5.6241776
H	-3.1606998	0.5982750	-3.9757025

O	1.4945016	-4.9335868	3.8648376
C	0.6899629	-2.4473414	3.9464935
C	-0.0531036	-0.2801965	5.5159060
C	-0.2009777	-1.5031156	3.4294280
C	1.2065577	-2.3288975	5.2413187
C	0.8330298	-1.2358216	6.0236435
C	-0.5706294	-0.4166746	4.2252846
H	-0.5977119	-1.6257969	2.4230052
H	1.8744320	-3.0965883	5.6314428
H	1.2279680	-1.1357319	7.0355568
H	-1.2664785	0.3246272	3.8311204
H	-0.3461558	0.5706117	6.1328607
Ir	1.6632090	-1.2943745	-0.3774068
H	2.9918912	-0.5149160	-0.2745344
H	7.8504082	-3.2428004	-0.1848040
H	1.0456829	0.1917386	-0.5818356
H	1.4741732	-0.8380288	1.1674432
H	3.4046027	-3.7273959	2.7704453
H	0.2213809	0.3063626	-3.7028606

Complex **3TSeq**

atom	X	Y	Z
O	0.004322	0.739050	-2.469445
O	3.064685	0.419996	2.423845
P	1.656864	-1.936827	-3.040854
P	3.576938	-2.517024	0.892184
C	1.895469	-3.728028	-3.435445
C	1.947870	-6.506591	-3.962618
C	1.991328	-4.677466	-2.399292
C	1.858660	-4.210168	-4.761070
C	1.903637	-5.587157	-5.024169
C	1.976861	-6.063905	-2.629090
H	1.786369	-3.488622	-5.590916
H	1.875334	-5.948653	-6.064554
H	1.938162	-7.590219	-4.166288
C	3.523777	-4.367065	0.855961
C	3.445445	-7.183310	0.638607
C	4.223089	-5.177780	1.776311
C	2.779584	-5.008735	-0.156298
C	2.729243	-6.409551	-0.290993
C	4.180977	-6.575945	1.671982
H	4.822293	-4.713401	2.577226
H	4.730650	-7.197013	2.397244
H	3.418219	-8.282402	0.552606
C	2.599128	-1.050617	-4.345029
C	4.044401	0.359181	-6.302449
C	1.914851	-0.271789	-5.297896

C	4.009057	-1.109381	-4.360421
C	4.728069	-0.409199	-5.341626
C	2.640932	0.429134	-6.276737
H	0.815019	-0.219506	-5.253545
H	4.547899	-1.697308	-3.596828
H	5.829702	-0.455731	-5.352239
H	2.104436	1.038400	-7.022838
H	4.611398	0.914043	-7.068779
O	2.068001	-4.218342	-1.065251
C	1.900777	-6.975974	-1.423368
H	0.825814	-7.026445	-1.113538
H	2.221417	-8.008674	-1.674336
N	-0.009593	-1.732410	-3.337550
N	3.370766	-2.180042	2.591424
C	5.329349	-2.067289	0.551745
C	7.967607	-1.291759	-0.061079
C	5.830114	-0.830316	1.017459
C	6.151842	-2.907453	-0.231747
C	7.468299	-2.519549	-0.531683
C	7.146424	-0.449492	0.709728
H	5.184215	-0.162680	1.612506
H	5.768637	-3.872647	-0.601825
H	7.531228	0.516479	1.076373
H	9.001363	-0.989802	-0.297442
S	-0.668912	-0.582994	-2.328108
S	2.777215	-0.721389	3.319361
O	-0.816345	-1.132404	-0.931816
H	-5.386309	-1.975358	-3.085651
C	-4.612387	-1.211310	-3.270513
C	-2.635725	0.744040	-3.737553
C	-3.320225	-1.393634	-2.750331
C	-4.920226	-0.058420	-4.016780
C	-3.934931	0.919240	-4.244404
C	-2.342144	-0.416605	-3.003507
H	-3.077445	-2.286134	-2.154218
H	-5.937906	0.080977	-4.418485
H	-4.178968	1.829445	-4.818213
H	-1.847576	1.498691	-3.888853
O	3.333875	-0.804711	4.686735
C	0.995590	-0.940972	3.399303
C	-1.757944	-1.321205	3.532473
C	0.464184	-1.696388	4.460115
C	0.180233	-0.354692	2.416413
C	-1.208815	-0.562620	2.485392
C	-0.925377	-1.879726	4.521991
H	1.132458	-2.118721	5.226705
H	0.619019	0.251498	1.610887
H	-1.850464	-0.139018	1.697061

H	-1.361815	-2.464395	5.348585
H	-2.847963	-1.481257	3.581086
Ir	2.113897	-1.903172	-0.622840
H	2.279794	-0.355331	-0.403809
H	8.109281	-3.184535	-1.134364
H	1.228413	-1.929135	0.693007
H	4.037145	-2.604698	3.254520
C	-1.106898	-4.620534	-2.049252
O	-1.304603	-5.779624	-1.732873
O	-1.287309	-4.138018	-3.280398
H	-0.757340	-3.840244	-1.311205
H	-0.885006	-3.183301	-3.340714

Complex **3TSax**

atom	X	Y	Z
O	-0.607184	1.524599	-3.867128
O	1.016398	-0.293009	2.465608
P	1.233058	-1.768002	-3.295806
P	3.114867	-1.999704	0.205461
C	1.037946	-3.594898	-3.620716
C	0.890069	-6.409115	-3.930536
C	1.153306	-4.478727	-2.539684
C	0.812473	-4.165425	-4.891212
C	0.731815	-5.559432	-5.042102
C	1.101983	-5.878025	-2.645235
H	0.703781	-3.499588	-5.762432
H	0.552284	-5.993681	-6.039091
H	0.842696	-7.503700	-4.058557
C	3.200253	-3.861107	0.338752
C	3.209544	-6.697401	0.359490
C	4.091558	-4.571213	1.170648
C	2.309381	-4.622719	-0.429113
C	2.288632	-6.026843	-0.465081
C	4.093170	-5.975399	1.183823
H	4.789875	-4.009261	1.812015
H	4.792472	-6.517456	1.841565
H	3.222878	-7.800432	0.365449
C	2.679561	-1.343143	-4.362857
C	4.905754	-0.573269	-5.913118
C	3.857987	-2.121173	-4.352368
C	2.625049	-0.172325	-5.148776
C	3.737721	0.209146	-5.918305
C	4.963989	-1.739796	-5.128172
H	3.915319	-3.036390	-3.738194
H	1.702794	0.431989	-5.149492
H	3.687156	1.125478	-6.529913
H	5.879241	-2.356067	-5.119052

H	5.776135	-0.273595	-6.520701
O	1.343256	-3.950822	-1.221881
C	1.279214	-6.696714	-1.378659
H	0.297082	-6.769294	-0.847008
H	1.588066	-7.736705	-1.616202
N	-0.060356	-1.009959	-4.052028
N	3.294807	-1.472782	1.860082
C	4.820236	-1.526962	-0.343973
C	7.331597	-0.646431	-1.284753
C	5.161548	-0.154278	-0.285536
C	5.738849	-2.449792	-0.891163
C	6.989127	-2.007331	-1.357656
C	6.415536	0.275653	-0.749084
H	4.435463	0.582052	0.106448
H	5.486128	-3.520910	-0.951232
H	6.671148	1.347064	-0.698509
H	8.313444	-0.302669	-1.650560
S	-0.819949	0.169757	-3.293373
S	2.150292	-1.019274	3.062377
O	-0.578061	0.145728	-1.750120
H	-4.784656	-2.827765	-3.461817
C	-4.414371	-1.789462	-3.507833
C	-3.470813	0.863694	-3.640683
C	-3.035751	-1.537872	-3.405066
C	-5.320122	-0.723671	-3.674387
C	-4.847876	0.599631	-3.740535
C	-2.580838	-0.210732	-3.473098
H	-2.311878	-2.360409	-3.288865
H	-6.400892	-0.926970	-3.759568
H	-5.555915	1.435259	-3.875937
H	-3.073489	1.888754	-3.702090
O	3.012649	-0.427715	4.107057
C	1.519531	-2.595058	3.690052
C	0.528263	-4.980914	4.740815
C	2.354738	-3.385594	4.499013
C	0.194759	-2.964860	3.411233
C	-0.297792	-4.169814	3.944230
C	1.851769	-4.588282	5.019292
H	3.377992	-3.049248	4.730700
H	-0.434979	-2.307741	2.793487
H	-1.338006	-4.470364	3.737944
H	2.492901	-5.218076	5.656983
H	0.135233	-5.921866	5.159099
Ir	1.024997	-1.882113	-0.928386
H	7.701877	-2.736334	-1.777548
H	0.409062	-2.141881	0.569153
H	4.232820	-1.177164	2.162607
C	1.574927	1.313492	-0.083933

O	0.513275	2.008591	-0.417645
O	2.588416	1.719907	0.443213
H	-0.520265	-2.183426	-1.313373
H	1.466805	0.179646	-0.368755
H	-0.092051	1.381494	-0.975361

References

S1 S. Oldenhof, B. de Bruin, M. Lutz, M. A. Siegler, F. W. Patureau, J. I. van der Vlugt and J. N. H. Reek, *Chem. Eur. J.*, 2013, **19**, 11507.

S2 R. Ahlrichs, *Turbomole*, *version 6.5*, University of Karlsruhe, Germany, 2013.

S3 PQS, version 2.4; Parallel Quantum Solutions: Fayetteville, AR, 2001. The Baker optimizer (see: I. Baker, *J. Comput. Chem*., 1986, **7**, 385) is available separately from Parallel Quantum Solutions upon request.

S4 P. H. M. Budzelaar, *J. Comput. Chem.*, 2007, **28**, 2226.