Supporting Information

Tris(pyrazolyl)methane Sulfonate Complexes of Iridium: Catalytic Hydrogenation of 3,3-Dimethyl-1-butene

C. M. Nagaraja, Munirathinam Nethaji, and Balaji R. Jagirdar*

Department of Inorganic & Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Contents

1. Figure S1. Variable temperature ^{1}H NMR spectral stack plot of [Ir(Tpms)(C_2H_4)$_2$] **1**

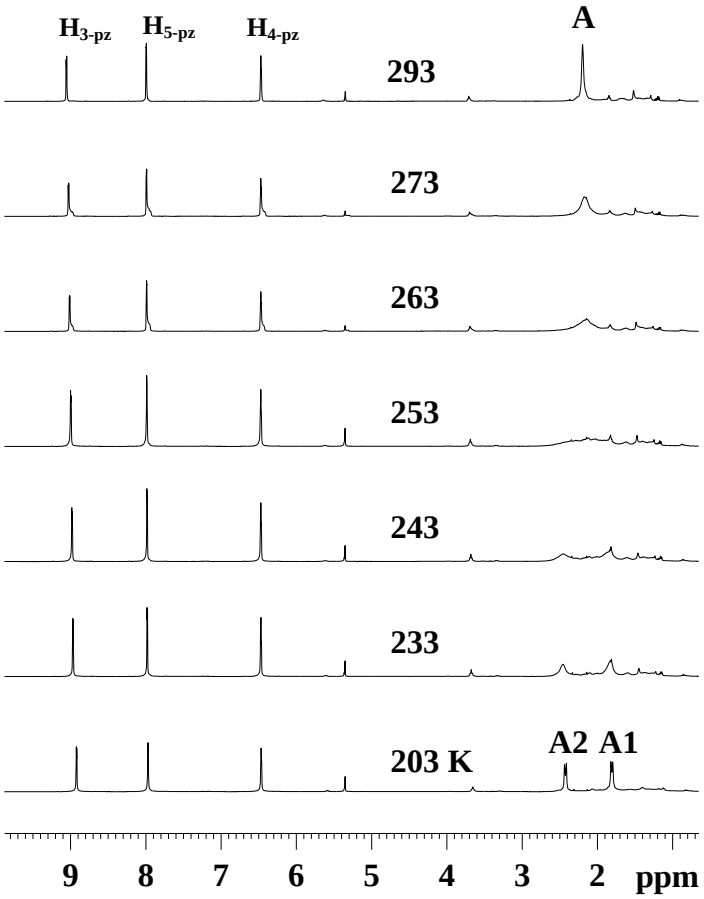
2. Figure S2. ^{1}H – ^{1}H NOESY spectrum of [Ir(Tpms)(C_2H_4)(PPh_3)] **2** at 223 K

3. Figure S3. ^{1}H NMR spectral stack plot for the hydrogenation of 3,3-dimethyl-1-butene using [Ir(H)$_2$(Tpms)(PPh_3)] **3** as a catalyst

4. Figure S4. Optimized geometry of intermediate **6a** at the B3LYP/LANL2DZ level of theory

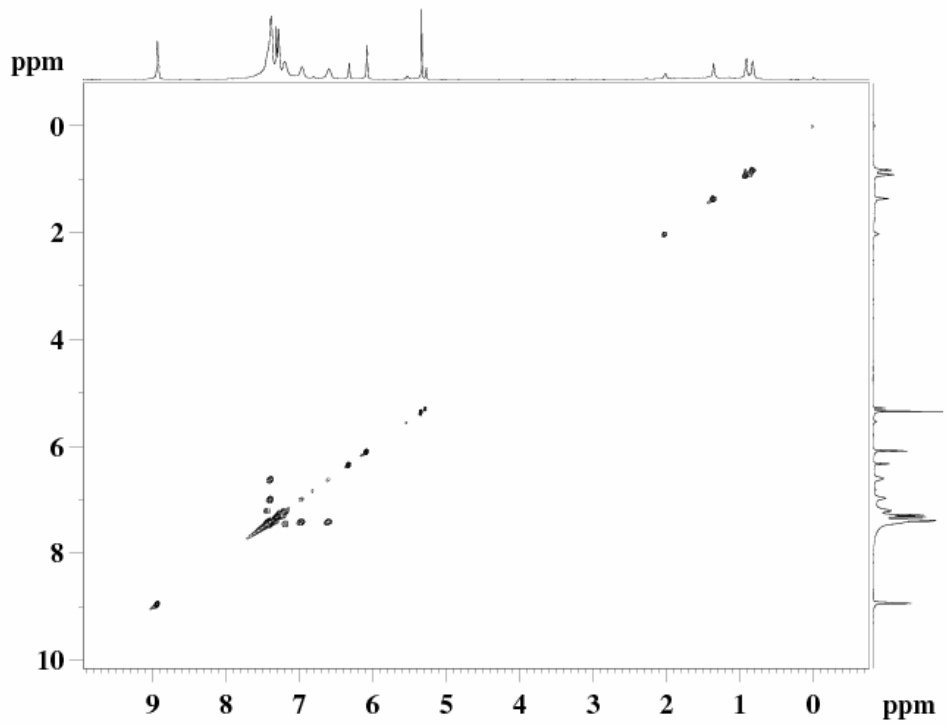
5. Total energy (E, in a.u.) and Cartesian coordinates of all the molecules at the B3LYP/LANL2DZ level of theory

Figure S1. Variable temperature ^{1}H NMR spectral stack plot of [Ir(Tpms)(C_2H_4)$_2$] **1** in CD_2Cl_2. **A**: resonance due to C_2H_4 at room temperature splits into two doublets **A1** and A**2** at low temperature



The broadness of the ^{1}H NMR resonance due to the ethylene moieties at room temperature is indicative of fast rotation of the two C_2H_4 ligands about the Ir-C_2H_4 bond at a rate faster than the NMR time scale. As the temperature of the sample was lowered, the broad signal at δ 2.16 broadens further, goes into the base line, and decoalesces at ca. 243 K into two new doublets at δ 1.77 and δ 2.39 (Figure S1). The observed spectrum is similar to the one reported by Cramer et al. *J. Am. Chem. Soc.* **1969**, *91*, 2519.

Figure S2. ^{1}H – ^{1}H NOESY spectrum of [Ir(Tpms)(C_2H_4)(PPh_3)] **2** at 223 K showing the correlations between the hydrogens on the equatorial pyrazolyl groups and the phenyl hydrogens of PPh_3



The ^{1}H–^{1}H NOESY spectrum shows cross peaks between the hydrogens on the equatorial pyrazolyl groups of Tpms and the phenyl hydrogens of PPh_3. This suggests that the PPh_3 ligand is in close proximity to the equatorial pyrazolyl groups: it occupies the axial position and the ethylene ligand, equatorial position of a tbp structure.

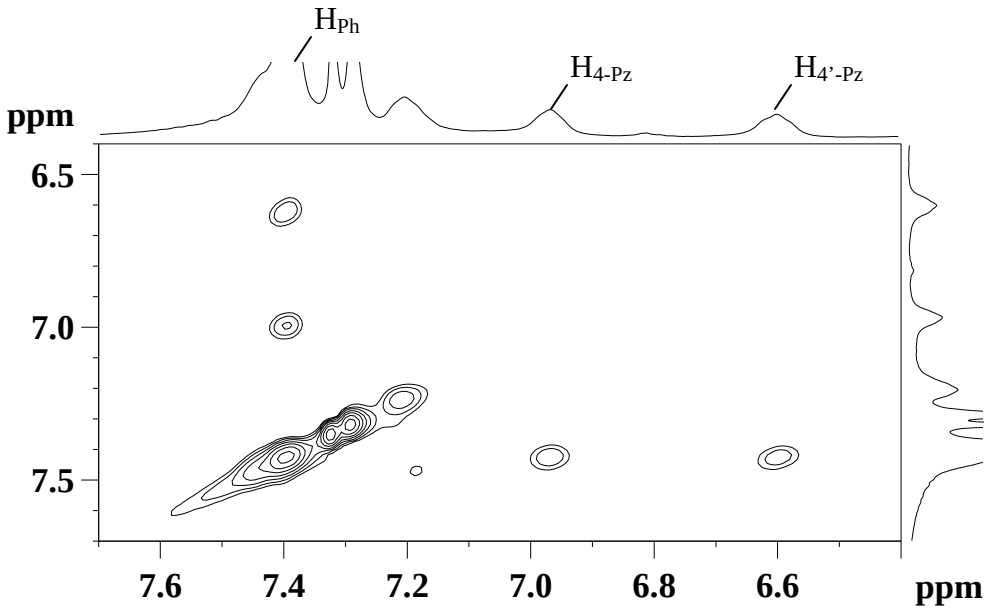


Figure S3. ^{1}H NMR spectral stack plot for the hydrogenation of 3,3-dimethyl-1-butene using $[Ir(H)_2(Tpms)(PPh_3)]$ **3** as a catalyst

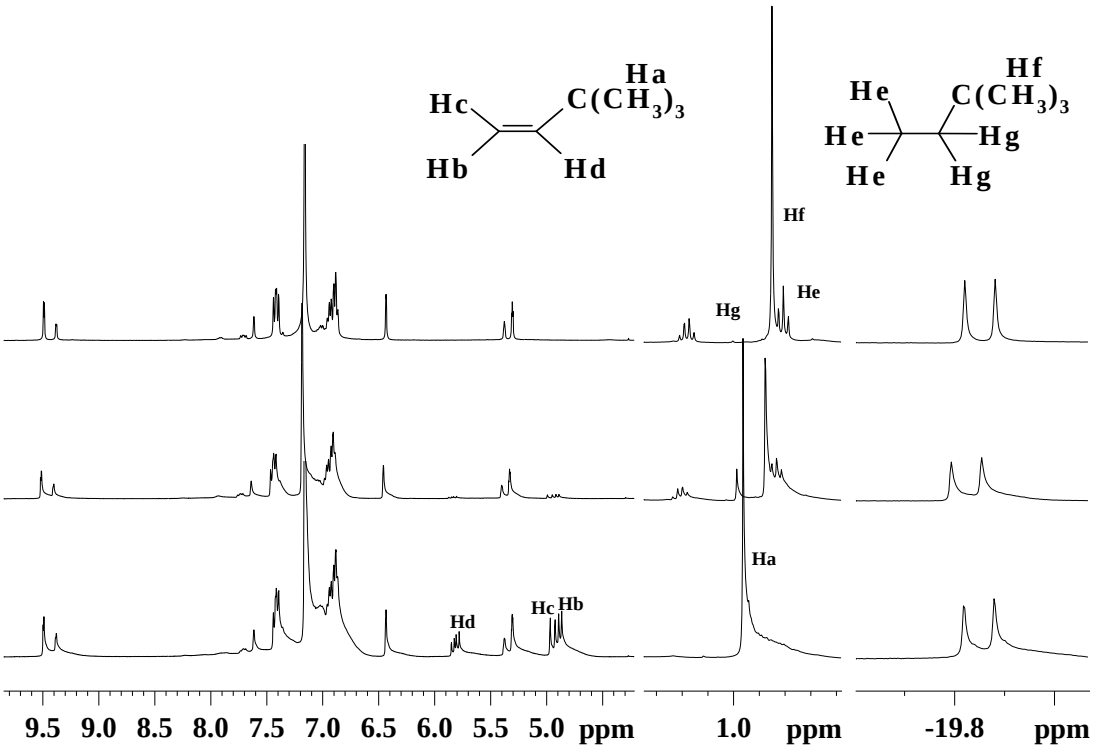
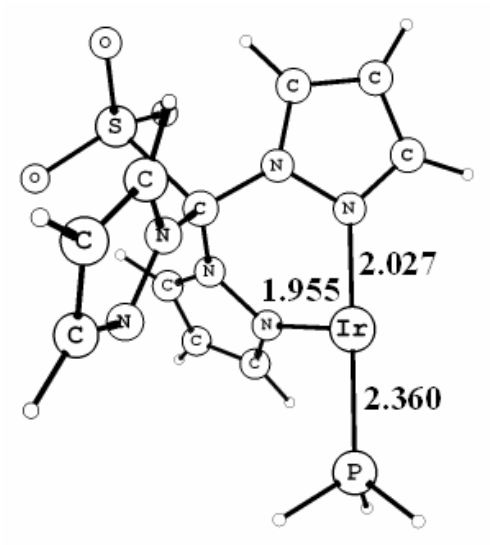


Figure S4. Optimized geometry of intermediate **6a** (bond lengths in Å) at the B3LYP/LANL2DZ level of theory



Total energy (E, in a.u.) and Cartesian co-ordinates of all the molecules at the B3LYP/LANL2DZ level of theory.

3a
E = -1063.28884

77	1.657411	.349649	-.110881
15	3.465667	-1.084337	.344112
16	-3.366014	-.407571	.126659
8	-3.795969	-.134057	-1.417995
8	-3.438390	-1.960688	.631134
1	3.687395	-1.628518	1.657607
8	-3.803578	.720626	1.213492
1	4.751663	-.484505	.137286
7	.236045	1.725378	-.552884
1	3.668197	-2.300677	-.397124
7	-.716198	-1.018555	-.973722
7	-.720550	-.252308	1.388834
6	-1.267906	-.089151	.029087
7	.582391	-.801611	-1.517015
7	.582050	.233470	1.702838
6	.177458	3.005134	-.968749
1	1.082825	3.564541	-1.145512
6	-1.954400	2.302491	-.753183
1	-3.023285	2.180178	-.720054
6	-1.277895	-2.144890	-1.544253
1	-2.255476	-2.497770	-1.255677
7	-1.081884	1.286600	-.416205
6	-1.289187	-.819851	2.513029
1	-2.271031	-1.265629	2.487738
6	-.376282	-.700267	3.555625
1	-.519925	-1.029097	4.572694
6	-1.178322	3.404312	-1.106493
1	-1.543640	4.368329	-1.421824
6	-.364235	-2.655932	-2.459854
1	-.503309	-3.522381	-3.086832
6	.764437	-1.792499	-2.416871
1	1.676977	-1.831619	-2.991894
6	.759172	-.037557	3.014047
1	1.673643	.261765	3.502952

4
E = -1143.14814

77	-1.938456	-.176733	-.360006
15	-3.885251	1.119851	-.590294
16	2.299495	-.268277	1.935099
8	3.242267	-1.595597	1.763790
8	3.091543	1.122920	2.280926
1	-3.850778	2.551123	-.492376
8	.859446	-.488684	2.666651
1	-4.974670	.863172	.306052
7	-.344243	-1.473708	-.445419
1	-4.567730	.993620	-1.836595
7	2.828861	.294052	-.866680
7	.862385	1.279752	.004010
6	1.663510	.070597	-.044110
7	2.608097	.484019	-2.242520
7	-.519064	1.378966	.138170
6	-.424059	-2.794123	-.729667
1	-1.392040	-3.258076	-.823950
6	1.750795	-2.303625	-.709200
1	2.826596	-2.282173	-.699855
6	4.181927	.362769	-.549138
1	4.547351	.254813	.458996
7	1.014256	-1.163085	-.449589
6	1.448158	2.521102	.179053
1	2.517130	2.642498	.162925
6	.433389	3.438226	.407559
1	.543935	4.494508	.590957
6	.862877	-3.352249	-.900650
1	1.109888	-4.378232	-1.118607
6	4.852903	.598459	-1.740853
1	5.919067	.707794	-1.865891
6	3.839817	.663358	-2.752605
1	3.954144	.830186	-3.814277
6	-.765381	2.684886	.377656
1	-1.777177	3.031094	.510843
6	-2.771903	-1.389557	1.541117
1	-2.245122	-2.338094	1.490673
1	-3.851356	-1.439302	1.422985
6	-2.138544	-.270842	2.059820
1	-1.102705	-.311700	2.388983
1	-2.713206	.608716	2.344785
1	-1.630543	.163225	-1.891652
1	-2.863867	-1.313152	-1.011292

5
E = -1143.18739

77	1.557110	-.032355	-.196851
15	3.130446	-1.663063	.390238
16	-3.728304	.105266	.172767
8	-4.133438	.261931	-1.396168
8	-4.063613	-1.329801	.867205
1	3.148602	-2.176398	1.731683
8	-3.925670	1.425053	1.105153
1	4.508991	-1.308650	.261515
7	.234739	1.427516	-.778242
1	3.141082	-2.911056	-.315277
7	-1.263500	-1.148051	-.778808
7	-1.086311	-.126533	1.401756
6	-1.617989	.006760	.045959
7	.088669	-1.376242	-1.072236
7	.303283	-.146651	1.579313
6	.376960	2.627846	-1.367913
1	1.360889	2.985451	-1.626750
6	-1.829599	2.343638	-1.050157
1	-2.902811	2.415067	-1.000647
6	-2.054697	-2.083024	-1.417659
1	-3.127564	-2.090540	-1.325349
7	-1.142019	1.244560	-.574752
6	-1.724298	-.200982	2.624363
1	-2.797157	-.201759	2.716054
6	-.736361	-.269793	3.601640
1	-.891462	-.333739	4.666679
6	-.890769	3.236631	-1.557196
1	-1.095187	4.195745	-2.004752
6	-1.205804	-2.923661	-2.130381
1	-1.498603	-3.761075	-2.743219
6	.110564	-2.444192	-1.891431
1	1.049475	-2.807566	-2.280073
6	.503319	-.227964	2.907815
1	1.506860	-.242091	3.304612
6	2.808748	1.427590	.691466
1	2.155431	2.290633	.901532
6	4.036717	1.909756	-.113844
1	4.735934	1.088901	-.327774
1	3.739325	2.330181	-1.084158
1	4.597291	2.687440	.430774
1	3.153660	1.075024	1.681651
1	2.390982	.122196	-1.551501

6

E = -1063.28884

77	1.657411	.349649	-.110881
15	3.465667	-1.084337	.344112
16	-3.366014	-.407571	.126659
8	-3.795969	-.134057	-1.417995
8	-3.438390	-1.960688	.631134
1	3.687395	-1.628518	1.657607
8	-3.803578	.720626	1.213492
1	4.751663	-.484505	.137286
7	.236045	1.725378	-.552884
1	3.668197	-2.300677	-.397124
7	-.716198	-1.018555	-.973722
7	-.720550	-.252308	1.388834
6	-1.267906	-.089151	.029087
7	.582391	-.801611	-1.517015
7	.582050	.233470	1.702838
6	.177458	3.005134	-.968749
1	1.082825	3.564541	-1.145512
6	-1.954400	2.302491	-.753183
1	-3.023285	2.180178	-.720054
6	-1.277895	-2.144890	-1.544253
1	-2.255476	-2.497770	-1.255677
7	-1.081884	1.286600	-.416205
6	-1.289187	-.819851	2.513029
1	-2.271031	-1.265629	2.487738
6	-.376282	-.700267	3.555625
1	-.519925	-1.029097	4.572694
6	-1.178322	3.404312	-1.106493
1	-1.543640	4.368329	-1.421824
6	-.364235	-2.655932	-2.459854
1	-.503309	-3.522381	-3.086832
6	.764437	-1.792499	-2.416871
1	1.676977	-1.831619	-2.991894
6	.759172	-.037557	3.014047
1	1.673643	.261765	3.502952

6a

E = -1063.29965

77	1.850646	.463421	.056666
16	-3.416849	-.233567	-.473663
8	-3.639096	-1.843296	-.579231
8	-4.029657	.515486	.845525
8	-3.528167	.600951	-1.874402
7	.806519	-.598220	-1.210859
7	-1.120961	-.766205	1.223416
7	-1.031660	1.343751	.057347
6	-1.330148	-.088435	-.028278
7	-.510634	-2.023673	1.256420
7	.304666	1.773383	.082590
6	1.172073	-1.309586	-2.301745
1	2.203580	-1.331543	-2.615506
6	-1.052167	-1.537541	-2.113493
1	-2.092904	-1.815593	-2.176292
6	-1.567847	-.373443	2.474264
1	-2.116830	.542296	2.621157
7	-.592449	-.718744	-1.107315
6	-1.869212	2.440216	.071915
1	-2.941884	2.333734	.080817
6	-1.072372	3.581193	.115760
1	-1.416715	4.602386	.136811
6	.038621	-1.918038	-2.888393
1	.016945	-2.551512	-3.759968
6	-1.226624	-1.391080	3.355067
1	-1.431699	-1.426457	4.413817
6	-.581821	-2.385102	2.553005
1	-.176181	-3.338929	2.858853
6	.267805	3.125511	.107870
1	1.186146	3.692968	.103584
15	3.629331	-1.078238	.221636
1	4.679311	-.781038	1.150208
1	4.445485	-1.422378	-.911359
1	3.291796	-2.396004	.666533

Ethylene

E = -78.57820

6	.000000	.674180	-.000293
1	-.926011	1.246265	.000880
1	.926011	1.246265	.000880
6	.000000	-.674180	-.000293
1	-.926011	-1.246265	.000880
1	.926011	-1.246265	.000880

Ethane

E = -79.81887

6	.000000	.771682	-.000001
1	-.512050	1.167460	.886879
1	1.024071	1.167552	-.000003
1	-.512069	1.167470	-.886870
6	.000000	-.771682	-.000001
1	.512069	-1.167470	-.886870
1	.512050	-1.167460	.886879
1	-1.024071	-1.167552	-.000003